THIRTIETH ANNUAL INTERNATIONAL PITTSBURGH COAL CONFERENCE

ABSTRACTS BOOKLET

COAL - ENERGY, ENVIRONMENT AND SUSTAINABLE DEVELOPMENT

September 15 - 18, 2013
Beijing, CHINA
Beijing International Convention Center

Hosted By:

The Division of Energy and Mining Engineering of
Chinese Academy of Engineering

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北京低碳清洁能源研究所
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On behalf of the Thirtieth Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation to Mrs. Heidi Peck for her dedication and professionalism; and Dr. Laurent Sehabiague and Mr. Omar Basha for their invaluable assistance in preparing this Abstracts Booklet.

Thank you,

Badie I. Morsi

Badie I. Morsi, Editor
Professor and Executive Director of the Conference

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SESSION 1
Coal Science: General – 1

Effect of Grinding Medium on the Surface Chemical Property and Flotation Behavior of Coal Middlings

Weining Xie, Yaqun He, Tao Zhang, Linhan Ge, Xiangnan Zhu, Shan Wu,
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Industrial practice indicates that grinding plays an important role in the mineral processing. Grinding in rod and ball mills with medium of steel or ceramics followed by flotation is the common practice in ores, but is unusual in coal preparation plant. The combination of these two operations is crucial for improving the recovery of clean coal, especially for the recycle use of coal middlings, for mineral liberation will happen because of the size reduction through the grinding of coal middlings. Meanwhile the surface physicochemical property will also be changed and the flotation activity will be further affected. In the current study, the effect of grind medium on chemical valance of the elements and the subsequent flotation behavior was investigated. Phase composition analyses of coal middlings conducted by the D8 Advance X-ray Diffractometer showed that kaolinite, quartz, illite, smectite were the main associated minerals and dolomite and pyrite were minor. The coal middlings were ground by the wet-milling with medium of iron and ZrO_2 ceramics to -0.5mm respectively. The chemical valence of elements analyzed by the X-ray photoelectron spectroscopy manifested that FeOOH was investigated on the surface of product ground by the wet milling with iron medium, while no change of the chemical valence was found on the surface of other product. Oxidizing atmosphere of the wet milling with iron medium lead to the change of FeS_2, which is due to the pyrite liberation to FeOOH. Local surface of coal ground by the wet mill with iron medium was replaced from hydrophobic to hydrophilic compared with the wet mill with ZrO_2 ceramics medium. The optimized timed-release flotation research depicted that when the ash content of the float clean coal was 11.50%, the clean coal yield ground by the wet milling with ZrO_2 ceramics medium was nearly 16% higher than that ground by the wet milling with iron medium.

Mercury and Fluorine in the Late Permian Coals from Eastern Yunnan Province, China

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and Safe Mining, CHINA

Yunnan is the second largest coal province in southern China. Estimated coal resource is more than 24.6 billion tons in 2006, of which 70% occurs in the Late Permian age and is located in the eastern area of Yunnan including northern Zhengxiong, middle Xuanwei and southern Enhong.

For the investigation of distributions, modes of occurrence, and origins of mercury and fluorine, a total of 56 coal samples of drill cores were collected from 11 coal mines, including the Mahe, Yujingshan, Daying, Shizhuang, Guanyingshan mines in the northern Zhengxiong, the Shuanghe and Xiangshui mines in the middle Xuanwei, the Dahe, Wayuchong, Taoshuping and Changxing mines in the southern Enhong.

The results show that the mercury content apparently varies in the three areas. The coals in the northern Zhengxiong have the highest content (91 to 398 ng/g, 212 ng/g on average). Whereas, mercury in the middle Xuanwei coals are mostly lower than 120 ng/g with an average of 51 ng/g, with the exception of the C16 coal in the Xiangshui mine, with an abnormal content of 1234 ng/g. Mercury in the southern Ehhong coals, ranging from 4 to 1012 ng/g with an average of 119 ng/g, is much higher than that of the middle coals. Mercury in these coals is closely associated with sulfur, which is derived from marine influence on the deposit during peat accumulation and/or early diagenesis.

The distribution of fluorine is quite different from that of mercury. Coals from the northern, middle, and southern areas, have an average fluorine content of 85 µg/g, 43 µg/g, and 77 µg/g, respectively. All these contents are lower than that of the average Chinese coals (130 µg/g) and the worldwide coals (88µg/g) reported by Dai et al (2012) and Ketris and Yudovich (2009), respectively. Based on the high correlation coefficient of fluorine and P_2O_5(r=0.85), it is inferred that fluorine in these coals occurs in phosphate minerals, probably of terrigenous origin. However, the higher fluorine in the Changxing coals is probably attributed to the input of the hydrothermal fluids.

Deformation-Metamorphism Characteristics of Coal and the Corresponding Energy Changing Process

Yiwen Ju, Xiaoshi Li, Guochang Wang, Mingming Wei, University of
Chinese Academy of Sciences, CHINA

Coal is an organic rock which is sensitive to geological environmental factors such as temperature and pressure. Various tectonothermal events of the geological evolution must have caused a series of changes in physical, chemical structures of coal and thus formed different tectonically deformed coals. The effect of tectonic stress would induce the brittle and ductile deformation of coal, as well as its dynamic metamorphism at different degrees. Therefore, the research about tectonic deformation and dynamic metamorphism of coal is not only of important scientific significance but also very significant for the evaluation in resources of coalbed methane and the prediction of dangerous coal and gas outbursts. Based on the existing research results, different tectonic deformation and dynamic metamorphism in coal have been intensively studied through the Ro, max, XRD and NMR (CP/MAS+ TOSS). Also the mechanism of dynamic metamorphism about coal under tectonic stress has been discussed. The results show that, tectonic stress has a more important influence on chemical structure in ductile deformational coal than in brittle deformational coal. The aromatization and the degree of ring condensation in brittle deformational coal have increased obviously. It means that, C polycondensation in ductile deformational coal is stronger than that in brittle deformational coal. Under the influence of tectonic stress to the brittle deformation of coal, the rapid mechanical friction on the plane of fracture in the brittle deformation of coal can be translated into heat energy causing the changes of its chemical structure and composition of coal; while as to the ductile deformation coal, the accumulation of local regional strain energy can result in the failure of its chemical structure. Thus, the dynamic metamorphism of different deformational mechanisms would have taken place.

Mercury Removal Technology, Today and Tomorrow

Robert Nebergall, Cabot Norit Activated Carbon, USA

The development of technologies for the reduction of mercury emissions from coal derived flue gas has taken substantial steps forward over the last ten years. Beginning with state or provincial regulations requiring high mercury removal efficiencies, and now a nationwide requirement in North America, much work has been completed. With the Legally-Binding Instrument for the Global Control of Mercury Pollution now signed, the need for a broader understanding of available solutions will increase worldwide. A broad spectrum of success has been demonstrated across numerous technologies with activated carbon being the most successful in achieving high removal rates across the broadest number of applications and fuels. With the newest regulation requiring emission rates on the order of 1 ug/dscm, optimization of any utilized technology has become critical.

This presentation will walk through a number of currently available technologies for removing mercury. It will review a history of the development of sorbent technologies leading up to the state of the art products addressing the latest challenges in effectiveness.

Thermal Analysis of Chinese Lignite Pyrolysis Using Thermogravimetry and Differential Scanning Calorimetry

Zhihang Guo, Qinhui Wang, Zhongyang Luo, Kefa Cen, Zhejiang University, CHINA

This paper presented a thermal analysis using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to characterize the heat effects from the devolatilization of three typical Chinese lignites under inert atmosphere. Actual specific heat resulting from pyrolysis reactions was evaluated by subtracting coal enthalpy from apparent heat flow. Results showed that there were three devolatilization peaks during the pyrolysis processes of each coal sample. Each devolatilization peak for all coal samples appeared at similar temperatures. Three endothermic peaks appeared in the vicinity of the three devolatilization peaks. Thermal effects during the pyrolysis of Chinese lignites were endothermic in nature over the temperature range studied. Accumulative reaction heat during pyrolysis process was calculated by integrating specific reaction heat. Accumulative reaction heat first increased with pyrolysis temperature, and then reached an asymptotic value after 600ºC. All coal samples had almost similar tendencies of accumulative reaction heat except for the overall heat value, which was slightly small for XLT lignite. This work offered information about actual reaction heat of Chinese lignite.

SESSION 2
Coal Mining: Ground Control in Mining - Session 1

Development and Applications of Rock Bolting Materials for Coal Mine Roadways

Hongpu Kang, Jian Lin, Yongzheng Wu, China Coal Research Institute, CHINA

Rock bolting has been the primary supporting method for roadways in Chinese coalmines. The complete rock bolting technique includes bolting design, materials, machinery, practical procedures, quality control and on-site monitoring methods, and rock bolting materials play an important part on the technique. Rock bolting materials involve bolt rods, accessories, anchorage materials, surface control components (straps, wire mesh) and cable bolts. The development of a variety of rock bolting materials for coal mine roadways is introduced. The functions and properties of rock bolting materials and components are analyzed. Especially, the mechanical properties of the high strength rock bolts and cable bolts are described thoroughly, and the underground practices of these rock bolting materials are introduced. Finally, the existing problems of the rock bolting materials are analyzed, and their development trends in the future are proposed.

Experiments on Effects to Rock Bolt Pretension by Thread Rolling Accuracy

Yan Lixin, China Coal Research Institute, CHINA

Pretension is a key factor affecting the performance of rock bolt. It is usually applied on the bolt by tightening the nut. The efficiency of the torque-to-pretension conversion is significantly influenced by the thread rolling accuracy. In this study, the influence of the thread rolling accuracy upon the pretension is investigated. Factors influencing the thread rolling efficiency, i.e., rock bolt material quality, rolling technic and equipments, are examined. To study the relationship between torque and pretension, a laboratory table was specially designed and a series of tests were carried out on the rock bolts with different thread accuracy. The result indicates that the higher the thread rolling accuracy, the higher the coefficient of torque-to-pretension conversion. And the coefficient can be improved by daubing lubrication oil on the thread. In China, the rock bolt thread encounters the issue of low rolling accuracy which results in coarse thread surface. As a result, the efficiency of the torque-to-pretension conversion is greatly reduced. In addition, the rock bolt is susceptible to break at the thread end. Essential approach to resolve these issues is to significantly improve the thread rolling accuracy by adopting advanced equipment.

Simulation Analysis of the Bolt Support in Inclined Shaft Through the Soft Rock Strata

Pengfei Jiang, Tiandi Science & Technology Co, Ltd., CHINA

Taking +150 inclined shaft going through the soft rock strata at Muchengjian mine as the background, and based on the analysis of the deformation and failure feature of the roadway surrounding rock in the soft rock strata, this paper makes X-Ray Differaction (XRD) phase analysis of the soft rock; using finite difference numerical software FLAC^{3D}, it stimulates and makes comparative analysis of the stress and deformation distribution characteristics of the roadway surrounding rock with bolt support with different intervals, and the support of the high-strength bolt with high pre-tension stress in the inclined shaft through the soft rock strata. The results show that the roadway surrounding rock in the +150 inclined shaft at Muchengjian mine is swelling soft rock prone to softening, degradation and swelling in water, which is bad for the roadway support; different types of rock strata have significant different impact on the stress and deformation of the roadway surrounding rock; for the soft rock roadway, the increased pre-tension stress of the bolt can cause higher compressive stress in the roadway surrounding rock and reduce the tension failure of the surrounding rock ; compared with the end anchorage, the full-size anchorage with high pre-tension stress can cause the overlap of the conical compressive stress zone and enhance the roadway overall support.

Technology Research on Weakly-Cemented Sandstone Roadway Supporting in Lignite Coal Mine and its Application

Fan Mingjian, Tiandi Science & Technology Co. Ltd, CHINA

The paper select a lignite coal mine in Yimin-River as the engineering background. The mine is located in the northeastern Inner Mongolia of china. The coal mine strata is characterized by broken loose structure, low cementation intensity, fractured joints, easily weathered, high content of clay minerals, low anchoring strength and so on. Owing to the characteristics of its surrounding rock, it is greatly difficult to effectively control the deformation and failure of roadway surrounding rock using ordinary supporting technology. The ordinary supporting system combining low-intensity bolts, matel-meshes and U-shaped steel brackets can not solve the difficulties. The paper is based on the results of surveying in geology and production conditions, geo-mechanical on-site tests, clay mineral composition analysis and the maximum anchoring force test of roadway surrounding rock in the lignite coal mine. Considering the weakly-cemented sandstone conditions, the paper offered some supporting principles, such as compressed-arch with high strength, full-face and timely supporting, full encapsulation with high pre-tension, high-strength Surface-protection and supporting stress spread efficiently. The roadway with weakly-cemented sandstone in the lignite coal mine was supported effectively by the supporting system with high pre-stressed bolts and cables. The convergence rate of roadway with new supporting system reached less than 3%.The new supporting manner cancelled steel-frame, reduced labor intensity and achieved higher technical and economic benefits. The research results can be applied to other mines with similar engineering conditions.

Research on Testing and Comprehensive Assessment Methods of Coalmine Goaf Treatment Effect

Zhang Gang-yan, Tiandi Science & Technology Co., Ltd., CHINA

Based on practice of many projects, the paper concluded comprehensive methods and techniques on improving the testing and assessing of the project quality and effect under complex geological conditions, formulated comprehensive testing and assessing methods of “geophysical prospecting + drilling + borehole color TV + drilling fluid leakage monitoring + rock mechanics test”, achieving a comprehensive analysis and assessment system from an isolated point to a whole range and from qualification to quantification, which could be shared by similar projects from home and abroad.

SESSION 3
Gasification: General – 1

State of the Gasification Industry – The Updated Worldwide Gasification Database

Chris Higman, Higman Consulting GmbH, GERMANY

The most recent gasification database was published in 2010 and provided information on 182 commercial real and planned gasification projects. This database has been updated and now includes over 100 more projects, the majority of which have been built over the last 5 years or are already under construction. The database includes not only coal and oil based units but also a considerable number of plants based on biomass and waste. This paper presents the results of the database update together with an analysis of trends that are derived from it. Information from the database will also be available for a poster in the form of a world map.

Modeling of Coal Gasification in a Low-Temperature, High-Pressure Entrained-Bed Reactor

Ting Wang, University of New Orleans, USA; Ming-Hong Chen, Yau-Pin Chyou, Institute of Nuclear Research, Atomic Energy Council, TAIWAN

It has been reported that a newly introduced Entrained Slagging Transport Reactor (E-STR) gasifier can reduce capital and operating costs, while improve operability. E-STR is a product modified from the existing E-Gasifier design. The major modifications include the following features: (a) the horizontal cylinder in the E-Gasifier is removed, (b) the oxidant is entirely fed at the 1st stage with only the recycled char (no coal slurry), (c) the coal/slurry mixture is entirely fed at the 2nd stage, (d) the operating pressure is much higher and temperature is lower than the counterparts in E-Gas^{TM} gasifier, and (e) due to the reduced operating temperature, catalyst is used to convert tar or heavy volatiles. Comparing to the cross-type configuration of E-Gas^{TM}, the design of E-STR excludes the first-stage cylinder. Therefore, several critical issues under high-pressure operation can be simplified, such as welding, sealing, maintenance and operation cost. The savings can be employed for the catalyst on low-temperature tar cracking process.

Considering the lower operating temperature in E-STR gasifier, the objective of this study is to modify the existing E-gasification simulation model by incorporating a tar condensation and re-evaporating sub-model. The commercial CFD software, ANSYS/FLUENT, is used in this study. Eulerian-Lagrangian approach is adopted to simulate the heterogeneous reactions involved with coal and char particles. The interaction of momentum, mass, and heat transfer between the solid coal particles and the fluid flow is predicted by the Discrete Phase Model. Finite-rate/Eddy-dissipation model is used to compute the species transport with nine assigned chemical reactions. The bituminous coal (Illinois #6 coal) is used in our model.

The results of E-Gas^{TM} and the preliminarily E-STR model are compared. Similar syngas compositions and outlet temperature were observed between E-Gas^{TM} and E-STR without char recycling. For E-STR, higher interior temperature is obtained near the second-stage injector, since all coal slurry was fed at the 2nd stage rather than the separate injection in E-Gas^{TM}. This also led to longer particle resident time at the 2nd

stage for E-STR. Preliminary modification on gemoetry and fed configuration results in completed comsumption of char. For the E-STR, however, due to the changed gaisifer configuration and operating condition, some char will be un-reacted and recycled. Therefore, the reaction mechanisms of char are modified. A comprehensive investigation shows that a 15% char recycling rate leads to reasonable cold gas efficiency (CGE) and outlet temperature without hot spot within the reactor. In the present study, the actual thermal property values of the volatiles are not known, so different condensation and re-evaporation tempertaures are used for paramtric study to test the functionality of the newly implemented volatile condesation and re-vaporation. The result shows that incorporating the tar condensation model results in a formation of about 8 % liquid volatiles and the outlet temperature increases about 355 K, due to the release of latent heat. When the re-vaporization model is implemented, the liquid volatiles evaporate with an amount depending on the setpoint of evaporation temperature. It is concluded that the volatile condensation and re-evaporation sub-modles have been successfully developed and implemented. These sub-models will be useful in the condition that the gasifier temperature is intentionally kept low, like the E-STR gasifer.

Several attempts have been made for reducing the reactor temperature by chaning the feeding mass distribution between the first and second stages, the oxygen/coal ratio and the operation pressure. In the case of feeding mass distribution, 20% coal-slurry is introduced at the 1st stage inlet and char is recycled at the 2nd stage inlet. This modification leads to lower interior temperature near the 1st injector, but higher temperature at the 2nd stage. To test the effect of oxygen/coal ratio, the value is reduced to one half (0.46) compared to that of base case (0.92). The result shows that the temperature at the 1st stage is higher, while the outlet temperature decreases from 1463 K to 1097 K. Furthermore, the case using higher operation pressure (70 atm) results in higher temperature at the 2nd stage, higher mole fraction of H_2 and CO in exit syngas and similar outlet temperature. It can be concluded that reducing the oxygen/coal ratio is an effective way to reduce the reactor temperature. As long as the interior temperature is low enough, the effect of liquid tar would be significant. The molar ratio of H_2/CO is 0.663, 0.716 and 0.929 for the baseline case, the case of 70 atm and the case of reduced oxygen, respectively. The results indicate that high pressure and less oxygen fed lead to more favorable higher H_2/CO ratio for synthetic natural gas (SNG) production.

Dry Solids Pump Program Status

Alan Darby, Aerojet Rocketdyne, USA

Since 2007, Pratt & Whitney Rocketdyne with support from DOE NETL, has been developing a Dry Solids Pump (DSP), and its related feed system hardware, to replace conventional gasification plant lock hopper systems. The DSP represents a unique solids transport design to transition solids feedstock from low pressure day bins to high pressure gasifier feed tanks without lock hoppers or generating a slurry mixture. The DSP reduces plant capital and operational costs over lock hopper systems.

In 2012, DSP testing began with the ultimate goal to achieve 400 ton per day (tpd) capacity while discharging coal into a 1200 psi feed tank. The PCC presentation will summarize the operational theory of the DSP, pictures of pump assembly, compare economic benefits over conventional lock hoppers, and present DSP testing results to date. As the test team approaches the pump design goals, the test data confirms the operational theory of pumping coal into a high pressure tank. The end product is a commercial DSP that can deliver 1000 tpd of feedstock into high pressure feed tanks.

Additionally, a short summary of our demonstration program status will be presented. PWR is pursuing a partnership with a China project developer to host a 400 tpd demonstration plant. The project will demonstrate the integration of PWR’s Compact Gasifier and Dry Solids Pump for future commercial gasification plants.

ITM Oxygen Technology for Clean Energy Applications

Andrew Mak, Edward P. (Ted) Foster, Phillip Armstrong, John M. Repasky,
VanEric E. Stein, Air Products and Chemicals, Inc., USA

In the late 1980’s Air Products identified a family of perovskite ceramic materials with high flux and separation selectivity for oxygen ions. These materials have become the basis for a novel class of air separation technologies, referred to as Ion Transport Membranes (ITMs). Along with partners and through cooperation with the U.S. Department of Energy, Air Products has made substantial progress in developing ITM Oxygen technology into a cost effective method of oxygen production. ITM Oxygen integrates well with advanced power generation processes, as well as traditional energy-intensive industrial processes requiring oxygen.

The team has successfully demonstrated expected performance and required reliability of commercial-scale modules over a wide range of process conditions and operating scenarios in a prototype facility that produces up to 5 tons-per-day (TPD) of oxygen. Next phase pilot unit is being commissioned in 2013. This Intermediate Scale Test Unit (ISTU) is designed to produce up to 100 TPD of oxygen integrated with turbo-machinery and co-production of power. Data from the 100 TPD unit will provide the design basis for a much larger plant that could produce 2000 TPD. In parallel, work is underway to expand ceramic fabrication capacity to support these advancements at commercial scale. Recent studies with U.S.-based Electric Power Research Institute (EPRI) and several power companies have confirmed the economic benefits of ITM Oxygen technology toward large-scale gasification and oxy-combustion applications, as well as traditional energy-intensive industrial applications.

This paper will present an overview and update of the ITM Oxygen development effort, including commercial-scale ceramic modules, next-phase scale-up designs, ceramic manufacturing expansion work, and developing commercial process integrations and economic analyses toward gasification, oxy-combustion, and other energy-intensive industrial applications. A commercialization timeline will be discussed.

Enhanced Hydrogen Production from Steam Gasification of Coal with In-Situ CO_2 Capture in a Pressurized Fluidized Bed

Nai Rong, Qinhui Wang, Hongtao Fan, Yongjie Meng, Zhongyang Luo, Kefa
Cen, Zhejiang University, CHINA

Steam gasification of a typical Chinese bituminous for hydrogen production in a lab-scale pressurized bubbling fluidized bed system with CaO as CO2 sorbent was conducted over a temperature range of 660-750 °C whilst varying gasification pressure from atmospheric pressure to 4 bar. The production gas composition was examined and correlated to the critical gasification variables such as pressure (P), mole ratio of steam to carbon ([H2O]/[C]), mole ratio of CaO to carbon ([CaO]/[C]) and temperature (T). The experimental results indicated that the H2 yield is enhanced by the increasing temperature, pressure, [H2O]/[C] and [CaO]/[C]. The presence of CaO sorbent transferred the CO2 in the production gas to solid CaCO3, thus shifted the reforming and water gas shift reactions beyond the reaction equilibrium restrictions and enhanced H2 yield. H2 concentration was as high as 78vol% (dry basis) under the condition of 750 °C, 4 bar, [Ca]/[C]=1 and [H2O]/[C]=2, while the CO2 (2.7 vol%) was almost in-situ captured by the CaO sorbent. This study demonstrated that CaO could be as a substantially excellent CO2 sorbent for the pressurized steam gasification of bituminous coal. With the presence of CaO, H2-rich syngas was obtained at relatively low temperature and pressure comparing with conventional steam gasification of coal.

SESSION 4
Clean Coal and Gas to Fuels: General - 1

Application of Selective Fischer-Tropsch Synthesis in CTL and CBTL: Slip-stream Evaluation and Technoeconomic Analysis

Santosh Gangwal, Southern Research Institute, USA

This project seeks to advance coal to liquids (CTL) and coal-biomass to liquids (CBTL) processes by demonstrating cost-effective, novel cobalt-based hybrid Fischer-Tropsch (FT) catalysts that selectively convert syngas derived from the gasification of coal and coal-biomass mixtures predominantly to gasoline, jet fuel and diesel range hydrocarbon liquids , thereby eliminating expensive upgrading operations. The project also seeks to evaluate the impacts of adding moderate amounts of biomass to coal on liquid products and CBTL economics, and compare CBTL carbon footprint with petroleum based fuels production processes. This technology development effort is supported by the U.S. Department of Energy. The selective cobalt-based FT catalyst will be provided by the Chevron Energy Technology Company. The National Carbon Capture Center (NCCC) at Wilsonville, Alabama will be the host site for the slip-stream testing and Nexant will support the technical and economic analysis effort. The project will implement a skid-mounted CTL and CBTL bench-scale FT synthesis reactor system to produce liquid transportation fuels. The fixed-bed catalytic reactor system incorporates a high activity catalyst with a novel, highly efficient, heat removal system that enables much higher hydrocarbon productivity per unit volume of reactor versus conventional high alpha FT catalysts. The project will use an existing air-blown transport gasifier (also known as TRIG™) operated by the NCCC to provide slip-streams of both coal- and coal-biomass derived syngas. Southern Research has designed and fabricated the bench scale skid mounted FT reactor system to receive the raw syngas, clean it to cobalt FT catalyst specifications, and produce liquid FT products at the design capacity. Southern Research will carry out a suite of analyses to characterize all liquids from the CTL and CBTL test runs and compare the property differences/similarities and product quality produced by coal vs. coal-biomass blends. A preliminary technical and economic analysis is being carried out to evaluate the relative economics of CTL and CBTL processes and cost reduction due to selective liquid production, and to determine the potential of moderate biomass addition to coal for reducing the carbon foot print of the CBTL process compared to petroleum-based fuel production processes.

Coliquefaction of Lignite, Wheat Straw and Plastic Waste in Sub-Critical Water

Baofeng Wang, Yaru Huang, Shuguang Zhao, Lirong Li, Jinjun Zhang, Shanxi Normal
University, CHINA

Coliquefaction behavior of Jingou lignite, wheat straw and plastic waste in sub-critical water is investigated. The effects of blending ratio of lignite, wheat straw and plastic waste, temperature, initial nitrogen pressure, residence times and additives on product distributions are also studied. The result indicates that blending ratio of lignite, wheat straw and plastic waste, liquefaction temperature, initial pressure, residence times and additives all could influence the product distributions during coliquefaction. When the blending ratio of Jingou lignite, wheat straw and plastic waste is 5:4:1, there exists synergism effect for oil yield, and the oil yield and the gas yield are all the highest at this ratio. The total conversion increases when the temperatureincreases from 260℃to 300℃and then decreases. For the oil yield, when temperature increases from 260℃ to 280℃, oil yield decreases, while when the temperature increases from 280℃ to 320℃, the oil yield increases. The initial nitrogen pressure and residence times influence differentially on the products yield and there are optimal initial nitrogen pressure and residence time for each product to get higher yield. The traditional catalyst for coal liquefaction has no obvious catalysis for coliquefaction of lignite, wheat straw and plastic waste in sub-critical water.

Pressure Influence on the Analytical Pyrolysis of Coals

Christian Berndt, Steffen Krzack, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

Coal is not only of interest for power generation. The limited availability and, associated therewith, rise in costs of crude oil and natural gas makes coal mining more attractive again, since many branches of industry excessively rely on these fossil fuels.
In contrary to gasification, which completely decomposes the structure of organic molecules to permanent gases using them to synthesize compounds of interest, pyrolysis maintains a part of the natural synthesis and the geological refinement of solid fuels. Besides coke, coal tar is an important pyrolysis product that can be used in various industries, for example as source of basic organic chemicals like aromatic compounds for the, at present, crude oil-based petrochemical industry. Therefore, an optimum has to be found between a high tar production and a satisfying tar quality in order to provide commercially relevant hydrocarbons and to assess the applicability of tar for this purpose. Hence, a thorough analysis of all condensable volatile matter, which is released during the conversion process, is necessary and helps processing the tar for subsequent application. On top of that, a detailed study on the composition and chemical structure of coal tar enables to understand the mechanisms of pyrolytic reactions. This knowledge is essential to predict both the behavior of coal during conversion processes and product distribution and compositions via modeling.
Feedstock properties, process conditions, and reactor designs are the parameters, which influence the complex mechanisms of the thermochemical decomposition of coal and therefore the formation of condensable volatiles during pyrolysis. Especially the pyrolysis behavior under elevated pressure and its influence on the chemical composition of tars is a less investigated topic.
Thus, pyrolysis experiments of German brown coals and international bituminous coals were conducted in a mini high-pressure pyrolysis reactor system (Pyroprobe 5200HP, CDS Analytical) directly connected to a GC-FID/MS. This combination of devices allows a fast acquisition of experimental data with a minimum of raw material and reproducible process parameters. Hereby the pressure influence (up to 30 bar) on the formation of gas chromatographic detectable coal tar compounds was determined. It is not possible to detect all components of tars this way, but it includes the determination of compound classes like BTEX, other alkylated benzenes, phenols, alkanes/alkenes, PAH and sulfur containing aromatics, which are of high interest with regard to tar quality. The obtained results of tar composition are considered in regard to the content and structure of organic and inorganic matter of the coals.

SESSION 5
Shale and Coal Bed Gas: General – 1

A Next-Generation Simulator for Unconventional Oil/Gas Production

Dongxiao Zhang, Peking University, CHINA

The increase in the demand of petroleum resources, higher prices, and the newly available and more sophisticated production technologies including the advances in hydraulic fracturing, well stimulation and treatment, have motivated petroleum production companies to operate and develop harder-to-access oil/gas resources such as tight sand, shale gas, shale oil, coal bed methane, and gas hydrates. The production of such resources involves complex mechanisms that are different from those for conventional oil and gas and are thus not included in existing reservoir simulators. In this presentation, flow mechanisms are discussed and a next generation reservoir simulator is presented for unconventional oil and gas production.

Production Characteristics and Stimulation of Low-To-Moderate Coalbed Methane Producing Well: Taking Hancheng Pilot Area as an Example

Shao Xianjie, Dong Xinxiu, Wu Ze, Sun Yubo, Xu Hao, Liu Yingjie, Wang Haiyang, Li Shicai, Yanshan University, CHINA

China coal reservoir is characterized by a high degree of coal metamorphism, complex structure, low porosity and permeability, thin single layer which are most thin interbedded. The high ratio of low-to-moderate producing wells seriously affects the scale development benefit. So it is an urgent matter to improve single well production. Taking Hancheng pilot area as an example, the production characteristics and influencing factors of low-to-moderate producing wells are analysed. The low-to-moderate producing wells can be divided into four types: the wells of medium and low methane without water production; the wells of medium and low methane accompanied by low water production; the wells of high, extra-high production of water without methane production and the rapid decreasig wells. The influencing factors of coalbed methane well productivity mainly include: thin production layer , poor physical property and low potential; the fracture and fault communicate and formation water channels along the fault which restrain the methane production; poor cementing quality and production outside the casing, a large water production because of the shallow water supply; fracturing fracture does not meet the designed scale and the effective seepage radius is small; the unreasonable draining and producing system which causes the permeability stress sensitivity. According to the geological conditions and production performances of different wells, the corresponding technical measures are put forward, including optimizing the development layer series to increase the brought-in layer thickness; using multiple fracturing technology to improve seepage area; implementing casing workover to plug interstratified channels; plugging old wells and drilling sidetracking horizontal wells; optimizaing the draining and producing system to prolong the stable production period. The study results have been applied in the practical production and have achieved good results.

Production Performance Evaluation Index System Construction of Medium- High Rank CBM Wells

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In order to maximize the methane recovery from the coal seam, a set of perfect, scientific, and reasonable evaluation index system of the coalbed methane (CBM) development performance should be constructed, which can guide the compilation and adjustment of coalbed methane development plan and the implementation of stimulation measures. The principles of CBM wells development performance evaluation index system are put forward according to the development practice of China in nearly 10 years. All the indexes parameters reflecting the development performance are listed first of all, then 11 parameters will be eventually determined as the evaluation index after comparing the representative, the importance, the admission difficulty and the correlation degree between these indexes. According to the characteristics of China medium-high coal rank reservoir and the present development situation, the indexes are divided into four grades using quantitative method. Three levels are divided based on the index properties in order to design a reasonable hierarchical structure model and establish the multi-level development evaluation index system. According to the importance of each index to the upper level, by conducting multiple comparisons quantitatively among the indexes, a comparison matrix is constructed to calculate the weights of different indexes at all levels. This paper evaluates step by step using analytic hierarchy process, and finally gets the comprehensive evaluation results of single well. The practical application has achieved good results to provide scientific basis for the development of coalbed methane.

SESSION 6
Clean Coal Demonstration and Commercial Projects: General - 1

Application of Heat-Carrier-Free Regenerative Rotating Bed Technology on Low-Rank Coal Pyrolysis

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Based on the Lab-scale experiments and pilot tests, Beijing Shenwu Environmental & Energy Technology Co., Ltd has researched and developed a new coal pyrolysis technology, Shenwu Pyrolysis Process (SPP) technology, which via heat-carrier-free regenerative rotating bed technology is able to upgrade low-rank coal to obtain three primary products, upgraded coal, tar and gas. SPP can use low calorific value gas (>700 kcal/Nm^3) as fuel through the adoption of regenerative high-temperature air combustion technology. The heat loss in fume exhausted is low (temp. about 150°C) while thermal efficiency is above 85%. The characteristics also include: the large capacity, more than 1 million tpa processing capacity of single furnace; the features of easy heating control that could realize accurate temperature control in zones and sections for the pyrolysis of raw coal; no heat carrier solving some technical problems, such as high dust content in coal tar, likely blockage of pipeline and greatly increasing the subsequent tar processing cost etc. At present, the results of the tests have proved the readiness for commercialization of the SPP process. It has been considered as a world leading advanced technology on the appraisal meeting organized by the National Department of Energy in China in 2012. Meanwhile, different commercial projects of SPP used to pyrolyze low-rank coal, municipality waste and scrap tire are under construction.

US-China Advanced Coal Technology Consortium, US-China Clean Energy Research Center: Research Direction and Program Overview

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In November 2009, President Barack Obama and President Hu Jintao announced the establishment of the $150 million U.S.-China Clean Energy Research Center (CERC) to be funded equally by the two countries to support cooperative work in their individual countries. The Protocol formally establishing the Center was signed at ceremonies in Beijing by U.S. Energy Secretary Steven Chu, Chinese Minister of Science and Technology Wan Gang, and Chinese National Energy Agency Administrator Zhang Guobao. The CERC was designed to significantly improve the cooperation between the two countries in energy research and development in the areas of clean coal technology and carbon capture, sequestration and storage; clean vehicles; and building energy efficiency. In August, 2010, the USDOE announced the selection of the Advanced Coal Technology Consortium led by West Virginia University as the U.S. participants in the CERC for coal related issues; the China team was announced later that fall and adopted the same name. Initial five year joint work plans for the U.S. and China participants in all three areas were signed on January 11, 2011 during President Hu Jintao's visit to the U.S.

Since that time, the ACTC has made significant advances in developing new approaches to intellectual property (IP) management and collaborative research efforts. The research issues are broken into eight themes: Advanced Power Generation; Clean Coal Conversion Technology; Pre-Combustion CO_2 Capture; Post-Combustion CO_2 Capture; Oxy-Combustion Technology Development; Evaluation Technology of CO_2 Geological Storage Sites; Carbon Dioxide Utilization with Microalgae; and Systems Integration, Simulation and Assessment. In addition, the ACTC has included significant activities related to IP management and development and other communication and integration tasks.

Activities to date include some dominated by Chinese participants and some by the U.S. team. We are now seeing increasing activity in areas of mutual interest that are truly collaborative. The long-term value of the CERC and the opportunity for mutual benefit will depend largely on the value of the collaborative activities now underway.

This paper provides an overview of the program from the beginning through the midpoint of the initial five year project plan. It also provides an overall assessment of the program as well as a perspective from the leadership of both the China and U.S. consortia. The CERC has broken new ground in research relationships between the two countries; this presentation will lay these out and provide an opportunity for discussion of the path ahead.

U.S. Department of Energy's CCS Demonstration Projects

Gary J. Stiegel, Thomas A. Sarkus, DOE/NETL, USA

In 2009, President Obama made a commitment to reduce greenhouse gas emissions in the U.S. by 17% below that emitted in 2005 by 2020. Last year, the U.S. emitted 5.29 billion metric tons of CO_2 to the atmosphere. Of that, nearly 38% (2.039 billion metric tons) was emitted by the electric utility industry while 30% (1.48 billion metric tons) was emitted by the industrial sector. To assist in achieving the President's near-term goal and to position the country for large scale reductions in CO_2 emissions in the future, the U.S. Congress appropriated funding to the Department of Energy (DOE) to pursue large-scale carbon capture and sequestration (CCS) demonstration projects both for the utility and industrial sectors. Currently, the DOE is co-funding the development of eight large scale demonstration projects. Of these projects, one is an integrated gasification combined cycle (IGCC) plant, two are IGCC polygen plants, one is an oxy-combustion plant, and three involve the capture of CO_2 from industrial facilities. All but two of the projects will use the captured CO_2 for enhanced oil recovery while the remaining two will sequester the CO_2 in a saline reservoir. This presentation will provide a summary of each project and its current status.

US-China Efforts on Financing the Texas Clean Energy Project

Cynthia Wang, China International Capital Corporation Limited, CHINA; Eric Redman, Summit Power Group, USA

The Texas Clean Energy Project is a first-of-its-kind "poly-generation" coal gasification project with carbon capture. TCEP's three major commercial products are ultra-low carbon electric power, urea for fertilizer, and captured carbon dioxide for enhanced oil recovery in the Permian Basin of West Texas. Even though the individual components of TCEP represent commercial proven and/or warranted facilities and equipment, the integration of these components into a single plant producing three major but very different products presents unique challenges for financing. The US Government has provided significant direct financial support to TCEP, as have other Western contractors and investors. In 2012, the Summit Power Group as the developer of TCEP turned to China to help complete the project financing. Cynthia Wang, Managing Director of China International Capital Corporation, has led the effort to bring Chinese debt and equity to the project. She will describe some of the challenges involved, as well as the strategies chosen for dealing with them.

SESSION 7
Coal Science: General - 1

Purification of Crude Coal Benzene by Ozonization in Presence of Oxide Catalysts

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For production of pure benzene from crude coal benzene, the latter has to be purified mainly from sulfur containing admixtures and unsaturated compounds. At present the method of catalytic hydrotreatment on the aluminum-cobalt-molybdenum catalyst (ACM) is applied worldwide to decrease the content of impurities in benzene. The goal of this work was to establish the influence of ozonolysis in the presence of metal oxides on the composition of crude coal benzene.

In the experiments the crude benzene (CB) of Russian Technical Specifications 1104-241419-395-167-2001 was used. The ozonization was carried out at atmospheric pressure in the temperature controlled bubble type reactor with continuous supply of an ozone-oxygen mixture into CB in the presence of metal oxides: CuO and NiO. Ozone was produced by an OGVK-02K ozone generator of MELP Company, St. Petersburg. The process was conducted at ozone concentration in oxygen 30 mg/l, temperature 25°C for 1 hour. The volume of the processed CB was 50 ml.

The process of ozonization of crude benzene was accompanied by intensive formation of oxygen containing products and hence an increase of the acid number. Thus, the color of the liquid changed from initial bright yellow to the bright orange. As a result of ozonization a decrease of the content of unsaturated and sulfur compounds in the product was noted. For example, the value of a bromine number which characterizes the presence of products of compounds with unsaturated C=C bonds decreased by 37% at CB ozonization in the presence of CuO, and by 78% after the ozonization with NiO. The concentration of carbon disulfide, which makes the main share of sulfur-containing components in CB, decreased by 98% in both cases.

The data obtained by chemical methods were confirmed by the results of IR spectroscopic study. Absorption bands of CH=CH bonds (880-900 cm^{-1}) were practically indiscernible in case of CB ozonization in the presence of CuO and NiO as in the case of analytical grade benzene. Slight absorption of C-H aliphatic groups can be due to small amounts of monoalkylsubstituted benzenes, such as toluene. Weak absorption at 480 cm^{-1} can be caused by the presence of sulfur compounds. It was established that the application of the method of benzene purification with ozone resulted in obtaining the product similar by IR spectra to the analytical grade benzene.

Thus, on the basis of the obtained results it is possible to conclude that the use of ozonolysis in the presence of metal oxides promotes an increase of the content of the target benzene component in CB and a decrease of the contents of undesired by-products. The used transition metals oxides exhibited certain catalytic activity. On the whole, the obtained results show promise and call for continuation of the research.

Effects of Heating Rate and AAEM on the Production of NH_3 and HCN during Pyrolysis of Shengli Brown Coal

Shu Zhang, Yanping Bai, Panpan Zheng, Yonggang Wang, Deping Xu, Lei Bai, China University of Mining and Technology (Beijing), CHINA

This study is to examine the effects of heating rate and AAEM (alkali and alkaline earth metallic species) on the generation of NH3and HCN during the pyrolysis of Shengli brown coalsat two different temperatures of 773 and 1073 K.All the experiments were conducted in a fixed-bed/fluidised-bed quartz reactor. The results show that high heating rate and high temperature have substantially promoted the formation of both NH3 and HCN. By comparing the results from raw coal and acid-washed coal, it was found that reduction in AAEM (mainly Na and Ca in this case) could lead to less production of NH3, but more formation of HCN.

Mechanism of Interaction between Surfactants and Surface Functional Groups of Jincheng Coal by XPS Analysis

Zhiyuan Yang, Xiaoyuan Ren, Kun Zhang, Xi'An University of Science and Technology; BaoShan Guan, Branch of Langfang of Research Institute of Exploration and Development of Chinese Petroleum, CHINA

Coalbed methane (CBM) is a kind of clean energy and CBM is adsorbed in coal seam. The surfactants are widely used in CBM drilling and completion. The intensive research on the utilization of surfactants-based product in coal technology is in progress in many laboratories. Jincheng coal has been modified by treating with several kinds of surfactants such as anionic surfactant sodium dodecylbenzene sulfonate (SDBS), cationic surfactant cetyl trimethyl ammonium bromide (CTAB), non-ionic surfactant polyoxyethylenenonylphenyl ether(TX-10), and amphoteric surfactant Cocoamidopropyl Betaine (CAB). The impact of surfactant adsorption on Jincheng coal has been investigated. Jincheng coal was crushed into a fine powder and immersed in different surfactant solution of certain concentration for 48h, respectively, then were filtered and dried in vacuum before analyzed. The chemical compositions of the samples were monitored by X-ray photoelectron spectroscopy (XPS) after treated by different surfactants. C1s XPS spectra can be decomposed into four components corresponding to carbon atoms in different oxygen-containing functional groups, non-oxygenated C-C, carbon in C-O, carbonyl carbon C=O and carboxyl carbon O=C-O (COOH). The results show that the main form of carbon-functional groups is C-C on the coal surface. The C1s XPS spectra of the surfactant-treated (SDBS, CTAB and TX-10) coal shows the same functionalities but with less content of C-C and higher oxygenated carbons. The phenomenon indicates that surfactant-treated coal has much more oxygen containing functional groups. While the sample treated by CAB has a similar C-C content compared with raw coal, and the O1s XPS spectra analysis is basically identical with that of C1s XPS spectra. The results can be useful in studying other surfactant adsorption coal systems.

Change of Physical Structure and Hydrophilic Oxygen-Containing Functional Groups in the Process of Lignite Drying

Xiaoxia Jing, Xiao Liu, Zhiqiang Li, Yunlong Yang, Liping Chang, Weiren Bao, Taiyuan University of Technology, CHINA

The low rank coals with relative abundant reserve, especially lignite, have been playing an increasingly important role with the shortage of high quality coal resources in the worldwide. However, the using range of lignite is largely limited because of its high moisture content, low heat value and easy re-adsorption after drying. It is necessary to upgrade lignite prior to the large-scale effective utilization.

Some literatures have shown that the existence of plentiful pore structure and hydrophilic oxygen-containing functional groups lead to the characteristic of high moisture content and easily re-adsorbing of dried lignite. The physical structure and surface active groups of lignite involve irreversible changes after the removal of the moisture, which has a significant impact on re-adsorption of dried lignite. Current research mainly focuses on the drying technology of lignite, but the association between the change of physical and chemical structure during the process of drying lignite and the behavior of moisture re-adsorption of dried sample has still no comprehensive understanding.

Lignite from Chinese Huolinhe mine was firstly dried in a fixed-bed reactor in the presence of argon (400ml/min), and then the moisture re-adsorption of dewatering coal from different drying temperature and time was investigated in the constant temperature and humidity chamber. The effects of drying temperature (80-160^{o}C) and time (5-70min) on lignite drying efficiency and the re-adsorption behavior of dried coal were associated with the changes of physical and chemical structures during the drying process, which were detected by nitrogen adsorption and in-situ infrared instrument, respectively. The changes of surface area, pore volume and the amount of hydrophilic oxygen-containing functional groups with drying temperature and time were specifically analyzed. With increasing drying temperature and time, the drying efficiency significantly increased. The higher the drying temperature is, the shorter the equilibrium time is. The re-adsorption characteristics of dried lignite under different drying conditions are significantly different, and this is related to the drying degree of coal and the level of physical and chemical structure changes. Since the collapsing of vacated pore during drying process, surface area and pore volume of lignite are reduced to varying degrees. Carrying on peak fitting for in-situ IR spectrum, the relative changes of hydrophilic oxygen-containing functional groups were analyzed in detail and associated with the re-adsorption amount of dried lignite.

SESSION 8
Coal Mining:
Ground Control in Mining - Session 2

Development and Application of Resin Capsules in Chinese Coal Mines

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Development and application of resin capsules in Chinese coal mines were introduced in this paper and the category, feature, applicability and basic parameters of resin capsules were elaborated. The paper pointed out that unsaturated polyester resin capsules were the most widely used and the largest amount in Chinese coal mines. A kind of newly-developed low-viscosity resin capsule was applied to industrial test in Fengshuigou Colliery at Pingzhuang which had a water-resistant performance and were used for full-length anchorage, and the results showed that the high pre-stress and intensive bolting system could effectively control the violent displacements of the surrounding rock, and it provided an effective approach for the support of soft rock roadway. Finally the future developments of resin capsules were prospected.

Research on the Waterproof Coal Pillar Design for Coal Seam Group Mining Goaf

Yu-jun Zhang, Tiandi Science & Technology Co., Ltd, CHINA

The Xinqiang mine is the close distance coal seam group mining, which distance is about 20~30 meter. Because the disordered mining of the small coal mine early and unreasonable exploitation mode of itself, the mine has appeared multiple cracks and collapse pit on the surface, and mining areas were communicated with each other, connected network complex formed between the upper and the lower coal seam gob. With the mining depth increasing, the formation of shallow mining goaf water has become a major threat water to the deep extension of mining. Based on the actual situation of coal mining, The water retaining wall have been set on the connectivity of shallow mining area, which objective is to partition the hydraulic connection between the mining and the other undeveloped mining. In order to ensure the safety of deep mining, The reasonable security isolation coal rock pillar were set for overlying coal seam and side seam goaf water area , and determine the deep coal mining upper limit, to realize the safe mining of close coal seam mining under goaf. Research results show that: the key to the feasibility of mining the deep were the strength and resistance to water pressure of water sealing and the coal seam group mining failure coverage and degree. Only both the roof waterproof safety pillars and the same seam water pillar would consider, the deep mining feasibility and safety were ensured.

Synthesis Grouting and Anchoring Reinforcement Application in Deep Roadway

Wenzhou Li, China Coal Research Institute, CHINA

Taking synthesis grouting and anchoring reinforcement way of deep deformation roadway as project background of Lu'an coal mining district in China The reasons of invalid supporting way were analyzed; various factors of grouting that influenced to supporting were analyzed by means of numerical simulation. The underground test was introduced in detail, including grouting materials, grouting characters, supporting characters and monitoring data. Then the results of synthesis grouting and anchoring reinforcements were evaluated by peeping, roadway convergences and bolts load. Based on the results of studying, a new way for roadway repaired was put forward for deep roadway effectively.

Mechanical Site-Monitoring to Shotcrete Layer of Soft Rock Main Roadway Supported by Bolt-Shotcrete

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Based on the soft rock, water-trickling and hard-maintain difficulty conditions of main air-return roadway in Tarangaole Colliery,high pretension stress and intensive bolt-shotcrete support program was designed and mechanical property of shotcrete layer was specially monitored through utilizing a type of concrete stress meter with oscillating chord after the program was carried out in the roadway. It is indicated that the interior of shotcrete layer will emerge diverse stresses in axial, radial and tangential direction and its exterior will emerge contact pressures when the shotcrete layer gets in touch with surrounding rock and the earlier layer. With time prolonged, internal stresses in three directions whose average values were 0.517MPa, 0.043MPa and -0.059MPa respectively fluctuated and tended to stability. Nevertheless, two kinds of external contact pressures which were all compressive increased earlier and remained stable late while contact pressures of layer-surroundingrock were 0.266MPa and those of layer-layer were 0.648MPa averagely. Spatially, along the section of roadway, all of internal stresses distributed symmetrically and increased gradually from the top of arch to the waist of wall, but stresses in the foot of wall reduced partly. However, external contact pressures increased gradually from top to bottom and distributed unevenly along the surrounding of roadway. During the period of roadway excavating, the stress of shotcrete layer was less than its ultimate bearing capacity and the deformation of shotcrete was limited. The two aspects show that High Pretensioned Stress and Intensive Bolt-Shotcrete Support technology meets the surrounding rock control requirement of main air-return roadway in Tarangaole Colliery.

Study on Backfill-Mining with Aeolian Sand in Coal Mine at Desert Border/ Present Application Status of Coal Backfill in China

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Coal mining with backfilling has been widely used in China in the last ten years, Backfill-mining is an effective measure to mine coal resources under buildings and water-bodies and to realize green mining. On the basis of discussing backfill-mining technology in China, backfill-mining is classified into three types according to different backfill materials: bulk backfill, paste backfill and high-water backfill, which are described from the backfill materials, equipments, technologies and effects with the practical applications for example. Finally, restraining factors of backfill-mining and those countermeasures in China are proposed.

Coal occupies a significant position in the energy structure in our country, which accounts for about 70% in the energy consumption. Driven rapidly by the requirement, raw coal production is increasing at high speed, reached 3.24 billion tons in 2010, and ranked first in the world. Meanwhile, there are lots of issues in the process of coal mass-production and utilization, such as the rapid moving of the mine activities, coal mining under buildings, railways and water-bodies being badly in the need of solution; lower recovery, serious waste; mass destruction of the earth’s surface zoology and ground water; prominent issue of subsidence which poses the difficulties of comprehensive ecological improvement (Qian et al., 2003). Therefore, backfill-mining is proposed in proper regions so that harmonious development can be realized between coal mining and environment.

Backfill technology is a kind of roof controlling technology, using sand, macadam, slag and so on to fill gob in order to support surrounding rock, prevent or lessen its caving and deformation(Xu, 2003). In the last decade, Xingtai, Fengfeng, Xinwen, and fuxin mining groups proceeded the application of backfill-mining in order to recover coal resource under buildings and water-bodies, or dispose wastes such as coal waste. According to different backfill materials, backfill technology can be classified into three types in China: bulk backfill, paste backfill (paste-like backfill) and high-water backfill.

SESSION 9
Gasification: General – 2

Experiments and Simulation of Pressurized Ash Agglomerating Fluidized Bed Gasifier

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Coal gasification is still one of the most important technologies for high-efficiency coal utilization. The fluidized bed gasification has emerged as a promising technology to convert small sized crushed coal into fuel or synthesis gas. In particular, ash agglomerating fluidized bed (AFB) gasifier, developed by Institute of Coal Chemistry, Chinese Academy of Sciences, is an effective means to handle most of commercial coal with high ash content and high ash fusion temperature. Recently, a large pilot scale pressurized gasifier with a designed pressure (3 MPa) has been put into operation for many experimental studies. During gasifier development and process optimization, the model development is valid and helpful to reduce the technical and financial burden. In addition, the application of large scale pressurized AFB gasifier needs the support knowledge from simulative investigation of pressurized gasification process. The simulation of coal gasification performance in this pressurized AFB gasifier is also studied in this paper. Both hydrodynamics and reaction kinetics are considered simultaneously to yield a predictive model for pressurized AFB gasifier based on a combination of ASPEN PLUS and FLUENT software. Because the hydrodynamic parameters and reaction kinetics have been inserted into the model, few model input parameters are needed. Although various conditions will affect the hydrodynamic parameters, the model variables will be modified automatically in hydrodynamic correlations coupled with the powerful physical property database in ASPEN PLUS. So this advantage makes the model suit for different kinds of operating conditions and coal types in AFB gasifier if coal gasification reaction kinetics is available. Different sets of pilot-scale experimental data are used to validate this model. The model predictions are in good agreement with experimental data at syngas composition, carbon conversion, high heat value, cold gas efficiency and dry gas yield. In order to assist with the design, optimization and scale-up of the AFB gasifier, the effects of different operating conditions on gasification performance have been studied in this work.

Kinetic Studies for CO_2 Gasification of HOK Coke using Thermogravimetric Analyzer

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Gasification is an essential step in the process of energy production using coal. Deeper understanding of the kinetics of gasification facilitates efficient utilization of feedstock. Many parameters influence the gasification process such as the gasification temperature, pressure, coal composition and particle size. Many approaches to describe the gasification process have been previously discussed and models were developed in order to predict the gasification process. However, the precision of every model can be influenced by process parameters. The usage of cokes in this investigation of models helps to avoid the complexity of the pyrolysis step and its overlapping effects on the gasification. In this study, we used the high quality Herdofenkoks (HOK) coke from a german power generation company and thermogravimetric analyzer (TGA) to investigate different models of gasification by changing reaction temperature and CO_2 pressure. Furthermore, the usage of TGA (from the company Rubotherm) is relatively rapid, provides highly accurate plots and allows performing experiments under high pressures and temperatures. The parameters of gasification kinetics (i.e. activation energy and the reaction rate constant) for each studied model were calculated and characteristics of our coke were compared in each case accordingly.

Alkalis K/Na Migration Rule during Coal and Biomass Co-Pyrolysis Process

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Alkali metals can catalyze the coal gasification to decrease the gasification temperature and improve the gasification efficiency. But in the coal catalytic gasification process, the main problem is the higher cost owing to the alkali metals corrosion and the alkali metals regeneration. Additionally, during biomass thermal treatment, large amounts of alkali metals will be volatilized to gas phase resulting in the deposit formation and reactor corrosion. Thus, it is a good way to use the biomass alkali metals to catalyze the coal gasification. In our previous studies, it was found that the alkali metals in biomass tended to transform from the biomass to coal char in the coal and biomass co-pyrolysis process. In this paper, the influencing factors of the alkalis K/Na migration from biomass to coal char during coal and biomass co-pyrolysis process and the mixture char’s catalytic behavior was investigated. The minerals in coal favored the alkali metals K/Na in biomass trasferring to coal char in the co-pyrolysis process. Additionally, both the higher pyrolysis temperature and the small coal particles could enhance the alkali metals K/Na in biomass transformed to coal char. From the TGA results of the mixture char, the higher alkali metals K/Na contents in the mixture char is beneficial to the higher mixture char’s gasification reactivity.

Design, Modeling and Characterization of an Entrained Flow Reactor for Pyrolysis/Gasification of Coal and Biomass

Sarma V. Pisupati, The Pennsylvania State University and DOE/NETL; Aime Hilaire Tchapda, Vijayaragavan Krishnamoorthy, Nandakumar Krishnamoorthy, The Pennsylvania State University, USA

Accurate determination and description of chemical kinetics of solid fuels during combustion/gasification is an important factor in not only describing with accuracy their subsequent high-temperature chemistry, but also for commercial system design and optimization. Generally laboratory scale reactors are used to determine the kinetics. A high-temperature, high-pressure entrained flow reactor is being built at the Pennsylvania State University to study the pyrolysis and gasification kinetics, mineral matter transformations and interactions of coal and biomass ash with refractory materials. This paper describes the design, modeling, and construction details of two (feeder and main reactor) components of the reactor system. A coal and biomass feeder to feed the fuel into a high-pressure unit has been designed and built in house. An Eulerian approach or “two fluid” method was used to model the flow of particles in the feeder during the design. Simulation results that were carried out using Ansys – Fluent are presented and discussed in this paper. The feeder has been tested for both coal and biomass of various particle sizes. The flow of particles in the feeder was controlled by a vertical auger. The feeder was able to achieve the maximum feed rate of 5 g per minute of coal, 1.2 g per minute of switch grass, and 0.9 g per minute of sawdust with 10 L per minute of transport gas. No segregation of particles was observed when feeding mixtures of coal and biomass. The main reactor tube consists of a ceramic tube of 63 mm ID and 700 mm in length. The gas flow and the heat transfer simulations in the reactor were carried out using COMSOL software. The pyrolysis gasification modeling and simulation was carried out using Ansys-Fluent software feeds for separate feeds of coal and biomass. The modeling and simulation results are presented and compared in this paper with experimental data obtained in the reactor. The calculated residence time for fuels in the reactor was 0.5 s for coal and 0.3 s for biomass particles. Some recirculation of particles was observed at lower gas flow rates in the simulation results. Experimental data indicated that the conversion rate is highly dependent on particle size, ranging from 12 to 55% for coal and 30 to 70% for biomass within the residence time.

Influence of Devolatilisation Conditions on Char Chemical Structure and Intrinsic Reactivity

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Raman spectroscopy has been widely used to study chemical structures of chars and further our understanding of their behaviour under combustion and gasification conditions. This paper explores the impact of devolatilisation conditions (heating rate, temperature, pressure and residence time) on char intrinsic reactivity. Chars were made at 900°C and 1100°C using slow (0.1°C/s) and rapid (1000°C/s) heating rates, and 1 bar and 20 bar pressure. These chars were characterised for their surface area (using N2 and CO2 adsorption), and Raman spectra were used to understand the impacts of devolatilisation conditions on ratios of small to large features of the carbon matrix. The intrinsic reactivity behaviour of these same chars was then determined using a pressurised thermogravimetric analyser (TGA)

Overall Raman intensities of slow heating rate, long residence time chars were significantly less than those for chars made under fast heating rates with shorter residence times. Increasing pyrolysis temperature also led to a reduction in total peak area for chars from both coals, giving some insights into the effect of temperature and residence time on chemical functional groups present in char. There is also a greater ratio of small to large aromatic ring structures in the lower temperature chars, and in the chars made with faster heating rates and shorter residence times. These effects on the ratios of small to large structures are shown to be consistent with their impacts on intrinsic reactivity.

The effects of devolatilisation pressure were less clear. Increasing pressure has led to a decrease in total Raman intensity for chars from the lignite, and an increase for chars from the bituminous coal. This was accompanied by some impacts of devolatilisation pressure on reactivity, whereby the higher-pressure char was more reactive (on an apparent and intrinsic basis) than the atmospheric pressure char. Clearly, the effects of pyrolysis pressure are complex, and warrant further work.

SESSION 10
Clean Coal and Gas to Fuels: General - 2

Carbon Fibers Preparation by Low-Molecular-Weight Fraction Obtained from Low-Rank Coal or Biomass by Degradative Solvent Extraction

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Carbon fibers, as a high value-added carbon material, can be used widely for various purposes. However, the practical utilization of carbon fiber is limited by its high price which was caused by the high cost of its feedstocks as well as manufacturing cost. We have proposed a degradative solvent extraction method to separate various types of low-rank coals and biomasses to several fractions under mild condition. The low-molecular-weight fraction (LMWF), obtained in around 30% yield, can soften and melt completely at around 100oC like pitch. In this study, the LMWF was proposed to be used as low-cost precursor for carbon fiber preparation. The possibility was shown by the preliminery experiments. The LMWF spnning was performed easily because of the low softening/melting point of it. The spun fibers were then extracted by cyclohexane at room temperature to remove light fraction and stabilized by thermal treatment in air for aroud 10 h from 50 oC to 330oC. The final carbon fibers were obtained by carbonizing the stabilized fibers at 1000 °C for 1 h in N2. The diameter of the carbon fiber obtained was around 5 μm. The carbon content and oxygen content of the final carbon fibers were respectively higher than 92% and round 6.0%, similar to those of commercial carbon fiber. Thus, the LMWF obtained from low-rank coal or biomass by degradative solvent extraction can be a low-cost precursor for carbon fiber preparation.

Extraction and Analysis of the Phenolic Compounds from Coal Tar Oils

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Coal tar received from pyrolysis process of low rank coal at a relative mild temperature (500-550^{o}C) contains significant amount of phenolic compounds, which are high valuable to specialty chemical industry. However the composition of coal tar varies along with the source of coal and the pyrolysis process. Detailed analysis of the phenolic contents is essential for developing the proper process of phenols extraction and performing the fair economic evaluation of the coal tar oils.

In this study, phenolic compounds in two coal tar oils received from the pyrolysis of two low rank coals, Shenmu long-flame coal and Hulunbeir lignite (denoted as Shenmu coal tar and Hulunbeir coal tar, respectively) are investigated by both GC-MS analysis and lab extraction experiments. GC-MS analysis discloses that the phenolic compounds are enriched in the distillation fractions with boiling point below 260 ℃ (marked as phenol oils) of the both coal tar oils, but showing the notable difference in the overall concentration and species distribution. The overall content of phenolic compounds in the phenol oil takes 7.48% weight of the Shenmu coal tar (dry base), while maintains as high as 16.15% weight of Hulunbeir coal tar (dry base). The distribution analysis indicates that the content of long chain alkyl (C3+) substituted phenols is notably high as 22.63% weight of the total phenolic compounds in Shenmu phenol oil, while the content of dihydric phenols is unexpected high as 11.78% weight in the counterpart from the Hunlunbeir phenol oil. The lab phenol extraction with NaOH solution disclosed that almost all the phenolic compounds from the Shenmu phenol oil were extracted, however only 72.03% of the overall phenolic compounds in the Hulunbeir phenol oil were extracted. The significant variation in the extraction yield is caused by the content of dihydric phenols, which are relative low active to react with NaOH solution.

Influence of Liquefaction Conditions on Molecular Composition of Coal-Derived Liquids

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Characterization studies have shown that coal-derived liquids (CDL) are highly aromatic and have high polynuclear aromatic hydrocarbon (PAH) content. To produce on-specification transportation fuel from CDL, the aromatic content has to be reduced to 37% for diesel fuel and 21% for jet fuel. A high PAH concentration is also not desired in an aromatic gasoline blend. Coal-derived liquids, therefore, have to be hydrogenated. However, as the degree of condensation of PAH in CDL increases, the severity of hydrogenation required to reduce the aromatic content to desired levels increases. This has a negative impact on the economics of refining CDLs. Physical properties of coal liquids, such as viscosity, has been shown to be dependent on liquefaction conditions of temperature and time. This study was carried out to understand the impact of liquefaction conditions on the molecular composition of CDLs and in particular on the aromatic composition.

Thermal digestion of a Canadian lignite coal was performed in an autoclave reactor. An industrial hydrogenated coal tar distillate was used as solvent with a coal to solvent ratio of 1:2. Digestion was carried out under initial Hydrogen pressure of 4MPa at different temperatures and for different lengths of time. The reaction time was divided into two periods: heat-up time; the time required to heat the reactor from 25 ^{o}C to the operating temperature, and hold time; the time at the operating temperature before being cooled down. The tetrahydrofuran (THF)-soluble portion of the product was collected for analysis.

Preliminary results show that the micro carbon residue (MCR) content of the THF-soluble liquids increased from 1.6 wt% at 350 ^{o}C to 6.74 wt% at 415 ^{o}C when the hold time was 0 minutes. No significant increase in MCR was observed as the reaction temperature was increased to 450 ^{o}C, when the hold time was 0 minutes. An increase in the hold time from 0 minutes to 15 minutes resulted in an increase in the MCR content from 4.55 wt% to 6.33 wt% at 400 ^{o}C and from 6.7 wt% to 8.44 wt% at 450 ^{o}C. MCR content further increased to 17.9 wt% when the hold time was increased to 30 minutes at 450 ^{o}C. This is suggestive of an increase in concentration of heavier molecules in the liquids as the reaction temperature and hold time increases. High Performance Liquid Chromatography (HPLC) analysis reveals that the mono-aromatic and di-aromatic content decreased as the reaction temperature increased from 350 to 450 ^{o}C. This was accompanied with an increase in heavier PAH as well as the formation of new species of heavier PAH. Given that homolytic bond cleavage increases as reaction temperature increases, heavy PAH content is expected to decrease as reaction temperature increases. However, preliminary results indicate an increase in free radical recombination reactions and hydrogen disproportionation reactions as the liquefaction temperature increased from 350 to 450 ^{o}C. In a typical experiment, a 1.6 wt% reduction liquid yield was observed as the hold time increased from 15 minutes to 30 minutes at 450 ^{o}C. An increase in heavy aromatics content would be understandable if liquid yield increased, as this will imply a tradeoff between yield and quality. However there is an indication that increasing the severity and time of thermal digestion of lignite coal results in lower yield and quality of coal liquids.

SESSION 11
Shale and Coal Bed Gas: General – 2

An Experimental and Numerical Study of Gas Transport and Imbibition Processes in Coal Matrix

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The mixed transport and imbibition processes of gas in the coal seams are the fundamental phenomena in the process of CO_2 sequestration in unminable coal seams and Enhanced Coal Bed Methane (CO_2-ECBM) production process. The gas imbibition and transport processes in a water-wetted matrix-plug (cleat-free) under a confined stress of 20 MPa were experimentally investigated by applying pressure gradients of different single gas (He, Ar, CH_4 and CO_2) over the matrix-plug and monitoring the gas pressure changes with time in the closed up- and down-stream compartments. It was found that different gases presented different up- (P_1) and down-stream (P_2) pressure curves, which reflected the differences in their flow rates and imbibition mechanisms through the plug. In order to explain the experimental data and understand quantitatively the imbibition and transport processes, simple numerical approaches were established, in which two mechanisms, including gas dissolution and diffusion in the pore water, and gas sorption and diffusion in the coal matrix were considered. Unipore models (homogenous medium) with a linear boundary and a Langmuir sorption boundary were applied to interpret these two mechanisms, respectively. It was found that He diffuses through the micropores which are inaccessible to water in the matrix-plug, while Ar, CH_4 or CO_2 travels in the matrix-plug mainly with a combined process of sorption and diffusion. The effective diffusion coefficients of He, Ar, CH_4 and CO_2 in the matrix-plug were 6.6×10^{-10}, 7.5×10^{-13}, 5.0×10^{-13} and 1.2×10^{-12} $m^2\cdot s^{-1}$, respectively. It seems that both Knudsen diffusion and surface diffusion govern the transport of He and Ar, CH_4 and CO_2 in the matrix-plug.

Methane Adsorption Capacity of Coals: Novell Research by Low-Field NMR

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Methane adsorption capacity of coals is a key parameter in evaluating in-place gas resources and production potential of coalbed methane reservoir. As a conventional and standard method, the volumetric isothermal adsorption analysis of coal cores is commonly used for analyzing the methane adsorption capacity. Low-field nuclear magnetic resonance (NMR) is a relatively new technique used in logging and in the analysis of fluids contained in reservoir rocks, and it provides non-destructive analytical method of detecting hydrocarbons in reservoirs and characterizing the hydrocarbon gas. This paper investigates the potential for coal adsorption capacity characterization by low-field NMR.

A new experimental setup was assembled by integrating a modeling gas adsorption apparatus and a NMR measurement instrument. Methane isothermal adsorption experiments were performed for dry power and block samples by using the setup. The adsorption experiment was performed for eight experimental pressures for each sample, with the uppermost pressure of 7.82 MPa. The experimental result for free methane gas shows that the amplitudes of transverse relaxation time (T2) spectra are linearly correlated with the experimental pressures. This means that the mass of bulk methane is directly proportional to methane T2 amplitude, and thus bulk methane can be estimated by using the methodology. The modeling adsorption experiment suggests that a small amount of surface relaxation amplitude can be observed at T2 ranging from 0.1 to 1 ms. This might contribute from the adsorbed methane on coal. It was also found that a change of signal amplitude of adsorbed methane with increasing methane pressure in coal samples. Unlike the relationship between mass of bulk methane and T2 amplitude, the amplitude of T2 spectra of adsorbed methane increases with the increasing pressure to a very limited extend at the methane pressure up to 6.24 MPa, where the T2 amplitude hardly increases with increasing pressure. The result of NMR experiment for gas adsorption shows that methane isothermal adsorption follows the Langmuir adsorption equation, which is consistent with the result of conventional volumetric isothermal adsorption method. Moreover, the results of adsorption capacity analyzed from NMR method were also compared with those from volumetric adsorption method, by using same experimental pressure sets for a medium volatile bituminous coal sample. The Langmuir volume value obtained from NMR is 15.11 m^3/t, which has a 32% underestimation of the value when comparing with that of 22.30 m^3/t for conventional method. A possible reason is that the volume of specimen chamber for gas adsorption is not well coincident with the domain of magnetic field for NMR analysis in this study. The low-field NMR method is applicable for characterization of adsorbed methane by NMR, and it also provides possible for adsorption isotherm and gas content measurements of coals.

Evaluation of the Coalbed Methane Potential of Coal Reservoirs in Weibei Coalbed Methane Field, Southeastern Ordos Basin, China

Taotao Yan, Dameng Liu, Yanbin Yao, China University of Geosciences, CHINA

Coalbed methane (CBM) potential evaluation is one of the most important element tasks for target area choosing in the process of exploration and development of coalbed methane (CBM). In order to better understand the geological controls on coalbed methane (CBM) in Weibei coalbed methane field, southeastern Ordos basin, China, geological surveys and laboratory experiments were conducted. The geologic structures, coal-bearing strata, coal depositional environment and basin hydrodynamic factors were studied by both field geological research and laboratory tests. A Fuzzy analytic hierarchy (AHP) model for CBM evaluation was used to evaluate the CBM resources in this research. The best prospective targets for CBM production are likely located in the northeast and central Hancheng districts.

Coal Reservoir Fracturing Process and the Acoustic Emission Response Based on the Development of Coalbed Gas

Zhifeng Yan, Yiwen Ju , Quanlin Hou, Xiaoshi Li, Guochang Wang, Liye Yu, University of Chinese Academy of Sciences; Shuheng Tang, China University of Geosciences, CHINA

Coal reservoir fracturing is an important method to improve the efficiency and Productivity of CBM production. In this study we have done the mechanical properties test and acoustic emission detection on coal taken from the coal reservoir lives in the southern Qinshui Basin. Based on the experimental results, the coal reservoir fracturing is simulated by using ANSYS finite element simulation software. The results showed that: (1) The mechanical properties of coal reservoir have directional differences. The tensile strength in the vertical of the face cleat is lower than in the parallel. The limit of uniaxial compressive strength in the parallel of the face cleat is much greater than in the vertical, and its elastic modulus in the parallel much greater too; (2) If the ground stress conditions remains unchanged, following with the angle which formed between pre-existing cracks and the direction of maximum horizontal principal stress changed from small to large, the fracturing pressure of coal reservoir generally changed from small to big; (3) According to the acoustic emission and stress - strain curves, the fracturing process of coal can be divided into three processes: burst open (Ⅰ) , rupture (Ⅱ) and stable (Ⅲ).

Why Do We Need a Right Permeability Model for Unconventional Gas Extraction?

Jishan Liu, Yan Peng, University of Western Australia, AUSTRALIA

When natural gas is extracted from shale or coal gas reservoirs, the permeability of coal/shale evolves as a function of complex interactions between stress, flow and chemistry. Laboratory and field observations have demonstrated that these evolutions are quite significant. Because of these significant evolutions, a variety of permeability models were developed to address how coal/shale permeability can be managed in order to effectively extract the natural gas. These models were derived normally under a set of specific conditions, including (1) uniaxial strain, (2) constant overburden stress, and (3) local equilibrium between matrix and fracture pressures. Our comprehensive review concluded that these models have so far failed to explain experimental results from controlled stress conditions. We identified the absence of the effective stress transfer between matrix and fracture as the fundamental reason for these failures, and developed a rigorous approach to explicitly quantify this effect on the evolution of coal/shale permeability during gas extraction. We benchmarked the solutions generated by using the widely-used permeability models against our exact solutions. Through comparisons, we concluded that these permeability models could produce unacceptable errors.

SESSION 12
Clean Coal Demonstration and Commercial Projects: General - 2

Siemens Coal Gasification Technology

Wang De Hui, Siemens Limited China, CHINA; Frank Hannemann, Siemens Fuel Gasification Technology GmbH &Co. KG, GERMANY

By 2030 almost two-thirds of the power will be generated by thermal power plants, which are expected to remain the backbone of global power generation. Combined cycle power plants (CCPPs) are the most efficient and most operationally flexible fossil-fueled power generation today, and the ability to use coal or "difficult" liquid feedstock can significantly increase the market for gas turbine and combined cycle applications. Gasification is the key to converting this large energy reserve into a clean gaseous feedstock for power generation and the production of chemicals and clean fuels.

Siemens Coal Gasification Technology represents one of the market leading technologies and offers a number of unique features including high dense flow feeding, cooling screen application as well as a top-mounted combined burner. This provides a wider feedstock adaptability, such as bituminous, sub bituminous, petcoke, anthracite, lignite and even biomass and allows a variation in ash composition between 4 and almost 30% without addition adaptations. The carbon conversion rate is well below 98.5% and the combined burner provides a fast start-up and shut-down i.e. 1 hour from cold condition. Further on in the process, the gasifier reactor and the full water quench are integrated into one pressure vessel leading to a simple and cost effective design, which is best suited for downstream CO shift application. Optimized water utilisation also ensures Siemens gasification technology is more cost effective by minimizing auxiliary power consumption.

Since 2012 Siemens has completed the coal to polypropylene project in Ning Xia province with a “first of it’s kind” SFG 5 × 500MW gasification design. The plant has been in commercial operation and the longest continuous operation for each gasifier has achieved more than 80 days at full load, producing an effective gas rate of nearly 140,000Nm3/h. The raw gas composition on a dry basis (carbon monoxide plus hydrogen) can reach more than 93%, using sub bituminous coal with reactor feed ash content varying between 12% and 25%, and a moisture content of 5 %. In addition a carbon conversion rate of >98.5% has been achieved.

Although our gasification technology has proven commercial viability, further development efforts are needed to continuously improve economics and upgrade the technology. Examples are an advanced feeding system, a lower cost black water treatment system, upscaling of the gasifier and utilization of advanced monitoring and control systems to target better performance and lower investment cost.

Unlocking Potential Value from Low Rank Coal with TRIG™ Gasification Technology

Qianlin Zhuang, KBR; Kerry Bowers, Southern Generation Technologies, LLC, USA

Coal gasification technologies have achieved significant commercial success and advancement in China due to its rapid GDP growth, a limited natural gas supply, and high price of crude oil in the past decade. There are more than 100 coal gasification plants under engineering, construction, startup or commercial operation. Most of the synthesis gas (‘syngas”) produced from these gasification plants feeds the demand of downstream products such as fertilizers, chemicals, liquid fuels, etc. The majority of the applied coal gasification technologies are operated at high pressure and high temperature with coal ash discharged from the gasifier in a form of glass-like non-leachable slag. The high operating pressure allows large coal processing capacity of a single train gasifier, which benefits large scale gasification projects. This type of coal gasification technology, however, requires a relatively good quality coal. The price of good quality coal in China is subject to market pricing, which has increased quite significantly though it has come down a bit since the economic downturn.

In contrast, low rank coals, which constitute a significant part of the global coal reserves, are not commonly a traded commodity due to low heating value and/or high moisture content and thus typically available at low cost. Current energy markets in China and Asia, have created a certain demand for low rank coal to leverage this lower cost resource. KBR and its partner, Southern Generation Technologies, LLC of Southern Co., with support from US Department of Energy, have developed and demonstrated a low rank coal gasification technology, which is called TRIG™ (Transport Reactor Integrated Gasification). In addition to its unique capability of utilizing low cost coal, TRIG™ features high efficiency, high coal feed capacity, less water use, and superior environmental performance, which we believe offers a niche play in coal to fertilizers, chemicals, substitute natural gas, power generation, and other applications. This presentation will provide a detailed account of TRIG™, its features and status of commercial projects worldwide.

Recent Development and Deployment of U-GAS

T. Robert Sheng, Synthesis Energy System, Inc. (SES), CHINA

Synthesis Energy System, Inc. (SES) has constructed a coal-to-methanol plant using U-GAS technology in China. The gasification section consists of three trains, two operating and one spare, designed to convert 1400 metric tons per day of coal to syngas to be processed to produce 320,000 metric tons per year of methanol. The gasifiers are designed to operate at 10 barg and 1000 ºC. This plant is currently in pre-commercial operation phase and coal feed rate has reached up to 90% of design capacity. SES is reactivating its existing coal-to-methanol plant based on U-GAS technology in China. The reactivation and modification works will be completed in a few months. SES is also developing other coal-to-chemicals, coal-to-syngas for direct reduction of iron ore (DRI), coal-to-syngas for power generation, and coal-to-SNG/LNG projects using U-GAS technology. A few of these projects are in the final planning stage.

Pre-Commercial Demonstration of High-Efficiency, Low-Cost Syngas Cleanup Technology for Chemical, Fuel, and Power Applications

David L. Denton, Ben Gardner, Raghubir Gupta, Brian Turk, RTI International, USA

Gasification is a technology for clean energy conversion of diverse feedstocks into a wide variety of useful products such as chemicals, fertilizers, fuels, electric power, and hydrogen. Existing technologies can be employed to clean the syngas from gasification processes to meet the rigorous demands of such diverse applications, but they are expensive to build and operate and consume a significant fraction of overall parasitic energy requirements, thus lowering overall process efficiency.

RTI has developed a warm syngas desulfurization process that has been demonstrated at both lab and pilot scale. Results from the lab and pilot tests have shown that RTI’s technology can improve both efficiency and cost on gasification plants. A pre-commercial scale demonstration of the process is now required to mitigate the technical and scale up risk associated with commercial deployment. RTI has negotiated a cooperative agreement with the U.S. Department of Energy for a 50-MW demonstration of this warm syngas clean-up technology platform at Tampa Electric Company’s Polk Power Station IGCC with the goal of being ready for commercial deployment by 2015. The project is now nearing construction completion. The project scope also includes a sweet water gas shift (90% carbon capture conversion) coupled with carbon capture via an advanced activated amine system. This advanced activated amine system has enhanced capabilities for CO_2 capture, but has previously been excluded from use in coal- or petcoke-based applications because of its sensitivity to high-level sulfur exposure in such syngas. Because of the selective upstream sulfur removal by RTI’s warm syngas desulfurization process, the CO_2 capture target can be achieved by this amine process without the detrimental effects of higher sulfur exposure. Because the amine process does provide some additional non-selective sulfur removal at low levels, the integration of these two processes is expected to reduce overall sulfur in the treated syngas to very low (<100 ppb) concentrations, suitable for the most rigorous syngas applications. These integrated processes are also expected to achieve such overall sulfur reduction at costs substantially below that of conventional syngas cleanup processes, thus expanding the application of RTI’s warm syngas cleanup technology beyond power generation to applications such as chemicals, fertilizers, fuels, and hydrogen.

The goals of this project are to demonstrate that the warm gas desulfurization technology can remove >99.9% of H_2S and COS from coal/petcoke derived syngas, operate for 5,000 to 8,000 hours, and capture up to 90% of any CO_2. The results from this project will be used to establish performance criteria for stable commercial operation, including reliability, availability, and maintainability performance, and to provide extensive operating experience including startup/shutdown and operator training. The results from the demonstration project will be utilized to validate the current performance and economic models. This presentation will provide an overview of these integrated syngas cleanup technologies and their expected performance, the status of the pre-commercial demonstration project, and economic comparisons with conventional syngas cleanup technologies.

MicGAS™ Coal Biotechnology Demonstration of Turkish Coals for Production of Gas and Organic Humic Products

Daman S. Walia, ARCTECH, Inc., USA

MicGAS™ Coal Biotechnology approach for bioconversion of coals was demonstrated in mobile pilot units in Turkey for production of both gas and organic humic products for agriculture and environmental applications. Techno economic analysis from the demonstration tests and integration of it for application to deep unminable colas support an approach with a potential of production of energy and non-energy products with highly favorable economic as well as utilizing vast resources of coals into environmentally safe manner. This approach utilizes total value chain of coals, eliminates wastes and offers potential of zero to negative carbon emissions from coal use.

Results of demonstration tests and applicability tests of organic humic products for meeting large needs of agriculture, environmental and wastes recycling in Turkey were evaluated. A comparison of the products from the Turkish lignite with the ARCTECH’s current commercial organic humic products will be presented.

SESSION 13
Coal Science: General – 3

Comparison of Coal Characterization Procedures Performed According to GB and ASTM/ISO Standards

JC van Dyk, Sasol Technology R&D, SOUTH AFRICA; Tao Qiaozhen, Ningxia Laboratory, CHINA

In July 2010, Sasol Technology South-Africa, together with the Laboratory of Geology and Mineral Resources of Ningxia, China performed a detail coal characterization study in both laboratories. Ningxia Laboratory performs work according to Chinese GB Standards and is Chinese State Accredited towards GB Standards.

The purpose of the study was to gain a better understanding of the differences between GB Standards ASTM / ISO standards, for specific coal test procedures. The study was not to compare exact values of experimental procedures, but rather to confirm if specific GB Standards of selected coal tests will result in a constant difference (either higher or lower) due to the experimental or reaction conditions. Furthermore, it must be noted that this study was not a round-robin type exercise, but a general study to understand and confirm if Chinese GB Standards can be used for coal tests in future and be comparable with ASTM / ISO test conditions. Sasol Technology and Ningxia Laboratory agreed that an official in-depth evaluation of the GB Standards was needed, together with a high level comparison and of the GB Standards with the general ASTM / ISO standards.

Supercritical Fluid Extraction of Heavy Components of Low Temperature Coal Tar Using N-Pentane Solvent

Guangce Jiang, Xiongchao Lin, Haiyong Zhang, Yonggang Wang, China University of Mining & Technology(Beijing), CHINA

The present work was aimed at investigating the dissolving capacity of supercritical n-pentane to the major heavy components of low temperature coal tar. The supercritical fluid extraction (SFE) of heavy components (above 300oC distillation fraction) in low temperature coal tar was conducted with n-pentane solvent, and the heavy components in low temperature coal tar was thus identified to nine major groups: 2, 3, 4, 5-ring aromatic hydrocarbons, phenols, heterocyclic compounds, long chain hydrocarbons, ether/alcohol/lipid, and small aromatic with hydrocarbon chains; the dissolution tendency of them at different pressures (from 3.5 to 9 MPa) and temperatures (from 470 to 580K) were evaluated according to an empirical model. Results show that, the empirical model provides a reasonable consistency with the experimental data (AARD% less than 10%), and the dissolution tendency is correlated with both properties of solvent and molecular structure of coal tar components. The 2-ring aromatic hydrocarbons and smaller aromatics with hydrocarbon chain (12-18 carbons in total) can be extracted completely in all or most of experiments; while, 3-ring aromatic hydrocarbons and longer chain hydrocarbons (20-34 carbons in total) are able to be extracted completely only at high pressure and low temperature. The dissolution trend of 4-ring aromatic hydrocarbons is similar to the 3-ring aromatic hydrocarbons; higher temperature promotes the dissolution in the case of high pressure. Distinctly, the 5-ring aromatic hydrocarbons can achieve only partial extraction at higher pressure (more than 5.5 MPa), and it seems hard to be completely extracted within the range of the experiments. The heterocyclic compounds, ethers/alcohols/lipids and phenols with polarity are also difficult to be totally extracted, mainly because the n-pentane is a non-polar solvent. In addition, the substances with and without polarity demonstrates quite different dissolution characterizations under supercritical conditions.

Low Rank Coal Pyrolysis Behaviors and its Semicoke Reactivity

Aiguo Chen, Xianglong Zhao, Peng Gao, Yi Guo, Ke Liu, National Institute of Clean-and-Low Carbon Energy, CHINA

Two low rank coals (M_{ar}=3.6%-30.72%, A_{ar}=3.76%-9.07%, V_{ar}=27.51%-33.19%) from China were pyrolyzed at low temperature by using a lab-scale furnace. The proximate and ultimate analysis of raw coal were determined. The fuel ratio (the ratio of volatile matter to fixed carbon) and molar H/C of raw coal, heating rate and pyrolysis temperature's impacts on the yields of semi-coke and coal derived liquid (CDL) were investigated and analyzed. The CO_2 reactivity and oxygen adsorption performance of semi-coke were examined. The results show that CDL yield mainly depends on raw coal's properties. As increasing heating rate (5-10ºC /min) and pyrolysis temperature (520-600ºC), CDL yield increases, semi-coke yield decreases. For selected coals, between 520 ºC to 600 ºC, the impact of heating rate to yield of CDL is stronger than pyrolysis temperature. Heating rate and pyrolysis temperature has also important influence on oxygen adsorption capacity of semi-coke. CO_2 reactivity of semi-coke was measured and used to evaluate semi-coke's application performance.

Improving Tar Yield and Quality by Enhancing Heat Transfer and Regulating Gas Flow in Fixed Bed Coal Pyrolysis

Rongcheng Wu, Chun Zhang, Guangwen Xu, State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, CHINA

Coal pyrolysis is considered to be the most effective way to use coal volatiles by its efficient production of tar and pyrolysis gas, but it represents a complicated physiochemical process so that the tar production from coal via pyrolysissuffers still many challenges after 100-year technical studies, such as having high content of heavy components and low yield of light tar. By noting that the heat and mass transfer in the pyrolysis reactor and the extraction method of gaseous pyrolysis product from the reactor can all significantly affect the final yield and quality of the generated tar, this study investigated the tar production characteristics of coal pyrolyis in an indirectly heated fixed bed pyrolyzer that treats 100 kg coal in each test and uses internals immersed in the coal bed to enhance the heat transfer from the reactor wall to the interior of the bed and to regulate the generated gaseous pyrolysis product to flow from high temperature zone to low-temperature zone. Yilan sub-bituminous coal was tested, and the produced tar was evaluated in terms of both yield and quality shown mainly by the content of heavy components that have boiling points above 360 ℃.The results demonstrated that the use of such particularly-designed internals increased the heating rate for the coal bed by more than 1.5 times. Comparing the reactors with and without the internals, the realized tar yields were 7.34 wt.% and 3.85 wt.% and their contents of light tar (boiling point below 360 ℃) were 70.6% and 64.8 %, respectively. The main components of the tar were found to bed phenols and BTX. Parametric investigation clarified that varying the coal moisture content in 5.1 wt.% and 9.5 wt.% only slightly influenced the tar yield, while changing the coal particle size resulted in notable effect on the distribution of pyrolysis product. The larger the particles size, the lower the tar yield. As a consequence, the tar yield and quality of coal pyrolsis are subject not only to the properties of coal and the conditions of reaction such as temperature but are also adjustable by controlling the flow and transfer conditions inside the reactor.

SESSION 14
Coal Mining:
Environmental Hazards, Remediation and Control

Introduction to Coal Mined Land Reclamation in China

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Coal is the most important energy in China. With the excavation of coal resources, a lot of land was damaged and serious environmental problems were produced. Thus, coal mined land reclamation has become the important task for achieving the target of green mining in China. This paper introduced the impact of coal mining on land and environment. Damage of land and water resources were serious due to coal mining in China, e.g. subsidence land has reached to more than 1 million ha. Some other environmental problems such as village movements, geological disasters and water and air pollution were also introduced. Based on the legislation and practice of land reclamation in China, history of mined land reclamation in China was also introduced. Furthermore, some major technologies related to subsidence land reclamation, surface mined land reclamation and ecological restoration of coal waste piles were discussed, which focused on discussion of the characteristics, advantages and disadvantages of typical reclamation technologies. Finally, some new land reclamation technologies and models such as concurrent mining and reclamation, and filling reclamation with yellow river sands were introduced.

Investigation to Define Treatment Requirements for Acid Mine Drainage during Closure of a Fly Ash Reservoir

Bruce M. Sass, John Seymour, Geosyntec Consultants; Alan R Wood, American Electric Power; J. Brady Gutta, West Virginia University, USA

American Electric Power's (AEP) Gavin Plant is located on the Ohio River near the Appalachian Coalfields. The Plant is configured with two 1300 MW bituminous coal-fired, supercritical steam units (ca. 1974–75). Coal combustion residue (CCR) was initially disposed in a flyash reservoir that was constructed near several small abandoned coal mines. A network of sluice pipes conveyed water-entrained flyash from the plant to a flyash reservoir for disposal. Sluicing and disposal of flyash ceased in 1994, when flue gas desulfurization (FGD) units were installed at the plant. Henceforth, FGD sludge and flyash were disposed in a solid waste landfill, not associated with the flyash reservoir.

Coal mining in the vicinity of the Plant began in the late 1800s and largely ended in the 1990s. Coal was excavated using contour mining techniques along rock slopes where the coal bed was exposed and of economical thickness. Today, benches and highwalls are remnants of contour mining throughout this region. Underground mining methods, including room and pillar and auger mining, were commonly used when the overburden became too thick for contour mining. These deep depleted coal mines and resulting mine spoils are now a source of acid mine drainage (AMD) that mingles with stormwater runoff within the drainage basin that feeds into the flyash reservoir. Engineering & design for closure of the reservoir is in progress.

The purpose of this investigation was to characterize existing conditions near the flyash reservoir to assist in defining near-term treatment options and/or requirements during the multi-year closure construction time-frame. During closure construction, water in the reservoir will be gradually lowered, then eliminated entirely after closure, thereby removing the current buffering and dilution effects of the pond. AMD could detrimentally impact surface water flowing from the closed facility after an engineered, "green" cover is installed.

AMD associated with former coal mines and mine spoils mingles with stormwater runoff within the drainage basin. Site reconnaissance and field investigations were conducted in 2012 to accurately identify AMD sources, flow rates and chemical characteristics of the drainage. The reconnaissance effort led to delineating acidic (pH < 4) surface waters in shallow pools and stream channels near the highwall. These acidic streams appear to coincide with known drift entries, auger borings, and air shafts that had previously existed along the highwall.

AMD flow rates were measured over a four month-long period by deploying V-notch weirs at five locations in drainage ditches near the highwall. Water levels were monitored continuously in the pools created behind the weirs using pressure transducers. The pressure transducer data were converted to flow rates using software supplied with the instruments (Levelogger® by Solinst). At two locations pH, specific conductivity, temperature, and oxidation-reduction potential were continuously monitored using YSI Model 6000XLM water quality meters and associated probes. Flows were relatively constant over the four month period, during which the cumulative precipitation was approximately 300 mm. The impact of precipitation on AMD was assessed by comparing meteorological data from the nearby Plant with

measured flow rates and water quality parameters. Recordings of continuous water quality measurements provided additional information about the nature of the acidic seeps.
Laboratory analysis of stream samples provided detailed chemical information that was used to assess the amount of alkalinity required to neutralize major hydrolysable metals, such as ferrous and ferric iron, aluminum, and manganese. Based on chemical analyses, the calculated acidity of the AMD is between 400 and 500 mg/L, as calcium carbonate ($CaCO_3$). The maximum typical AMD flow rate at is 20 L/min in each of the major drainage ditches. Based on the acidity range and the estimated maximum AMD flow rate, consumption of calcium carbonate equivalent is estimated to be between 4 and 5 metric tonnes (MT) per year. This estimate was corroborated by calculations using AMDTreat software (Ver. 5.0.1 + PHREEQ). In addition, a geochemical speciation code was used to provide additional insights into the AMD chemistry and to simulate treatment processes with various neutralizing agents. Presently, AEP is assessing options for AMD treatment, during construction and in the post closure time-frame.

Study of Rock Burst Hazard Predication Based on Acoustic Emission Monitoring

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According to the using of ARES-5/E system in coal mine of China, the paper introduced the principle of AE monitoring technique, and analysis method of AE events. Through analyzing the results of AE monitoring, the coal or rock dynamic disasters can be predicted accurately. The field application of AE monitoring system shows that the dangerous state of monitoring area can be evaluated accurately.

Experimental Relation between Stress, Gas Desorption and Thermal Expansion in Coals

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When coal is recovered by mining, or fluid recovered or injected, complex interactions of stress, gas sorption and thermal expansion have a strong influence on the mechanical and transport properties of coal. These include influences on gas sorption and flow, coal deformation, porosity change and permeability modification. Although these interactions have been studied comprehensively, direct observations are rare. This study presents the direct observation of these interactions in coals obtained from Baijiao coal mine in Southwest China. A special method was developed to measure thermally-induced deformation of coal, as well as the desorbing gases emission. The test procedure yields uniaxial compression at a temperature range from 20^oC to 40^oC with an interval of 5^oC. The results show that the thermal effect controls the evolution of coal volume with two distinct stages of deformation. During the first stage, the thermally-induced volumetric expansion dominates the deformation of coal sample. During the second stage, the shrinkage of coal matrix predominates the deformation of coal sample as a result of the ongoing desorption of adsorbed gas. Such a transition process from expansion to shrinking may weaken the cohesive bonds of coal grains. The loading results reveal that flow of the desorbing gas is closely related to the overall deformation of the stressed coal, and both the uniaxial compressive strength and the Young's modulus of coal samples tend to deteriorate with temperature. Finally, we discuss the adsorbed gas release associated with the deformation of coal mass. These test results may help us understand the interactions of stress, gas sorption and thermal expansion and their implications to the safety of deep coal mining and the effective extraction of coal seam gas.

Mine Hazards – Assessing the Risk

Tana Levi, Jean Saurat, Guy Boaz, CRL Energy Ltd., NEW ZEALAND; Basil Beamish, CB3Mine Services Ltd., AUSTRALIA

There are numerous hazards associated with exploring, developing and mining mineral resources. Many of these hazards are resource specific and there is a need to better understand the underlying causes and effects to allow the identification, management and mitigation of the risks. The principle stakeholders include mine owners, mine workers, regulators, mine rescuers and researchers. CRL Energy Ltd., is currently working to understand these conditions. There are some high priority areas of study relevant not only to New Zealand, where there is a need to carry out and integrate fundamental studies with working situations such as: methane gas content, outbursts and explosions, gas drainage technologies, spontaneous ignition, friction ignition and mine fires, rock reactivity and gas monitoring.
This paper will mainly focus on spontaneous combustion – which is a very real and significant hazard for coal mine operations with the occurrence of such events often leading to severe outcomes and major disruption to production. Tragic events, such as those surrounding the Pike River Mine disaster that recently rocked the mining industry in New Zealand, will lead to the legislation around mining becoming increasingly more stringent. Spontaneous Combustion Management Plans (SCMP) and Trigger Action Response Plans (TARP) are leading practice and aid in the timely assessment of, and response to, the state of self-heating in coal during production, stockpiling and transport in the coal industry. For hazard identification purposes it is important that these plans are backed by comprehensive results with regards to the evaluation of the specific coals propensity to spontaneously combust. In the past, R70 testing has been the benchmark in this field and an extensive data bank of previous heating events exists. CRL Energy Ltd., and CB3 Mine Services Ltd., have built on this test and developed it to closer replicate site specific parameters for individual mines. This has been achieved by developing the SponComSIM™ test which tests the as-received coal, rather than dried coal, thus incorporating the effects of moisture. Seasonal variations can be replicated with the use of a humidity controlled oven. SponComGas™ is a gas evolution test which enables the early detection of a spontaneous combustion event. Results from these new tests and case study's are outlined and interpreted in the paper.

Reaching for Bulk Samples through Aquifers at Thar Coal Fields in Pakistan

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Thar coalfield is the biggest in Pakistan and is recognized as the one of the largest in the world. The deposit is located in the south-eastern corner of Sindh province in the desert of Thar. The field is spread over 9000 square kilometers. The size as estimated by joint exploration of the geological survey of Pakistan and United States geological survey is ground 175 billion tons at comparatively shallow depths (150 meters) but covered by aquifers.
All attempts at reaching the coal deposits for obtaining bulk samples have been unsuccessful mainly due to the presence of aquifers above and below the lignite. The first perched aquifer is persistent throughout the thar coalfield at a depth of 50-90 meters from the surface. As a first attempt at obtaining bulk samples an eight feet diameter shaft was sunk in the ground. Pumping of ground water was unsuccessful. Finally the plan was abandoned. Now a fresh approach of Test or Development Mine is being planned. Surface diameter of the Test Pit will be 670 meters while the top of the coal seam after digging will be 100 meters with a slope angle of 30 degree for upper dune sand, 35 degree for recent alluvial deposits and 40 degree for bora formation and coal. The over burden at a depth of 150 meters will be around 51 million M^3.
The aquifers in Bara Formation are continuous under high hydrostatic pressure which can release enormous amount of water. It is possible that rather taking water out of the Pit it would be more advantageous to live with it. Coal and some of the ground may be removed by dredging or dragline to obtain the bulk coal samples for evaluation and downstream processing like IGCC, gasification and FTD.

SESSION 15
Gasification: General – 3

Experimental Study on Co-Pyrolysis/Gasification of Deoiled Asphalt with Lignite

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In order to find an efficient and feasible technological rout to dispose and utilize deoiled asphalt (DOA, a byproduct of solvent deasphalting process), the co-pyrolysis/gasification of DOA with lignite was investigated. A series of isothermal co-pyrolysis experiments were conducted in a fixed bed reactor to observe the characteristics of the chars yields and the pattern of the blends. Then a set of non-isothermal experiments were performed by thermogravimetric system to evaluate the gasification characteristics of the chars of lignite, DOA and the blends. It was observed that the DOA has the lowest reactivity for its low surface area, high graphitic carbon structure and low ash content. The reactivity of the co-pyrolysis chars was found higher than that of the calculated, this clearly demonstrating that the synergetic effect is existed during the co-gasification process.

The Effect of Drying Temperature on Moisture Resorption Capacity of Lignite

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Evaporative drying of Baori lignite was conducted in a rotary kiln at 130～380 ℃. The concentration of hydrophilic oxygen functional group, pore structure and equilibrium moisture content (EMC) of treated lignite were determined with the ion exchange method, nitrogen adsorption isotherms and desiccator experiment to compare with that of raw lignite. Moreover, the influences of hydrophilic oxygen functional group and pore structure on the EMC value were investigated. The results show that both the pore structure and hydrophilic nature of products determine its EMC value. At 130～330 ℃, the EMC value decreased with the disintegration of pore structure, the hydrophilic factor could be neglected for the "bridges" were formed between clusters of water molecules at 97% relative vapor pressure, namely, the pore was filled by water molecules completely.

However, the EMC value increased a little at 380 ℃ with a considerable increase of pore volume. Because no hydrophilic groups exist on the new formed pore surface, so they are unable to provide adsorption sites for water molecules. FT-IR spectroscopy and SEM photograph provided some additional evidence regarding the changes in lignite structure due to the drying treatment.

Experiments on the Riser Exit Configurations in a Cold Dense Transport Bed

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Pulverized Coal Pressurized Dense Transport Bed Gasifier, as one of the emerging gasification technologies, is applicable for coal of low rank, high ash and high melting point. The influence of seven exit configurations (L-shape, T-shape, 15°V-smooth shape, 15°V-abrupt shape, 30°V-smooth shape, 45°V-smooth shape, 45°V-abrupt shape) on the hydrodynamic behaviors was investigated in a cold dense transport bed (0.10 m-ID×17 m-high). The solid circulation rate G_s was up to 924 kg/(m^2·s) with the Geldart group B silica sand (ρ_p =3092 kg/m^3, d_p =106 μm). Specially, at the high G_s (803~924 kg/(m^2·s)) conditions, no increase of solid concentration was observed through the riser with any of the seven configurations. It was obviously different from the previous published results under the low G_s conditions. Also the composition of the pressure drop near the exit region was analyzed, which was divided into the elbow part, the connection part and the variable diameter part. For reducing the pressure drop of the elbow part and connection part, the exit configurations with the big inclination angle (≥30°) were beneficial to the increase of G_s. The pressure drop of the reducing pipe (ΔP_{vd}) accounted for the most proportion of the total pressure drop. A semi-empirical model of ΔP_{vd} was proposed, which could be used to obtain the real-time G_s conveniently.

New technology of High Concentration Coal Water Slurry (CWS) Preparation Technology from Low Rank Coals and Lignite for CWS Gasification

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A new technology for preparation of coal water slurry (CWS) with high concentration from low rank coals and lignite by dry method with optimum particle size distribution（PSD）was developed based on two principals: high bulk density with optimum PSD and conversion of interior bound water into free water by grounding coal to less than several μm and developing new additive. The coal loading in CWS using the new technology can reach 68% for Shenmu coal and 58% for lignite about 10% higher in comparison with conventional method, which will greatly increase the economic and social benefits. The recent progress using this new technology is introduced in this paper. The dry mill with capacity of 80 t coal/h has been developed. The major advantage is that the lignite with water content of less than 40% can be directly fed to the mill without pre-dry. Various low rank coals and lignite are tested for several coal chemical plants. The reformation of the existed plant and the technology for construction of new plant are also introduced.

Hot-State Experimental Research on a Novel Coal-Based Two-stage Gasification Process

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A novel coal-based two-stage combined gasification process with heat recovery via chemical reaction was proposed by Institute of Clean Coal Technology, East China University of Science and Technology, which was aimed at the insufficient heat recovery of high temperature gas for existing entrained-flow gasifiers. The effects of coal types (lignite, petroleum coke and anthracite), the mass of coal added (1000g, 1200g, 1400g and 1600g), and coal particle sizes (5-8mm, 8-10mm, 10-15mm and 15-20mm) for the second stage on gasification efficiency were researched in an experimental two-stage hot-state gasifier. In addition, the influence of gas compositions from the first stage was also examined. The effective gas concentration (H_2+CO), low heat value (LHV) of syngas and carbon conversion rate as well as CO_2 and H_2O conversion rate were analyzed and compared under different operating conditions. Experimental results showed that the two-stage gasification process can lower the syngas temperature in the gasifier, and improve the effective components of the syngas significantly. The reactivity of lignite was better than petroleum coke and anthracite. The optimum amount of coal added to the second stage was 1400g, which occupied 10% of the handling capacity for the first stage, and the optimum coal particle size for the second stage was 8-10mm. The carbon conversion as well as CO_2 and H_2O conversion rate in the gasifier presented an increase trend with the increase of invalid components (CO_2+H_2O) in syngas from the first stage. Furthermore, the process had good environment benefits by reducing the emission of CO_2.

SESSION 16
Clean Coal and Gas to Fuels: General - 3

Techno-Economic Analysis of Jet Fuel Co-Production with Electricity from Coal and Biomass in the Ohio River Valley of the United States, with Capture of CO_2 and Storage via Enhanced Oil Recovery

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There are limited number of potential low-carbon alternative fuels with the energy density and other characteristics needed for jet aircraft engines. One option is co-processing of coal and biomass via gasification and Fischer-Tropsch (FT) synthesis with capture and storage of byproduct CO_2. With sustainably produced biomass, synthetic jet fuel from such a system can have lower lifecycle greenhouse gas emissions than petroleum-derived jet fuel.

Detailed steady-state performance simulations are developed for plants that gasify coal and biomass in separate reactors and convert the resulting syngas via FT synthesis and syncrude refining into synthetic jet fuel plus gasoline. Unconverted syngas and off-gases from synthesis and refining are used to fire a gas turbine combined cycle, which additionally uses heat recovered from the synthesis reactor and elsewhere to augment steam production for the bottoming steam cycle. Byproduct CO_2 is captured and sold for use in enhanced oil recovery (EOR), as a result of which the CO_2 is permanently stored underground. The plant design utilizes fully-commercialized equipment, such that it is plausible that a plant of this design could be constructed within the next 5 to 10 years.

Each plant is designed with a capacity to produce 13,000 barrels per day of liquids from 584 tonnes per day (dry basis) of corn stover biomass plus 6,000 to 8,000 tonnes per day of Illinois #6 bituminous coal. The two designs are distinguished by the amount of co-product electricity produced. The process simulations provide a basis for estimates of greenhouse gas emissions and capital costs.

Nth plant economics are estimated on the basis of delivered corn stover prices for a plant that would be sited in the Ohio River Valley (ORV) of the United States. Captured CO_2 is assumed to be sold into EOR markets via an anticipated pipeline system connecting the ORV to Gulf Coast or Permian Basin oil fields. The ORV has historically been well populated with coal-fired power plants. Many of these are at or near the end of their operating lives and/or are being challenged to remain economically competitive in the face of tightened air emissions standards and low-cost electricity from natural gas combined cycles resulting from low natural gas prices. These conditions are leading to further depression of coal mining areas due to reduced coal demand. The combination of these factors makes the ORV a particularly relevant context for examining the feasibility of coal-biomass co-processing for liquids production. Internal rates of return, levelized costs of fuel, and levelized costs of electricity are calculated. Sensitivity analyses are presented around key economic and policy variables, including assumed future oil and carbon emission prices.

Modeling Comparison of High Temperature Fuel Cell Fueled with Carbon and Hydrogen

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Coal is not only the most abundant fossil fuel in the world but also well distributed world-wide. It is necessary to develop the clean coal technologies to improve the problems existing in conventional coal-based energy conversion systems such as low efficiency and pollution matter emission. Coal-based fuel cell or direct coal fuel cell are the alternative power-generation systems and have the prospect for directly converting chemical energy stored in coal into electricity more benignly and efficiently. The theoretical efficiency of fuel cells fueled with carbon, which is the main component of coal, can reach 100% through $G(T)/\Delta H=1-T\Delta S/\Delta H$. In this study, a mathematical model is proposed to compare the effect of the carbon-based fuel cell on the performance of the high temperature fuel cell with that of existing hydrogen-based fuel cell system. The ideal voltage and three major irreversibilities are simulated for calculating the performance. These three major irreversibilities cause the voltage losses to the high temperature fuel cells and they are calculated by using the Nernst equation, Butler-Volmer equation, Ohm's law and ordinary and Knudsen diffusion in the mathematical model. The voltage losses, cell voltage and power density of fuel cells on carbon are compared with that of hydrogen. The results indicate that the voltage losses and open-circuit voltage of hydrogen are more than that of carbon and the cell voltage of the hydrogen decreases to zero with increasing current density, but the power density of carbon is larger than that of hydrogen. This results show that the performance of the high temperature fuel cells fueled with carbon is better than that of hydrogen.

Simulation Analysis of Coal to Substitute Natural Gas Process

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Nowadays, the growing energy demand and limited fossil reserves have forced us to consider the utilization of coal due to their abundant reserves especially in China. Coal to substitute natural gas (SNG) has been well known as a more efficient way than the other conversion routes such as coal to liquid fuels or coal to dimethyl ether. In 1980s, the Great Plains Synfuels Plant in North Dakota (United States) erected the first and only commercial SNG from coal process based on the Lurgi gasification and methanation technology with the feed of North Dakota lignite. In this work, the coal to SNG process is simulated including air separation unit, gasification unit, gas conditioning unit, gas cleaning unit and methanation unit by ASPEN PLUS. The key parameters of the process have been confirmed and optimized by the sensitive analysis of a series of evaluation indicators such as Wobbe Index for the quality of SNG, energy efficiency for the energy consumption, the emission of carbon dioxide and the consumption of water for the environment effect. Based on the process model, the effect of different coal rank, gasifier type and methanation reactor is studied and the results indicate that the lignites and high pressurized fixed-bed gasification technology benefits for the coal to SNG process due to the high methane content and high hydrogen to carbon monoxide molar ratio in the syngas. Moreover, fluidized bed methanation reactor can increased the energy efficiency because of the centralized energy utilization and simplified process compared with the traditional fixed bed methanation reactor.

Sensitivity Analysis of the Mutli-step Reaction Model for CaC_2 Formation from Coal and Lime

Steven L. Rowan, Ismail B. Celik, Jose Antonio Escobar Vargas, Suryanarayana R. Pakalapati, West Virginia University, USA; Matt Targett, LP Amina, CHINA

Calcium Carbide is a valuable precursor to the production of many common industrially-valuable chemicals. In industrial settings, it is typically formed by heating stoichiometric mixtures of calcium oxide (lime) and coal-derived coke inside large high temperature electric arc furnaces. Once produced, the calcium carbide (CaC_2) is then treated with water to form acetylene, which is used to manufacture pvc and other compounds. Several efforts have been made over the last five decades to study and characterize the reaction kinetics of calcium carbide formation. Among the factors believed to effect the rates of formation and disassociation of calcium carbide are: particle size, pellet compaction, reaction temperature and heating rates, and the initial molar ratio of lime to carbon.

Much of the previous literature relating to calcium carbide formation has attempted to apply simple single-mechanism, first order reaction rate models to experimental data in order to obtain information on the chemical kinetics of calcium carbide formation. Inherent in these models is a number of limitations; primary among these being that the previous models only allowed the initial formation reaction to proceed in the forward direction. In addition, these previous models do not incorporate the additional reactions which may lead to the disassociation of calcium carbide after its initial formation, or the effects of particle size, pellet size and heating rates.

In an effort to address these limitations, a multi-step reaction (MSR) model has been proposed and shown to provide predictions that closely match the previously-published experimental data. In this paper, a parametric analysis has been carried out in order to explore the effects of varying the initial stoichiometric ratios of reactants, as well as variations in particle heating rates due to differences in particle size, upon the apparent kinetic rates of formation and disassociation of calcium carbide, as predicted by the MSR model.

Methane Production by Hydrogenation of Low-Rank Coal in a Fixed Bed Reactor

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The aim of this paper is to investigate the hydrogasification characteristics of three low rank coals in a fixed-bed reactor, focusing on the production of methane. Coal hydrogasification experiments were carried out at a heating rate of 15 °C/min up to 700 °C with a holding time of 1 hour under various hydrogen pressures up to 5 MPa. It was observed that the coal hydrogasification was clearly characteristic of a two-stage process, volatile matter hydrogenation occurring in the heat-up stage and char hydrogasification occurring mainly in the isothermal stage. The accumulated yields of methane obtained under hydrogen of 5 MPa were 4.7, 4.0 and 1.4 times as much as those under that of 0.1 MPa, respectively, for YX lignite, ZD sub-bituminous coal, and XD lignite. An elevation in hydrogen pressure not only facilitated the char hydrogasification but also the volatile matter hydrogenation reactions. The promoted hydrogenation reactions by pressure were also due to the significantly increased residence time of volatile matter in the reactor. Analysis of the tar composition indicated that the tar obtained at ambient hydrogen pressure contained more of long alkyl chain hydrocarbons and larger polyaromatics, whereas that obtained at 5 MPa was enriched with benzene, toluene, and xylene (BTX), reflective of the facilitated decomposition of volatile matter under pressure. The formation of CO decreased with hydrogen pressure increasing, indicating its hydrogenation reaction to turn to carbon or CH_4. The change of CO_2 with pressure was not a monotonous trend, implying the trade-offs of some competition reactions. The char hydrogasification rate was essentially proportional to the hydrogen pressure, but depending on coals. ZD sub-bituminous coal demonstrated a higher rate of char hydrogasification. Elemental analysis of the char collected after gasification showed that the char obtained at 5 MPa had a higher H/C molar ratio and a lower N/C molar ratio than that obtained at ambient pressure. The kinetics of hydrogenated chars showed increased pressure and long solid residence time would decrease the char reactivity towards CO_2.

SESSION 17
Shale and Coal Bed Gas: General - 3

Possibilities of Increasing the Effectiveness of Mining Methane Drainage in Conditions of Low Permeability of Coal Seams

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There is very low permeability of coal seams in Polish coal mines. For this reason pre-mining methane drainage is conducted to a small extent, which rarely brings expected results. Methane emission from roof and floor sub-economic seams has the greatest share in total methane emission to workings. Effective CMM capture is used from goaf in advance or after mining. However, due to longwall mining and ventilation systems, it is not always possible to capture methane from strata.

This paper presents a method of increasing the permeability of coal seams and a method of drilling boreholes towards goaf. Initial results of the effectiveness of methane capture after applying these methods are presented.

A Tale of Two Mudrocks – Reservoir Quality of the Marcellus Shale and Point Pleasant-Utica in the Appalachian Basin, USA

Timothy R. Carr, West Virginia University, USA

Paleozoic organic-rich mudrock (“shale”) units were deposited on the eastern margin of the United States of America from the initial Cambrian rifting to the assembly of Pangaea after the Devonian. Two of these organic-rich shale units the Ordovician Point Pleasant-Utica and Devonian Marcellus mudrocks of the northern Appalachian basin are some of the most active shale gas and liquids plays in the world, and a significant component in the United States energy market. Unconventional hydrocarbon plays are often referred to as statistical plays due to their high degree of heterogeneity, and present challenges for characterization and exploitation. Productivity depends upon an inter-related set of reservoir, completion and production characteristics. Key controls on success are regional geology, maturity, sequence stratigraphy, and past and present stress regimes. In particular the geographic and stratigraphic distribution of organic matter, silica, and carbonate are important for fracture stimulation. The distribution of these key elements has been modeled at the basin and local scales. A 3-D mudrock lithofacies model was constructed using sequence stratigraphy to constrain mineral composition, rock properties and organic content. Core analysis and log data were used to calibrate the model from core scale to well scale and finally to regional scale. Geostatistical approaches were used to develop a quantitative relationship between conventional logs and lithofacies, and to model the distribution of mudrock lithofacies in three-dimensions. Controlled primarily by dilution, organic matter productivity, and organic matter accumulation distribution of organic-rich mudrock lithofacies was dominantly affected by water depth and distance to shoreline. Maturity in the Point Pleasant-Utica and Marcellus as mapped at a regional scale has a strong influence on porosity development and subsequent gas and liquid productivity. Finally, present and past stress regimes are important for orientation of fracture stimulations and influence the orientation of horizontal well bores. The controls on mudrock reservoir quality are subtle and heterogeneity present in Point Pleasant-Utica and Marcellus results in regional and local well production variations. The proposed regional 3-D models can aid in recognizing geologic and engineering targets, designing horizontal well trajectories, targeting fracture stimulation strategies and understanding shale depositional environments and processes. The proposed approach can be extended to other organic-rich shale reservoirs.

The Impacts of Shale Gas Development on Coal in the U.S. Electricity Industry

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The dramatic rise in liquid and natural gas production is changing the energy structure in the United States (U.S.). One region of focus in the development of shale gas is the state of West Virginia where the Marcellus shale gas basin underlies most of the state, in addition to being a major coal producing state. The Marcellus shale gas basin also crosses under Pennsylvania and New York; in these three states from 2005 thru 2011, shale gas wells increased from 27 to over 11,0000. The boom in upstream shale gas development resulted in a decreased price of natural gas shifting energy demand away from coal in the short run—the development of shale gas is impacting the coal industry in the U.S. and the long term effects of shale gas on the energy mix are uncertain. Some of the market impacts between shale gas and coal are compounded by stricter environmental regulations sometimes resulting in the closure of coal mines and the early retirement of coal-fired power plants, which—even if only short term decreases in production result—can generate social and economic problems in the long run.

This paper details a brief history of the explosive development of Marcellus shale gas and provides a discussion of the subsequent impacts on the coal industry in the United States. Given the dominant role of coal in China's energy supply and the presence of large shale gas reserves in the country, this paper can serve as a guide to the Chinese coal industry on the economic repercussions for the U.S. coal industry of the development of the shale gas industry; and for the developing Chinese shale gas industry, this paper can provide information to help current and future shale gas development move forward efficiently. For both China and the U.S., this paper highlights the trade-offs involved in the development of coal and gas resources and markets, which assists in providing background information for assessing future energy trends and strategies. By focusing on future energy markets and broader environmental concerns, it is possible to introduce and perform analysis to predict the future of coal industrial development in the United States.

Integrated Approaches of Conventional Log Suite Interpretation for Unconventional Shale-Gas Reservoir Evaluation

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The conventional log suite constitutes the major available data for shale-gas reservoir characterization, although increasingly 3-D seismic volumes and advanced log suites (e.g., pulsed neutron spectroscopy, PNS) are acquired. Essentially, reliance on conventional log suites for shale-gas evaluation will persist through the next several decades. Therefore, it is necessary to develop an integrated approach to efficiently approach conventional log suite interpretation to evaluate critical reservoir factors for shale-gas exploration and development. Two key factors for identifying highly productive zones and areas, and understanding depositional processes of organic-rich shale are "fracability" and gas content. The ability to effectively stimulate a reservoir is to a large extent influenced by mineral composition, and gas content is controlled by total organic carbon (TOC). Both mineral composition and TOC content have strong but complex response in several conventional logs, which are the target of this research.

It is difficult with a conventional log suite to recognize all the minerals measured, so we simplified the mineral composition model. For example, feldspar and quartz are grouped together while all clay minerals are grouped as clay. It is important to understand the effects of well borehole condition on conventional logs. Trace minerals such as barite and pyrite are present commonly in shale-gas reservoirs, and small concentrations have large effects on logs such as the photo-electric index and density. The effects of barite are removed by using envelop line technology. Porosity and water saturation also influence the interpretation of mineral composition and TOC content. Thus, in order to improve the accuracy of interpretation results of mineral composition and TOC content, we have developed a protocol to use all available conventional logs and consider all these effects together.

In this paper, an integrated framework and approach is developed to evaluate shale-gas reservoirs based on conventional log suite. Available core data and advanced PNS logs are used to demonstrate the quality of interpretation results.

The Main Characteristics Shale Gas Reservoir and its Effect on the Reservoir Reconstruction

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Shale gas reservoir is unconventional gas reservoir where shale gas is mainly adsorption and free state, a small amount of dissolved occurrence. Meanwhile, heterogeneity is strong, and physical property characteristics of low porosity, low permeability. In order to get the ideal output, shale gas well need transformation after completion. Hydraulic fracturing technology which is commonly used in conventional reservoir transformation method is also used for coal bed methane and shale gas and other unconventional reservoir reformation. With the rapid rise in energy and environmental problems, supercritical carbon dioxide development and fracturing liquid propane gradually come into the reservoir horizons and are expected to replace hydraulic fracturing technology in large-scale and industrialized exploitation. Based on the previous studies, this paper discussed characteristics of shale gas reservoirs from the rock structure and thickness, rock composition, geological environment and petrophysical characteristics, besides its restricting factors are also analyzed, then affections on reservoir reconstruction of these characteristics were discussed in detail. This will not only contribute to complete the reservoir transformation theory in shale gas, but also has important practical value in improving the efficiency of shale gas production and drilling.

Production Analysis of Desorption in Shale Gas Development

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Natural gas production from shale gas reservoir has increased dramatically in the United States over the past ten years due to the significant improvements in completion and stimulation technologies. Previous studies and field experience have shown that shale gas is stored as free gas and adsorbed gas in reservoir, and the adsorbed-gas proportion exhibits a large variation, from 20% to 85%, in different shale gas basins according to the accumulation conditions. The production of shale gas can be divided into three stages: The free gas in natural fractures is produced firstly, then the free gas in fracture and intergranular porosity flows through fractures to well, with the pressure depletion, finally the desorption starts to contribute to the production. Gas desorption is considered to be one of the reasons why shale gas wells usually have a long and stable production at a relatively low rate.

Analyzing the effects of gas desorption on production will improve our understanding of shale gas production mechanisms and reservoir management strategies. The original amount of free and adsorbed-gas in place were analyzed in literature, providing initial assessment for the importance of adsorbed gas for a certain reservoir. Numerical and analytical simulators were used to investigate the difference between the production performance with or without considering the desorption mechanism. However, the effect of gas desorption changes with production time and pressure, and no previous study addressed the questions that how much of the well production is from the original-adsorbed-gas at a certain time and in what conditions and when the desorption process will dominate the production.

In this work, we present an approach to dynamically analyze the production of free and adsorbed gas, which quantifies the amount of original-adsorbed-gas in final production in shale gas development, using the Unconventional Oil and Gas Simulator (UNCONG) developed by our group. Through components subdivision, the free and adsorbed gas can be distinguished in production. Field cases of Barnett and Antrim Shale are analyzed, the proportion of original-adsorbed-gas in production with time and the desorption distribution in the entire reservoir are calculated. The results show that the desorption gas dominates the production in Antrim Shale while it only takes a small part of production in Barnett Shale.

This work provides an intuitive, convenient method for dynamic production analysis of desorption in shale gas development, contributing to reservoir resources and production evaluation, production mechanisms understanding, and shale gas production simulation.

SESSION 18
Clean Coal Demonstration and Commercial Projects: General - 3

Development of Coal Pyrolysis and Combustion Poly-generation System

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To realize comprehensive utilization of coal, a new poly-generation system combined coal combustion and pyrolysis has been developed for clean and high efficient utilization of coal. Coal is first pyrolysed in a fluidized pyrolyzer and produced gas is then purified and used for chemical product or liquid fuel production. Tar is collected during purification and can be processed to extract monocyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) etc. and to make liquid fuels by hydro-refining; semi-coke from the pyrolysis reactor is burned in a circulating fluidized bed (CFB) combustor for heat or power generation. The system can realize coal multi-product generation and has a great potential to increase coal utilization value. A 1MW poly-generation system pilot plant and a 12 MW CFB gas, tar, heat and power poly-generation system was erected. The experimental study focused on the two fluidized bed operation and characterization of gas, tar and char yields and compositions. The results showed that the system could operate stable, and produce about 0.12 Nm^3/kg gas with 22 MJ/Nm^3 heating value and about 10 wt % tar when using Huainan bituminous coal under pyrolysis temperature between 500~600˚C. The produced gases were mainly H_2, CH_4, N_2, CO, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. The CFB combustor can burn semi-coke steadily, whether the pyrolyzer run or not, and produced 12 MW electricity. On basis of this, a 300MW coal pyrolysis and combustion poly-generation demonstration project was designed and the 1st phase project operation result showed the feasibility of the system.

Advanced Ultra-Supercritical Steam Power Plants

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In its World Energy Outlook 2009, the IEA estimates that long-term world power generation installed base will increase by 73% up to 2030, while electricity generation will increase at the same pace. In this reference scenario, fossil fuels represent the major share of power generation by 2030, with slightly more than two thirds of the electricity generated in 2030 from coal, oil, or gas. Demands on scare resources and impacts to the environment (solid, liquid, gaseous emissions including CO_2) will be coincident with this increase in fossil power capacity. Improvements in generation efficiency are a “no-regrets” action which reduces these demands and potential impacts. Improvement to generation efficiency has been steady over the history of the power generation industry and shall continue with all methodologies exploited. In the case of the steam power plant this will include reduction of stack losses, improved combustion, coal drying, advanced controls, reduction in auxiliary power demands, improved steam turbine aerodynamics, flue gas heat recovery, and other measures, as well as increases to the underlying thermodynamic cycle by increases in steam temperature and pressure. While there is no specific technical definition of A-USC, Alstom defines A-USC as steam conditions beyond today’s state-of-the-art (~600 – 625^{o}C) and requiring the employment of nickel alloys. The strength of such alloys allows a significant jump in steam conditions with a target of 700 – 760^{o}C allowing a significant (~7-10%) efficiency benefit for the incremental investment in application of these materials over today’s state-of-the-art plants.

Alstom is the World leader in advancing A-USC steam power plant technology and has on-going developments for the boiler and steam turbine components and of the optimized integrated plant. These developments complement Alstom’s advancements in environmental controls and carbon capture and sequestration technology, with efficiency improvements reducing the size of the associated equipment for a given amount of power produced. Achieving 700-760^{o}C steam temperatures requires new materials and new fabrication techniques. Alstom is a founding member of the European EMAX consortium and the USA USC Materials Consortium. Alstom continues its active involvement in materials validation in laboratory environments and in field testing. Currently Alstom is overseeing two high temperature steam test loops in operating utility boilers (one in Germany and one in the US). Alstom was a leader in the Comtes700 components test facility which successfully tested large scale boiler components and valves. In these programs, Alstom has gained considerable know-how and experience in materials properties, welding, fabrication, design, design rules (including relevant industry code standards), and is ready to progress to full scale demonstration.

FutureGen 2.0: Commercial-Scale Oxy-Combustion Plant Advances Toward Construction

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Significant project development and technical accomplishments over the past year have positioned FutureGen 2.0 as likely to proceed to construction. FutureGen 2.0 is a commercial-scale, near-zero emission power plant which utilizes oxy-combustion technology coupled with fully integrated CO_2 storage in a deep saline geologic formation.

FutureGen 2.0 will repower an idled fossil-fueled power plant in Meredosia, Illinois with oxy-combustion technology. The plant design output is 168-MW gross. The plant will be fueled with a blend of high-sulfur bituminous and low sulfur subbituminous coal. During steady-state operations the plant is designed to capture 98% of the CO_2 in the full flue gas stream and purify it to a level of 99.8%. Other conventional emissions will be reduced to near-zero levels. At an 85% capacity factor, the plant will capture 1.1 million tonnes per year of carbon dioxide. The carbon dioxide will be compressed and pumped forty-eight kilometers to a deep geologic storage site. The target injection reservoir for CO_2 storage, which is located at a depth of 1200 to 1350 m, is the Mt. Simon Sandstone. Confining beds of the overlying Eau Claire shale formation form a 126 m thick caprock. Based upon completed geologic characterization of the target injection reservoir and the overlying caprock, as well as 3D simulations of CO_2 injection and redistribution, it has been concluded that the site is a suitable geologic system for storage.

In 2012, the initial phase of design, including an assessment of the existing power plant infrastructure and drilling of a geologic characterization well, was completed. The results of this work were then used to prepare a detailed cost estimate and project schedule. The level of engineering and cost estimating far exceeds the level of detail performed in a typical pre-FEED, leading to greater confidence in the forecasted project cost. In January 2013, the FutureGen Alliance signed an asset purchase agreement that provides the rights to the necessary assets at the Meredosia Energy Center to complete the project. Also during early 2013 the CO_2 pipeline permit and CO_2 storage permit applications were filed with the regulating agencies. In June 2013, the Illinois Commerce Commission approved a 20-year power purchase agreement (PPA) for the plant’s operation. The PPA includes cost recovery for base plant operations as well as the associated carbon capture and storage (CCS) costs substantially increasing the likelihood the project will reach financial close and a construction start. With these and other accomplishments now complete, an additional $140 million has been authorized to complete the required design and permitting work required to reach a final construction start decision in mid-2014. The plant is scheduled to be online is 2017.

The presentation will include a technical description of the project and its status with respect to key project development activities, such as design, permitting, liability management, stakeholder involvement, and the power purchase agreement.

Demonstration of Coal Refining (COALREF$^®$) Technology in Commercial Scale

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Low rank coal (LRC) accounts for over 40% of the total coal reserves in China and US. The high efficiency and clean utilization of LRC plays an important role to meet the strong energy demand, reduce SOx/NOx/Hg and PM2.5 emissions. It is very important for China to develop advanced LRC utilization technologies. Various LRC upgrading technologies have been studied and developed over past decades, mainly in the directions of drying upgrading, pyrolysis polygeneration and gasification. But as today, there are no mature technologies for the efficient utilization of LRC in commercial scale. Driven by the strong energy demand and great market potentials, National Institute of Clean-and-low-carbon Energy (NICE) developed the first generation Coal Refining (CoalRef®) technology. The CoalRef technology aims to efficiently produce high value liquid and solid products from LRC by using the principle of Oil Refining. The CoalRef technology is the integration of drying, pyrolysis, quenching/cooling, deactivation process, and further processing of gas/liquid/solid products to clean fuel and chemicals. The upgraded coal is not only stable and has much higher heating value than the raw coals, but also has much lower sulfur and Hg content, and can be used for gasification and combustion in a much cleaner way. The valuable liquid products can be used directly or upgraded to high value fuels and chemicals.

Based on NICE’s Coal Refining technology, Shenhua Group is planning to build a 1 MMTA demonstration plant which is part of 10 MMTA Coal Refining project in China. The successful demo of this technology will have significant impact on the clean and efficient utilization of LRC in China and world.

Performance Prediction of a Pyrolysis Bridged Hybrid Power System

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Pyrolysis bridged hybrid power system (PBHPS) for low rank coal employs a pyrolyzer which is integrated with a Circulating Fluidized Bed (CFB) boiler to convert coal into gas and char. The pyrolysis gas is applied to gas turbine to generate electricity after purification, and char is fed into the CFB boiler and burned for conventional steam turbine electricity production. Another unique feature of the system is that the steam produced from heat recovery steam generator (HRSG) is superheated in the CFB boiler, then the superheated vapor enters into the steam turbine together with the steam produced from the CFB boiler. To this concept, an existing 50 MWe combined heat and power plant with CFB boiler was retrofitted by means of appending a pyrolyzer, 30 MWe gas turbine and HRSG. The structured system model had been set up by utilizing THERMOFLEX® software. In this research, net electricity efficiency of repowering system increased from original 14.8% to 20.3% with 80 MWe capacity. Off-design performance of the system had been taken into consideration. Three commercial gas turbines were used in the simulation and also discussed the overall efficiency of the plant at part-load. The work confirmed the benefit of merging gas turbines and conventional steam cycle units for coal fired plants.

SESSION 19
Coal Science: General – 4

Effect of Sodium Carbonate Additive on the Activation of Coal Wastes for Alumina Extraction

Yanxia Guo, Kezhou Yan, Yaoyao Li, Fangqin Cheng, Shanxi University, CHINA

Coal wastes such as coal fly ash, coal burning bottom ash and coal gangue as one of the largest solid wastes discharged in China have brought very serious environment problems. Coal wastes are aluminosilicates containing many amounts of Al_2O_3 (10~40 wt%) and SiO_2(40~60 wt%). Extraction of alumina from coal wastes is one of the most important high-valued utilization ways. The common alumina extraction method from them is acid leaching method. Coal wastes, however, containing the inert matters such as mullite, kaolinite, feldspar and quartz, are needed to be activated to inspire their chemical activities. It is found that Na_2CO_3 as the active additive of coal wastes could improve their alumina extraction significantly. The effect of the differences in mineral compositions on the activation of coal wastes is still unclear. In this study, coal fly ash and coal gangue as the typical coal wastes were used to extract Al_2O_3. It is aimed to investigate the effect of the differences in mineral compositions on the activation by Na_2CO_3. The results showed that Na_2CO_3 could improve the alumina extraction no matter for coal fly ash or coal gangue. All the aluminosilicates such as mullite, kaolinite, quartz and other aluminosilicate minerals in coal fly ash and coal gangue could be transformed into nepheline ($NaAlSiO_4$) which is easily to be leached by acid. The thermal behaviors displayed from TG-DSC curves for coal fly ash and coal gangue with the addition of Na_2CO_3 represented remarkable resemblances. It deduced that Na_2CO_3 could provide the charge compensate ion and facilitate the disaggregation or decomposition of aluminosilicates despite of the differences in the mineral compositions.

Effect of Heating Temperature and Additives on the Transformation of Alkali Metals in Zhundong Coal with High Sodium Content

Xuebin Wang, Limeng Zhang, Bo Wei, Houzhang Tan, Tao Yang, Zhongfa Hu, Xi'an Jiaotong University, CHINA

Zhundong coalfield is the largest integrated coal basin newly found in China but the content of sodium in Zhundong coal is high, and it induces severe problems of fouling and slagging. In the present paper, the existence and transformation of alkali metals in Zhundong coal was investigated when coal was heated at 500-900^oC and the effects of silicous additives were also discussed. Results show that most of Na in raw Zhundong coal and its residual ash exists as water-soluble species, but the other alkali metals liking K, Ca and Mg mainly exist as insoluble forms. Amount of sulfates containing alkali metals are found in ash for all the test conditions, which will not decompose until 1150 ^oC. In the ash prepared at 500^oC, there is a certain content of $MgCa(CO_3)_2$ which decomposes at higher than 600^oC. The residual Na in ash linearly decreases with the increasing in treating temperature, and the decreasing is mainly referring to the water-soluble Na because the changing in the content of acid-soluble Na and insoluble Na with treating temperature is inconspicuous. Moreover, the additions of siliceous additives play an effective role of capturing Na species at high temperatures, and with the increasing in the additive mass, the relative content of water-soluble Na is significantly reduced but more water-insoluble Na is kept in the residual ash. The present investigation and results should be useful to propose the efficient method to solve the fouling and slagging induced by alkali metals in Zhundong coal.

Process Analysis on Co-Pyrolysis of Lignite and Residue from Shendong Coal Direct Liquefaction

Yanli Xue, Xiaohong Li, Xiaoyong Xue, Qun Yi, Jie Feng, and Wenying Li, Taiyuan University of Technology; Xiaofen Guo, Ke Liu, NICE, CHINA

The co-pyrolysis concept of lignite and direct liquefaction residue (DLR) is proposed based on the resources utilization and the synergetic effect to upgrade the yield and quality of tar. Low temperature co-pyrolysis (500 - 600 ^oC) experiments were investigated by using a fixed-bed reactor under atmospheric pressure in high purity nitrogen. The initial pyrolysis temperature was designed as 550 ^oC and the ratio of DLR to lignite were 10%, 15% and 20% respectively. In order to expel the influence of the residual liquefaction catalyst ($Fe_{1-x}S$), the DLR was Soxhlet extracted with tetrahydrofuran at 100 ^oC in order to extract hydrogen-rich components, and extraction residue was named as THFIS.

Results showed that yield of tar produced at different blending ratio 10%, 15%, 20% were 7.1%, 8.75%, 8.35%, while the tar yield sum of lignite and DLR pyrolysis individually were 6.02%, 6.46%, 6.9%. There exists the synergetic effect between lignite and DLR during co-pyrolysis. By analysising co-pyrolysis of lignite and THFIS, it was found that synergetic effect is not from the remained liquefaction catalyst ($Fe_{1-x}S$), and is likely to come from hydrogen-rich component.The higher blending ratio will lead to more free radicals being stabilized, but excessive plastic mass hinder volatiles being driven out of the particles, hence, the yield of tar produced at 15% was maximum. Based on the synergetic effect, optimization of experimental conditions was suggested as the ratio of the DLR to coal, pyrolysis temperature and particle sizes of coal and DLR are 0.15, 550^oC and 0.425 - 0.85mm, respectively. Under the optimal operational conditions, tar yields of lignite and DLR co-pyrolysis was 8.75%, but hexane insoluble of the tar increase from 29.46% to 38.56%.

SESSION 20
Coal Mining: Monitoring and Controlling Gas in Mines

Mining Methane Drainage in Polish Coal Mines

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Methane drainage is used in Polish coal mines in order to reduce mine methane emission as well as to keep methane concentration in mine workings at safe levels. Due to mining and geological conditions in Polish mines, pre-mining methane drainage is conducted to a small extent. It is usually used to reduce outburst risk. Low permeability of coal seams allows for obtaining satisfactory effectiveness during and after mining a longwall. Development works also do not take into consideration pre-mining methane drainage.

This article presents two methods of methane drainage during mining. The first method is connected with drilling cross-measure boreholes from tail entries to an unstressed zone in roof or floor layers of a mined seam. That is the main method used in Polish mining, where both the location of drilled boreholes as well as their parameters are dependent on mining and ventilation systems of longwalls. The second method is connected with drilling top drainage headings in seams situated under or over a mined seam.

This paper compares these methane drainage methods with regard to their effectiveness in Polish mining conditions. High effectiveness of methane drainage system with different ventilation and methane drainage systems has been proven.

A Novel Technology to Control the Quality of Pre-Mining Methane Drainage

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Advances in our understanding of coal-gas interactions have changed the manner in which we treat coalbed methane: from mitigating its dangers as a mining hazard to developing its potential as an unconventional gas resource recovered through pre-mining drainage. This study presents a novel technology that has been developed and commercially applied to enhance the concentration of pre-mining methane drainage. The new technology involves the sealing of fractures around boreholes that may develop into air-leakage paths. Firstly fine expansive particles are injected to these fractures while gas concentration drops. These particles transport into in-seam borehole driven by the high pressure air. Then particles move randomly within the fractures. Meanwhile particles become to coagulate and block up fractures due to its swelling. As fractures are blocked, air is prevented from entering into the coal seam. As a result, an ideal gas concentration can be maintained and the duration of high drainage concentration is extended. Field testing shows the characteristics of fractures have been greatly changed after sealing. For the boreholes with an originally low gas concentration (0%~30%), the novel technology can increase the gas concentration by 10%~65% and extend the production time by two to three more months. The total amount of the extracted gas increased to 2000~3000 m³ per borehole.

The Global Methane Initiative and its Role in Increasing Coal Mine Methane Recovery and Use

Felicia Ruiz, Coalbed Methane Outreach Program, EPA; Clark Talkington, Advanced Resources International, Inc., USA

Coal mining is one of the principal sources of fugitive anthropogenic methane contributing 8 percent of total man-made methane emissions. In 2010, estimated worldwide coal mine methane (CMM) emissions totaled 589 million metric tons of carbon dioxide equivalent (MMTCO2E), or about 41.2 billion cubic meters (BCM) and emissions are expected to grow to 671 MMTCO2E (46.9 BCM) by 2030. Advancing CMM projects and realizing emission reductions requires the implementation of enabling regulatory and policy directives with sufficient drivers that foster best practices in the industry and promote actual project implementation and operation. The Global Methane Initiative (GMI) is playing a leading role in these efforts. Created in 2004, the GMI has now grown to 41 member states and the European Commission with over 1200 project network members representing private, non-governmental, multilateral, quasi-governmental, academic and public institutions. The Initiative works to reduce the informational, institutional, and other market barriers to project development through the development of tools and resources, training and capacity building, technology demonstration, and direct project support.

In the coal sector emission reductions are achieved through implementation of best practices, installation and operation of modern, efficient gas drainage systems, deployment of gas utilization equipment and destruction of ventilation air methane (VAM). These projects not only reduce greenhouse gas emissions but deliver important ancillary benefits including greater mine safety, incremental energy production and even profitable business silos for mining companies. Since its inception in 2004, GMI initiatives have played a key role in abating over 150 MMTCO2e from coal mines. These projects have in turn accounted for investments into the hundreds of millions of dollars supporting social and economic development in addition to mine safety and environmental protection.

Although the number of CMM recovery and use projects is growing and much has been accomplished in the last decade, there remains substantial opportunity to further reduce CMM emissions through widespread implementation of industry best practices for methane drainage and deployment of state-of-the-art equipment and operating practices. China, in particular, is very important to any global effort to reduce CMM emission because it is rapidly approaching 50% of global coal production with its mines producing 4 billion metric tonnes per year. Almost all of China's coal is produced from gassy underground mines, and over 300 mines in China use methane drainage. China also leads the world in CMM emissions which mirrors its coal production ranking. On the other hand, China has been at the forefront of CMM project development in recent years with many new projects coming on line including the world's largest VAM project. Still, there remains great opportunity in China for institutionalization of best practices and further project development to achieve even greater CMM emission reductions.

This paper will identify and evaluate existing global practices and trends for CMM recovery and use including possible new horizons for gas recovery. The paper will also examine the role of the GMI in catalyzing current and future project implementation with particular emphasis on China.

Micro-Seismic Monitoring for Uncontrolled Gas Emissions in Underground Coal Mining

Guangyao Si, Ji-Quan Shi, Sevket Durucan, Imperial College London, UNITED KINGDOM

Uncontrolled gas emissions (or gas outbursts) pose a serious threat to safety in underground coal mining throughout the world. In a recently completed research project funded by the European Commission Research Fund for Coal and Steel, a suit of monitoring techniques have been applied to monitor geophysical as well as geomechanical response of the coal seam being mined to longwall face advance at Coal Mine Velenje in Slovenia. In one longwall panel, over 2,000 micro-seismic events were recorded during the period between 27 April and 30 August 2011, as a direct result of coal extraction. Over the same period, there was also a recorded episode of relatively high gas emission in the area. In this paper, a detailed analysis of the processed microseismic data leading to and post this emission incident carried out at Imperial College is presented. Specifically, the analysis includes the spatial distribution of the microseismic events with respect to the advancing face, the histogram of the energy released (weekly) and its temporal evolution. Recognising that micro-seismic events occur as a result of the fracturing of coal/rock surrounding mine openings, an attempt has also been made to use fractal dimension, estimated from the spatial density of the recorded microseismic incidents, to characterise the build-up of fractures in the seam being mined ahead of the face, and to correlate it with the gas emission event.

Field Performance of Alternate Mining Geometries for Set-Up Rooms and Development Entries in Longwall Mining

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This paper discusses a numerical modeling and field study that focuses on: 1) Identifying mechanisms of instability in the set-up rooms (SR) and T-junctions, and 2) Implementing alternate 3-entry and 4-entry set-up room geometries. This was done to alleviate ground control problems (roof falls, rib sloughing, floor heave, etc.) and safety issues within set-up rooms (SR) layout and around the T-junctions of SR. 3-D numerical models using FLAC3D software were developed of the SR area and the adjoining gate and tail development areas. The numerical models were validated using field measurements of the current mining geometry. Analyses were then made of the linear and non-linear behaviour of coal pillars and immediate mine roof and intersections of alternate geometries within the SR area. The developed alternate geometries were implemented by the coal company with acceptance by the regulatory agencies. Over the last two years, three alternate geometries have been successfully implemented at two longwall faces. Field monitoring of roof to floor convergence, differential horizontal displacement of pillars, rosettes mounted in the roof (roof bolts) and on the wooden cribs have indicated significantly improved stability in SR as well as T-junction areas. The coal company has successfully maintained stable SRs.

SESSION 21
Gasification: General – 4

Research on Two Stage Gasification Reaction Property in a Pulverized Coal Gasifier

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The conception of two stage gasification is that gasification reaction is divided into two stages to finish. In the first stage, reaction temperature is higher than ash fluid temperature to ensure slag generated discharge from gasifier. In the second stage, reaction temperature is 1100~1200℃, gasification reaction continue to occur and more syngas generated, which improves gasification efficiency. Experiments of two stage gasification are carried on in a 2000t/d pulverized coal gasifier in Huaneng GreenGen Project. Different coal rate injected in the second stage is tested and the effect of H_2O and CO_2 ration in syngas to reaction is tested. The result shows when 5% coal is put into the second stage, total coal reaction rate is higher than 99% and gasification efficiency is improved 1%. Coal reaction rate of second stage is higher when H_2O and CO_2 ration in syngas is higher than 2.5%.

Study on Venturi Characteristics in the Dense Phase Pneumatic Conveying System

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Stably feeding coal to the gasifier at high density and pressure could be better realized adopting venturi in the conveying system. This paper discusses the role of venturi on the performance of pneumatic conveying of pulverized coal with the high density and pressure experimental system. Compared to general systems the conveying capacity can be effectively curbed and the pipeline pressure can be greatly raised moreover the system stability could be preferably optimized. In addition, in contrast to particle concentration, particle velocity presents the greater influence on the venturi pressure drop.

Modeling Based Development of Internally Circulating Gasifier for High Ash Coals

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Despite the enormous potential of coal gasification technology as environmental friendly technology, the wide industrial usage of this technology has not been achieved yet. The reduction of capital costs is the most important step towards economic competitiveness of gasification technologies compared to alternatives such as conventional combustion (for the case of electricity and heat supply) and oil based or gas based processes (for the case of chemicals production). To reduce the production and operation costs the so-called computer based modeling of new gasifier prototypes is required.

The present work focuses on modeling Internal Circulating (INCI) gasifier invented by researchers at IEC, TUBAF [1]. This gasifier combines advantages of different types of gasifiers to provide high carbon conversion rates, high cold gas efficiency and syngas yields at comparatively low construction and operating costs especially for conversion of high-ash coals.

The system is characterized by a mild transport regime with induced kidney shaped recirculation cells in order to increase the residence time. Oxygen is added as gasification agent leading to local temperatures above the ash fluid temperature. Formation of ash agglomerates will lead to an internal separation mechanism of fresh fine-grained feedstock and (partially) converted bigger agglomerates. The agglomerates will move downwards and form a moving bed in the lower part of the gasifier. Secondary gasification agents are added from below the moving bed in order to post gasify the agglomerates. Thus complete carbon conversion can be achieved.

The modeling work comprises two parts. First part is devoted to the thermodynamic-based simulation. In particular, the influence of manifold parameters of the INCI gasifier such as coal ash content, outlet temperature, etc. on the gasifier key performance indicators are investigated theoretically using the commercial software tool ASPEN Plus® [2]. Additionally we compare the performance of the INCI gasifier with conventional coal gasifiers. The analysis of results revealed that in the case of converting high ash coals, the INCI gasifier showed the best performance. The actual ratios of coal to H_2O and coal to O_2 in the INCI gasifier are closest to the thermodynamically optimal ratios for maximizing cold gas efficiency and syngas yield compared to other investigated gasifiers. The global thermodynamic maximum of cold gas efficiency for a particular high ash (25 wt%, wf) coal gasified at 30 bars is calculated to be approx. 85%. The INCI gasifier achieves approx. 85% whereas the investigated conventional coal gasifiers achieved between 61 and 79%. For the same case, the global thermodynamic maximum for syngas yield (H_2 + CO) is approx. 2.1 m^3(STP)/kg $coal_{waf}$. The INCI gasifier achieves 1.83 m^3(STP)/kg $coal_{waf}$ whereas the other investigated gasifiers achieved between 1.52 and 1.91 m^3(STP)/kg $coal_{waf}$.

Second part of the work presents the results of CFD simulations to illustrate the flow structure inside the gasifier in order to confirm the formation of recirculation cells. A Two Fluid Model (TFM) was applied to model the gas phase and solid phase. Here, the Kinetic Theory of Granular Flow (KTGF) was used to close the resulting set of equations. As a first step we investigated the cold gas flow in the lab scale unit. The comparison of numerical simulations with experimental data obtained using PIV measurement showed very good agreement. Additional calculations investigate the interaction between gas phase and particle phase. These simulations are based on a spouted bed experiment [3] as there are no own measurements. A spouted bed system was chosen as it comprises different volume fractions of solids in its different regions (core, annulus, spout), which is somehow similar to particulate flows in the INCI reactor. The simulation results are in qualitative agreement with experiments and the most influential model parameters are detected. Finally, cold and hot unreactive multiphase simulations in the INCI mesh were performed to demonstrate the flow pattern inside the reactor. The results are illustrated and discussed.

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Computational Fluid Dynamics Modeling for Coal Size Effect on Coal Gasification in a Two-stage Commercial Entrained-Bed Gasifier

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Computational Fluid Dynamics (CFD) modeling of coal gasification in E-Gas coal gasifier was conducted using a commercial code, ANSYS FLUENT to study coal size effect on gasification performance. The CFD modeling was carried out by solving the three-dimensional, steady-state Navier–Stokes equations with the Eulerian–Lagrangian method. Gas-phase chemical reactions were solved via the Finite-Rate/Eddy-Dissipation model. In order to solve char gasification reactions, the random pore model with bulk and pore diffusion effects was considered via a user defined function (UDF). For each coal size, species mole fractions, exit gas temperature, carbon conversion efficiency, cold gas efficiency, and distributions of gas temperature and species in the gasifier were calculated by the modeling. The CFD results were reasonable in terms of species mole fractions and temperature at the exit through comparison with operating data of Wabash plant. The carbon conversion efficiency and cold gas efficiency were the best with the coal size of 100 μm.

A Dynamic Modeling and Simulation of an Entrained Flow Coal Gasifier

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In order to better understand the information of an entrained flow coal gasifier, a mathematical model is developed to simulate the Texaco down flow entrainment pilot plant gasifier using coal–water slurries as feed stocks. The entrained flow gasifier is divided into three zones: the pyrolysis and volatile combustion zone, the char combustion and gasification zone, and the gasification zone. The model describes the physical and chemical processes occurring in an entrained coal gasifier. Temperature, concentration and slag profiles along the reactor were obtained by solving the mass and energy balances and taking into consideration heterogeneous and homogeneous reaction rates to describe different complex reactions. The prediction results from this model were in agreement with an experimental data. Parameter studies were made to provide a better understanding of reactor performance for various inlet feed conditions utilizing the model.

SESSION 22
Clean Coal and Gas to Fuels: General - 4

High Purity Hydrogen from Coal in a Novel Reactant Looping Gasification

Tomasz Wiltowski, Kanchan Mondal, Southern Illinois University, USA

A novel process on the production of a high purity stream of hydrogen from gasification products with concomitant generation of utilization-ready carbon dioxide stream is presented. For the implementation of this technology, three systems are envisioned a) Steam gasification with partial oxidation in the presence of magnetite in a fluidized bed, b) Reactant looping Separation for hydrogen enrichment and carbon dioxide separation in the presence of a Boudouard catalysts and a carbon dioxide capture agent (CDCA) in a fixed bed, and c) Final utilization of the enriched hydrogen by either emission free combustion or use as a chemical. In the first system, the coal is expected to be gasified by both steam and the iron oxide and the reduced iron oxide is constantly regenerated by the steam. The correct loading of the iron oxide provides sufficient enthalpy for the reaction to be carried out with low external energy input as well as reduce the formation of thermal NO_x (generally present in the flue gas when using air). The Boudouard reaction produces one CO_2 moiety and one C moiety from two CO moieties in an exothermic reaction. Thus, unlike the water gas shift, this reduces the amount of CO_2 to be captured in the hydrogen enrichment stage. The CO_2 is captured by the CDCA, yielding high purity hydrogen. If steam is added to this stage the purity of hydrogen may be further enhanced. Once the CO_2 breakthough occurs in this stage, air or steam is introduced to regenerate the Boudouard catalyst through an exothermic oxidation reaction and the heat is utilized to desorb the CO_2 from the CDCA. Thus, the operation of this system would result into two separate streams of (a) high purity hydrogen for use in fuel cells and (b) utilization ready CO_2. The thermodynamic evaluation of the above system shows the potential of achieving greater than 99 % hydrogen purity values in the product stream even at atmospheric pressures. Simultaneous coal gasification and hydrogen enrichment experiments were conducted in the pressurized fluidized bed reactor at one and 250 psi. The effects of temperature, pressure and steam partial pressures on the gasification and hydrogen enrichment processes are reported. Experiments were also conducted to evaluate the effect of Boudouard catalyst and CDCA loadings on the product gases. Both the gaseous yield and hydrogen purity was observed to increase due to the use of these solid oxides. Simple gasification produced a gas with a maximum purity less than 40 %. However, greater than 70 % pure hydrogen was obtained in most cases. The conditions were optimized to obtain nearly 99% pure hydrogen in the exiting stream. In addition, the gaseous yield was observed to increase two fold as a result of the use of the reactive solids in the bed.

Hydrogenation of Coal Tar on Dinickel Phosphide Supported on Alumina Catalyst

Shibiao Ren, Xianzhong Cao, Zhiping Lei, Zhicai Wang, Hengfu Shui, Shigang Kang, Chunxiu Pan, Anhui University of Technology, CHINA

As an important by-product in coke production, abundant high-temperature coal tar has been produced every year in China. Hydrogenation of high-temperature coal tar is one of the most viable process alternatives for the conversion of low-value coal tar into a valuable product such as high-clear fuel and aromatic compounds. In this work, we report the conversion of high-temperature coal tar into the valuable aromatic compounds (such as naphthalene) by selective hydrogenation of high-temperature coal tar over $Ni_2P/\gamma\text{-}Al_2O_3$ catalysts. Hydrogenation reaction was carried out on a fixed bed microreactor. The activity of $Ni/\gamma\text{-}Al_2O_3$ for hydrogenation of high-temperature coal tar was also tested as comparison. The results showed that naphthalene content in the hydrogenation products on both $Ni/\gamma\text{-}Al_2O_3$ and $Ni_2P/\gamma\text{-}Al_2O_3$ catalysts was enhanced. After reaction for 4h, naphthalene content increased from 10.2 wt% in coal tar to 14.7 wt% in hydrogenation products over $Ni/\gamma\text{-}Al_2O_3$, but 13.8 wt% over $Ni_2P/\gamma\text{-}Al_2O_3$ catalyst. However, naphthalene content decreased obviously over $Ni/\gamma\text{-}Al_2O_3$ with prolongation of reaction time and only about 12.5 wt% after reaction 8h. In contrast, $Ni_2P/\gamma\text{-}Al_2O_3$ catalyst had 13.5 wt% naphthalene content after reaction for 8 h and still 12.8 wt% after reaction for 16 h. It indicated that $Ni/\gamma\text{-}Al_2O_3$ had a higher initial activity than $Ni_2P/\gamma\text{-}Al_2O_3$ catalyst but $Ni_2P/\gamma\text{-}Al_2O_3$ catalyst showed long-lived activity. Since increase in reaction time had inactivation of both $Ni/\gamma\text{-}Al_2O_3$ and $Ni_2P/\gamma\text{-}Al_2O_3$ catalysts, catalyst reactivation was also carried out by washing out the used catalysts with toluene solvent. The reactivated $Ni_2P/\gamma\text{-}Al_2O_3$ catalyst showed almost the same activity as the fresh catalyst. But the reactivated $Ni/\gamma\text{-}Al_2O_3$ showed only about 12.7 wt% naphthalene content after reaction for 4h, which was lower than that of the fresh catalyst, indicating the reactivated $Ni/\gamma\text{-}Al_2O_3$ catalyst was not reactivated by washing with toluene solvent. It shows that high-temperature coal tar can be converted into the valuable aromatic compounds (such as naphthalene) by selective hydrogenation over $Ni_2P/\gamma\text{-}Al_2O_3$ catalyst.

Fischer Tropsch Synthesis in Supercritical CO_2 Atmosphere with Product Gas Recycle

Kanchan Mondal, Adam Sim, Madhav Soti, David Carron, Tomasz Wiltowski, Southern Illinois University, USA

The key challenge in applying the Fischer-Tropsch process to produce transportation fuels is to make the capital and production costs economically feasible relative to the comparative cost of existing petroleum resources. To meet this challenge, it is imperative to enhance the CO conversion while maximizing carbon selectivity towards the desired liquid hydrocarbon ranges (i.e. reduction in CH_4 and CO_2 selectivities) at high throughputs. At the same time, it is equally essential to increase the catalyst robustness and longevity without sacrificing catalyst activity. This paper focuses on process development to achieve the above. The paper describes the influence of operating parameters on Fischer Tropsch synthesis (FTS) from coal derived syngas in supercritical carbon dioxide ($ScCO_2$). In addition, the unreacted gas and solvent recycle was incorporated and the effect of unreacted feed recycle was evaluated. It was expected that with the recycle, the feed rate can be increased. The increase in conversion and liquid selectivity accompanied by the production of narrower carbon number distribution in the product suggest that higher flow rates can and should be used when incorporating exit gas recycle. It was observed that this novel process was capable of enhancing the hydrocarbon selectivity, reducing the parasitic loss of carbon efficiency due to carbon dioxide formation during FT synthesis reactions and increasing the life of the catalyst. The use of the supercritical CO_2 ($ScCO_2$) inhibited both methane and CO_2 selectivities while enhancing the rates of synthesis. In addition, the use of supercritical CO_2 was found to prolong the life of the catalyst presumably by removing the heat of reaction from the catalysts surface and solubilizing the waxes that tend to deposit of the surface. The effect of the process conditions on the life of the catalysts will also be presented. Fe based catalysts are known to have a high proclivity for producing CO_2 during FTS. The data of the product spectrum and selectivity on Co and Fe-Co based catalysts as well as those obtained from commercial sources will also be presented. The measurable decision criteria were the increase in CO conversion at H_2:CO ratio of 1:1 (as commonly found in coal gasification product stream) in supercritical phase as compared to gas phase reaction, decrease in CO_2 and CH_4

selectivity, overall liquid product distribution, and finally an increase in the life of the catalysts. Some of the notable findings include negative CO_2 selectivities while obtaining nearly 98 % CO conversion. Increasing the reactor pressure was found to favor longer chain growth. In addition, it is noted that the ratio between CO_2:syngas in the reaction mixture is an important factor in the liquid product distribution. The results from Fe-Zn-K, Fe-Co-Zn-K and Fe-Co-Ru-Zn catalysts on gamma alumina supports will be presented for recycled gas to feed gas flow rate ratio of 0, 0.5, 1, 2, 3, 4 and 5.

SESSION 23
Carbon Management: General - 1

CO_2 Capture RD&D Proceedings in China Huaneng Group

Shisen Xu, Huaneng Clean Energy Research Institute, CHINA

CO_2 capture is an important carbon management route to mitigate the greenhouse gas emissions in power sector. In recent years, China Huaneng Group has paid more attention on CO_2 capture technology development and launched a series of R&D and demonstration projects.

In the area of Pre-combustion CO_2 capture technology, GreenGen project initiated by China Huaneng Group (CHNG), is the first integrated gasification combined cycle (IGCC) power plant in China. Located in Tianjin, GreenGen aims at the development, demonstration and promotion of a near-zero emissions power plant which will improve coal power generation efficiency and realize near zero emissions of pollutants (SO_2, NO_x, particulate matters) and CO_2. As planed in Phase I of GreenGen, an IGCC plant of 250 MW has been built, which has successfully passed a 72+24-hour full-scale trial operation on 6 November 2012. Based on this plant, in Phase II, a pre-combustion CO_2 capture unit will be added and tested. Recently, with the help of process and unit modeling, the process comparison and selection of a 30MW_{th} capture system has been finished. Moreover, Process Flow Diagram (PFD), design of the key equipments, and the bidding for the large key equipments have been completed. Innovations in the absorbents and adsorbents for CO_2 will further enhance the process performance.

Regarding to Post-combustion CO_2 capture (PCC), in 2008, CHNG built an experimental flue gas capture pilot system at its Huaneng Beijing Thermal Power Plant with a capture capacity of 3000 tonnes of CO_2 per year, which is the first CO_2 capture demonstration plant in China. It is under operation since then and supports a series of solvent performance tests and material corrosion analysis studies. In 2009, Huaneng launched a PCC project at the Huaneng Shidongkou No.2 Power Plant in Shanghai with a capture capacity of 120,000 tonnes of CO_2 per year. This commercial demonstration project applies the low partial pressure CO_2 capture technology of CHNG its own. The construction was commenced on July 2009 and the plant was put into operation on 30th Dec. 2009. CO_2 with a purity of higher than 99.5% can be generated from the capture island, after the refining treatment CO_2 of food-grade purity can be produced. This demonstration is one of the largest coal-fired power plant PCC units in the world. Recently, Huaneng Clean Energy Research Institute (CERI) and Powerspan formed a joint venture, Huaneng-CERI-Powerspan (HCP). As one entity, HCP has completed the technology qualification program (TQP) required by Statoil to supply carbon capture technology for the CO_2 Capture Mongstad (CCM) project. During this qualification program, several test campaigns were conducted to demonstrate technology performance under operating conditions expected at CCM and to establish solvent degredation characteristics and absorber emissions during extended operations. Besides these activities mentioned above, feasibility studies and system design for large scale PCC system, have been undertaken by CERI and its partners from Australia, US and Europe.

Dynamic Simulation of MEA-Based Post-Combustion Carbon Capture System

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Coal-fired power plants are the primary targets to reduce CO_2 emission due to their largest CO_2 emission of single source, relatively centralized regional distribution and thus good potential of CO_2 reduction. Post-combustion carbon capture using aqueous MEA solution is the most likely technology to be deployed in coal-fired power plants. Some studies have focused on the dynamic modeling of MEA-based post-combustion carbon capture system recently to facilitate the CCS practice in coal-fired power plants, but a clear strategy is still lacking on how to handle the CO_2 capture units in transient mode.

In this paper, a dynamic model of MEA-based carbon capture system for coal-fired power plants was built up and validated to study its transient responses. The model was implemented in Invensys Simsci DYNSIM platform, and the stage efficiency was used to correct the assumption of vapor-liquid equilibrium in tower model. The pilot carbon capture facility set up at the University of Texas at Austin was simulated in this research. The local control systems of gas pressure, liquid level and flowrate were designed to keep the system working. The experiment data of Case 28 was used to validate the model. The comparison among the pilot test data, simulation of Aspen Plus using rate-based model and our simulation was carried out on the gas phase temperature profile inside the absorber and stripper. The results show that the steady state of developed dynamic model fits the measured data fairly well. This dynamic model was then used to study the dynamic character of CO_2 capture system, and under the flowrate disturbances of flue gas and lean solution, the transient response of CO_2 loading, CO_2 capture rate, CO_2 capture energy consumption were observed and analyzed for the purpose of disturbance rejection control.

Dynamic Modeling and Control of Post-Combustion CO_2 Capture Process Integrated with Supercritical Pulverized Coal Plant

Qiang Zhang, Debangsu Bhattacharyya, Richard Turton, West Virginia University, USA

The process of CO_2 capture and storage is a promising and effective way to control the emission of CO_2 from large-scale, stationary sources such as conventional, pulverized-coal, power plants. In this work, a liquid MEA-based, post-combustion CO_2 capture and compression system, was simulated in Aspen Plus and Aspen Plus Dynamics. The process was also integrated with the steam system of a 550 MWe supercritical pulverized coal power plant. The steady state simulation was carried out in Aspen Plus using rate-based separation processes for the absorber and stripper columns under a constraint of 90% capture efficiency. The thermal energy for CO_2 recovery was provided by extracting steam before the low-pressure turbine. With optimized parameters for the capture process, the integrated coal-fired power plant had a net power of 420.9 MWe and the efficiency was 30.08% (HHV), which was 9.22% less than the values reported in the case without CO_2 capture.

The steady state model developed in Aspen Plus was converted to a dynamic model in Aspen Plus Dynamics with appropriate modifications in the plant configuration for a pressure-driven dynamic simulation. The rate-based separation calculation method was also replaced by equilibrium-based method since rate-based unit operations are not supported in Aspen Plus Dynamic. A formulation for component efficiency was generated from the rate-based simulation in the face of typical disturbances such as changes in the flue gas flowrate and composition. This formulation was then applied in the dynamic simulation to minimize the discrepancy between rate-based and equilibrium-based absorber models.

For even modest sized power plants, the volume of flue gas generated requires that multiple parallel trains of absorption and stripping columns are needed in order to capture the majority of the carbon dioxide in the gas. For the current study, six trains of CO_2 absorption and stripping columns were coupled together to investigate the controllability of such systems. Due to the pressure-flow dynamics, a precise distribution of the flue gas between the trains is a challenge for this highly interactive system. Variations in distribution of the flue gas in the absorbers can lead to variations in CO_2 capture achieved in any column. Thus it can be difficult to achieve the overall goal of CO_2 capture. In addition, the control of liquid inventory and the regulation of the stripper efficiency pose further challenges. The presentation will include results from a number of control strategies for maintaining the desired CO_2 capture efficiency in the face of typical disturbances for this highly interactive process.

Aqueous Ammonia and Amino Acid Salts Blends for CO_2 Capture

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Aqueous ammonia (NH_3) is a promising absorbent for post combustion capture (PCC) of CO_2 because it has many advantages compared to amines based solvents, including low cost, a high CO_2 removal capacity, a low regeneration energy, and the potential of capturing multiple flue gas components (NO_x, SO_x and CO_2) and producing value added chemicals. However, aqueous ammonia has a low CO_2 absorption rate and the mass transfer coefficient (K_G) of CO_2 in aqueous ammonia is 3 or 4 times lower than those in standard monoethanolamine (MEA) base solvents at their respective operating conditions. This will lead to a high capital cost for the aqueous ammonia based CO_2 capture process. To enhance CO_2 absorption rate in aqueous ammonia, a number of amino acid salts were investigated as the potential promoter. Amino acid salts are low-cost, environmentally friendly chemicals. They have lower vapour pressure, are less sensitive to oxygen and more thermally stable than amines and react with CO_2 relatively fast. Screening tests of the potassium salts of amino acids on a wet wall column showed that sarcosine and L-poline give the highest mass transfer coefficients of CO_2. These two kinds of amino acid salts were further investigated. Effect of temperature, amino acid salt concentration, and CO_2 loading on absorption rate and ammonia loss rate is reported.

Investigation of Carbon Dioxide Desorption in Membrane Vacuum Regeneration Process

Mengxiang Fang, Zhen Wang, Qinhiu Ma, Zhongyang Luo, Zhejiang University; Shuiping Yan, Huazhong Agricultural University, CHINA

Amine based post-combustion capture (PCC) technology, which typically uses thermal method to achieve absorbent regeneration, is believed to be the most mature technology for CO_2 capture from flue gas. However, the major drawback of this technology is the high energy penalty, especially large energy required in stripper, due to high-grade steam to be extracted from turbine to heat the CO_2-rich solution. Aiming to reduce the energy demand of absorbent regeneration in the stripper, we developed a novel regeneration concept called membrane vacuum regeneration (MVR), in which the regeneration temperature decreases to around 343 K. In MVR process, a commercial polypropylene (PP) hollow fiber membrane contactor is used instead of traditional packed column stripper to gain a higher CO_2 mass transfer area. Reduced pressure and low-temperature sweeping steam are employed in the shell side of membrane contactor to enhance the CO_2 desorption mass transfer driving force. The MVR performance of different absorbents including amines and amino acid salts are studied at the condition of 348K regeneration temperature and 20kPa regeneration pressure. The results showed absorbents with lower basicity (pKa) usually present a better MVR performance that those with higher pKa. For example, N-methyldiethanolamine (MDEA), 2-amino-2-hydroxymethyl-1,3- propanediol (THAM) and triethylenetetramine (TEA) have advanced regeneration ratio and CO_2 capacity per mole absorbent. Most amino acid salts studied in this work show a relative low regeneration ratio, but the surface tensions of them are usually higher than amine solutions, which could reduce the possibility of membrane wetting in MVR process. To understand the CO_2 regeneration in MVR process, we investigated the effects of key operating parameters including liquid flow rate, regeneration pressure, regeneration temperature experimentally and theoretically. Increase of liquid flow rate will reduce the regeneration ratio of CO_2-riched absorbent but increase CO_2 desorption flux. Lower regeneration pressure and higher regeneration temperature will improve regeneration ratio but at cost of more energy demand. The long-term running of MVR process is also studied. It is observed that some slit-like membrane pores shrank longitudinally and became elliptical which result in the increase of mean membrane pore size after long-time contact of membrane with absorbents. This increase on membrane pore size leads to the decrease of minimum breakthrough pressure and the increase of membrane wetting possibility. The energy demand in MVR process is an important index. We theoretically analyzed the energy demands of different absorbents in MVR process. By comparing with conventional thermal regeneration, MVR process shows an approximate 30% reduction on energy consumption. Based on above studies, we concluded that for suitable absorbents MVR is an attractive technology for CO2 desorption with low energy demand.

SESSION 24
Combustion: Combustion Studies

Mild Combustion of a Lignite Coal in a Laboratory Scale Furnace

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The present study investigates the characteristics of MILD combustion of a pulverized lignite coal in a recuperative laboratory scale furnace. The lignite with particle size in the range of 38-180µm were injected into the furnace using either CO_2 or N_2 as a carrier gas. Gas composition was measured inside the combustion chamber using a water cooling sampling probe and on-line gas analyzers. The overall equivalence ratio (Φ) was fixed at 0,86. The furnace temperature was measured at different position in the furnace using N-type thermocouples. It was observed that MILD combustions were established without air preheat for both carrier gases and lignite with high ash content, suggesting that it may be possible extend the applicability of MILD combustion to low rank coals.

During MILD combustion, a very uniform and flat temperature profile was found. The average temperature for the case with N_2 as carrier gas was higher than with the CO_2 case, by approximately 160°C. This result is consistent with the higher carbon burnout obtained in the N_2 case after analyzing the ashes. The temperature contrast is due to the difference between N_2 and CO_2 specific heats and possibly due to endothermic reactions in the presence of CO_2 and carbonaceous material.

Chemical species distribution inside the furnace was similar for both cases. The main reaction zone was located near the central jet carrying the coal particles. There, volatiles of the lignite were quickly released followed by heterogeneous reaction of char and the formation of small gas molecules by breaking down of large hydrocarbons fragments. These chemical events were evidenced by an increase of CO, H_2, CO_2, NO concentrations and a low oxygen concentration (1-3% v) due to the recirculation of flue gases. Afterwards on a secondary reaction zone, CO concentration decreases and then remains constant upstream. Its concentration in the secondary zone was higher when CO_2 was the carrier gas, which agrees with the lower carbon burnout obtained from the ash analysis.

In the primary reaction zone the nitrogen of the coal was released in a highly sub-stoichiometric environment which favored its conversion to molecular nitrogen, so less NO was formed in this region. Further up of this zone, it appears that a moderate NO reburning mechanism has dropped the NO concentration. This behavior is consistent with the low NO emissions measured in the exhaust ≈ 200 ppm and shows the potential of MILD combustion with lignite coal for reducing emissions of NO to the environment.

Estimation of Combustion Reactivity of Different Coal Rank Chars by Physicochemical Properties

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During the coal combustion process, the combustion of char is extremely slower than the release of volatiles, which can be considered as the rate controlling step. However, the combustion of coal char is affected by many factors, such as particle size, charring condition, ash content, pore structure, and other physical properties. Thus the combustion reactivity of different coal chars is difficult to be estimated by one property. In this paper, the isothermal and non-isothermal combustion reactivity of 8 chars from different rank of coals and 2 fine chars derived from a pilot-scale fluidized bed gasifier were studied in a thermogravimetric analyzer (TGA). The BET surface area, micropore area, ash content and mineral constituents were correlated with the char combustion reactivity index and characteristic temperature, however, the results were not satisfied. So, a new method based on air chemisorption was used to test the active sites for combustion. The results show that the total and strong air chemisorbed volumes correlate the combustion reactivity very well. It means that the air chemisorption can be used to estimate the combustion reactivity of chars from different rank of coals.

Providing Explosion Safety in Intermediate Dustbin Systems when Burning Coals with High Volatile Content

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The existing practice for evaluating fuel explosion safety and for designing and operating dust preparation systems usually leads to errors. Underestimating a fuel’s explosion-proof characteristics can result in adverse effects, such as increased capital equipment costs and unnecessary high operating costs.

Assessment of the Spontaneous Combustion Potential of Coal Using the Pulse Flow Calorimetric Method: A 20-year Experience

Boleslav Taraba, University of Ostrava, CZECH REPUBLIC

The paper summarises 20 years of experience with the pulse flow (PF) calorimetric method established at the University of Ostrava to assess the spontaneous combustion potential of coals according to values of the oxidation heat q_{30} (W kg^{-1}). During the period, more than 200 coals with natural moisture content and of various rank were investigated, oxidation heat of q_{30} = 8.6 W kg^{-1} being found as a maximal value.

The relation between oxidation heat q^{30} and oxygen consumption determined using the method of thermal oxidation was analysed giving a heat effect of 520 kJ (mol O_2)$^{-1}$. Also, possible comparison between oxidation heats q_{30} and values of the initial rate of heating (IRH) of the adiabatic calorimetry is reported.

SESSION 25
Coal Science: General – 5

Behaviors of Radical Fragments in Tar Generated from Pyrolysis of Coal under Various Conditions

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It is well recognized that coal pyrolysis follows free radical mechanism. Most literature however studied mainly the free radicals in solid products. Free radical information about coal tar is very important not only for in-depth understanding on pyrolysis mechanism but also on optimization of the processes for high oil yield and stable operation. This paper reports our recent study on free radical concentration of coal tars generated from 4 coals under various pyrolysis conditions or subjected to various downstream conditions.

Preparation of Char-Water Slurry Using Various Coal Chars Derived from Pyrolysis and Hydrothermal Treatment

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This work aims at the study of the slurryability of a Chinese lignite and various chars derived from coal pyrolysis and hydrothermal treatment. Coal pyrolysis was conducted in an air-isolated atmosphere with a changing temperature from 300 °C to 700 °C. Hydrothermal treatment of coal was carried out in autoclave at temperatures from 150 °C to 300 °C with autogenous pressure from 0.8 MPa to 9.2 MPa. The results showed that the raw lignite had the poor slurryability, and the chars exhibited an improved slurryability depending on the pretreatment methods. The char obtained by pyrolysis at 400 °C was prepared to a char-water slurry with the char loading of 59 wt%, the apparent viscosity of 1208 mPa s, and the good stability. The char obtained from the hydrothermal treatment also showed the improved slurryability as compared to the YX raw lignite. The apparent viscosity was found to be correlated to the elimination of the hydrophilic carboxyl group by pretreatment for the char-water slurries. Rheological analysis showed that both the lignite-water slurries and the char-water slurries well fitted to the power low model, and the char-water slurries had a larger value of the rheological exponent (n) and a more gradual decrease in the n value with the solid concentration increasing than the lignite-water slurries.

Separation of Phenol from Oils with Quaternary Ammonium Salts via Forming Deep Eutectic Solvents

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Phenolic compounds, Phenol, one of the major industrial organic chemicals, is currently used in processes to produce phenolic resins, bisphenol A, caprolactam, alkylphenols, adipic acid and other products. Phenolic compounds are mainly derived from coal liquefaction oil, coal tar and petroleum, and also from biomass via pyrolysis as documented in recent reports. These processes provide mixtures containing phenols and oils (called neutral oil compared with phenols). Therefore, it is necessary to separate phenols from oils before further refining. The present method to separate phenols from oil mixtures is to chemically extract phenols using aqueous alkaline solutions (such as aqueous NaOH) and then to acidify the extract by mineral acids (such as aqueous H_2SO_4) to recover the phenols. The disadvantages of the method are the use of large amounts of both strong alkalis and acids and the production of excessive amounts of waste water containing phenols. Therefore, a method to separate phenols from oil mixtures using a non-aqueous method to avoid the above problems would be environmentally advantageous.

Deep eutectic solvents (DES) have a eutectic temperature very much lower than would normally be expected and are usually formed from mixtures of organic halide salts with hydrogen-bond donors (HBD), where a strong hydrogen bond is formed. [1] Currently, DES are being used in research as well as in industry because of they are non-toxic, non-reactive with water and biodegradable.

In this work, we found that choline chloride (ChCl) could form DES with phenol and cresols, which could be used to separate phenols from oils and there were no ChCl detected in the extracted oils, which provides an efficient way to separate phenols from oils with removal efficiencies from 90 % to 95 %.[2] ChCl shows a short eutectic equilibrium time and an in-sensitivity to eutectic temperature. Significantly, no ChCl was found in the upper oil phase at equilibrium with the eutectic solvent.

In order to know the effect of ammonium salt structure on DES and extraction efficiency, a variety of quaternary ammonium salts, including tetramethylammonium chloride (TMAC), tetramethylammonium bromide (TMAB), tetraethylammonium chloride (TEAC), methyltriethylammonium chloride (MTAC), tetraethylammonium bromide (TEAB), tetrapropylammonium chloride (TPAC), tetrabutylammonium chloride (TBAC), ammonium chloride (NH4Cl), and choline bromide (ChBr), were studied in separating phenols from model oils.[3] The results show that the quaternary ammonium salts that are composed of cations with appropriate chain length as well as high symmetry and anions with higher electronegativity were conducive to separate phenols from model oil mixtures. A maximum removal efficiency of phenol was attained by TEAC at a mole ratio of 0.8:1 (TEAC: phenol), with 99.9 % removal. Moreover, the extraction equilibrium was very fast and the extraction separation efficiency was not sensitive to temperature. Therefore, it can be effectively performed at room temperature. Significantly, TMAC can be easily recovered by DBE or DEE as an antisolvent and reused without mass loss and reduction in separation efficiency. While still unoptimised, the process shows that an anti-solvent could be used to recover the quaternary ammonium salts. In contrast with the traditional methods to separate phenol compounds from oil, this proposed method involving the formation of eutectic solvents with ammonium salts avoids the use of alkali and acid and the production of phenol containing waste water.

Acknowledgement: This work is financially supported by the National Basic Research Program of China (2011CB201303) and Shanxi Scholarship Council of China (2011-086).

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SESSION 26
Coal Mining:
Safety, Economics and Mining Technology

Field Performance of an SIUC Innovative Spray System for Continuous Miners for Coal Mine Dust Control

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The authors present here field performance of a scientifically-founded water spray system developed for continuous miners (CM) that significantly reduces respirable dust exposure for workers in the face area (Patent Pending). It includes engineered sprays around the cutting drum, outer bit-ring sprays, chassis sprays and side cutter boom sprays. About 3.6-4.5 m behind these sprays are additional sprays that spatially cover the area between the CM chassis and the mine roof and ribs. The spray system uses approximately the same volume of water as currently used on CMs and at similar operating pressures. The design considers coal dust wettability. Three Illinois Basin coal mines decided to implement these concepts on a CM during rebuild stage. Dust control performance of rebuilt CMs was evaluated using gravimetric dust sampling and real-time monitoring using multiple personal dust monitors (PDMs). The average results based on gravimetric sampling of almost 200 cuts show reduction in dust exposure for the miner operator, and the haulage unit operator of about 30% and 20%, respectively. Visibility in the mining areas is also significantly improved. Two coal companies have already implemented the system on their currently operating CMs and the third one should be making that decision soon.

Development of China’s Coal Mining Technology and Equipment

Wang Guo-fa, China Coal Research Institute, CHINA

Strategic position of coal in China and three development stages of long wall mining technology and equipment, together with the last ten years important development achievements of mining technology and equipment were discussed. It introduces the main technology innovations, technical characteristics and application effects of some important projects in the field, such as the completed technology and equipment for 6 million tons in one long wall face, the key technique and equipment of long wall face for 35º ～55º inclined seam, the completed technology and equipment for 10 million tons in high cutting long wall face, the top coal caving long wall mining technology and equipment for 20 meters coal seam. At last, it presents the development directions and prospects of China’s coal mining technology and equipment.

Top Coal Caving Method for Middle Hard Thick Coal Seam in Shendong Coal Field

Haiyong Yu, Tiandi Science & Technology Co., Ltd, CHINA

Erdos Dongsheng coal field belong to the Jurassic coal field with the best mining condition at the present time in China. The seam is stable with low gas, short rushing water, think layer rock and little ground pressure. Shendong has to face how to extract 7 to 9m middle hard thick coal seam recently. Top coal caving mining method was applied in Shendong Liuta coal mine. It was obtained successful results with maxim output reaching 640,000tons per month and 27,000tons per day. The key technology which was applied in this coal mine was high resistance powered support, great cutting height and low rate of cutting and caving.

Meso-Fracture Experimental Method of Coal Containing Gas Based on the Industrial Computerized Tomography

Baisheng Nie, Xiangchun Li, Junqing Meng, Hui Zhang, China University of Mining & Technology(Beijing), CHINA

The mechanical characters of coal is important for designing mining method and roadway support technology and disasters prediction such as coalburst, coal and gas outburst and roof failure in coal mines. The meso-mechanical behaviors of coal, especially cracks inner coal growth rules during the process of deformation and fracture under load, are necessary for designing revealing the mechanism of these disasters. On basis of the industrial computerized tomography(CT) scanning equipment the real time loading and monitoring system for coal or rock were developed and the experimental method was put forward. The deformation and fracture process inner coal were detected and lots of images inner coal were obtained. The meso-structure and micro-cracks growth of coal were got. The results show that CT technology can detect the inner of coal and coal is one kind of typical heterogeneous material; the fractures of coal happen mainly between the skeleton and matrix and on the weak region of the skeleton. These investigations can provide theoretical foundations for understanding mechanism of coal or rock dynamic disaster in coal mines.

SESSION 27
Gasification: General – 5

Simulation of a Catalytic Coal Gasification in Elevated Jetting Fluidized Bed

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A number simulation study is conducted for catalytic coal gasification in pressured jetting fluidized bed. The gasifier is divided into three parts: grid zone, bubble zone and freeboard zone. It is based on a steady-state model which takes account of pressured hydrodynamics, mass and heat transfers and catalytic reaction kinetics.

The model is first validated by comparing predicted results with experimental data in a pressured electric-heated 1t/d PDU with 0.2m internal diameter, and 3m height. The calculated vales show good agreement with experimental results on the bed temperature and gas composition. The prediction presents that the temperature of particle in jet almost reaches the maximum value when the oxygen is introduced, then sharply decreases and levels off due to high reaction rate of catalytic char combustion and large heat transfer coefficients under high pressure. The gas concentration in the grid zone increase slowly due to low particle hold up and short resident time. With synthesis gas introduced to annulus from the distributor, H_2 and CO immediately appear in jet due to the fast gas exchange between jet and annuls. The way to promote methane production by increasing bed height is practicable, although increasing the risk of slug. According to the calculated results, the maximum mean bubble size (0.1m) at 2.5MPa is less than about half of reactor diameter(0.2m), the bed operate in bubble zone. Moreover, sensitivity analysis by this simulation for some operation conditions such as catalyst loading amount, oxygen and steam flow rates, bed temperatures and bed pressures on methane formation are carried out. The simulation results are shown that key operation parameters are steam flow rate and bed pressure.

Advanced High Pressure Multipiston Feeder for Coal and Coal-Biomass Mixtures

Santosh Gangwal, Tim Hansen, Southern Research Institute, USA; Thomas Koch, Peter Friehling, TK Energy ApS, DENMARK

Commercially available coal feeding methods for gasification consist of injection of coal-water slurry, or dry feed lock-hoppers. Coal-water slurry can be injected at very high pressure to high-pressure gasifiers; however additional water required for slurry feeding precludes the use of coal-water slurry feeding for low rank coals. The injection of water reduces the energy efficiency of the gasification process and increases the oxygen consumption. Dry feed lock hoppers can handle dry coal feeds. But lock hoppers can only be utilized at relatively lower operating pressures, at which gasifier operation is less efficient. Also, there are other disadvantages of lock-hoppers such as bridging and high operating costs due to enormous consumption of inert gas. The development of cost-effective dry high-pressure fuel feeders can reduce gasification system costs, allow for increased versatility in feedstock use, and ultimately provide a more economical and efficient platform for production of power, fuel, chemicals and other products from both coal and renewable feedstock. High-pressure solid feed systems, such as the TK Energy multi-piston feeder, are being developed to enable dry pumping of all sort of solids such as low-rank coals in to high-pressure gasifiers, to allow co-feeding of coal with other advantageous fuels (such as biomass and waste), and to encourage higher pressure (and therefore more efficient) operation of dry-feed gasifiers. The up to date status and future development plans for the TK Energy high pressure multi-piston feeder will be described. The TK Energy feeder has been demonstrated at a scale of 10 m^3/h for feeding both coal and biomass across a 380 psig pressure barrier. The feeder has several potential advantages over lock hoppers and other dry fuel feeders that do not use lock hoppers. These include simpler design, higher fuel flexibility, lower capital costs, and significantly lower operating costs. Southern Research Institute and TK Energy have agreed to participate in a project for further development and scale up of the TK Energy feeder system.

Industrial Scale Fixed Bed Biomass Gasification Experiment

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An industrial scale fixed-bed updraft gasification R&D test run with several types of biomass sources was conducted in a commercial installation in Poland. The research project was developed as a cooperation between Sasol Technology R&D (South-Africa), Modern Technologies & Filtration (Poland) and University of Warsaw (Poland). The experiments were run in a commercial facility in Poland, which uses a gasifier to power an activated carbon regeneration unit. This plant has 15 years history of operation, proving that the fixed bed gasification technology is robust and mature for biomass gasification purposes. This research project is unique due to the scale of the test runs. The installed gasification chamber is ca. 3 MWth, which allows insight into pyrolysis, gasification and tar production on an industrial scale, whilst maintaining control of the process parameters using laboratory scale measuring equipment.

Four different types of biomass, namely Polish- and South-African wood pellets, torrefied pellets and sawdust from Poland, were tested in an industrial fixed-bed gasifier. Gasification products i.e., gas, liquid hydrocarbons, ash and other residuals were collected separately for each biomass feedstock.

It was observed that tar production from torrefied pellets is slower, lower in yield and technically more difficult compared to untreated biomass sources gasified at similar operating conditions. The dry and highly reactive torrefied pellets created a fixed-bed with a strong tendency to combust rather than gasify. For this reason the temperature inside the gasifier was higher for torrefied pellets (up to 1200^{o}C) and the gasification rate and tar collection rate were 50% lower. Apart from reduction in the air supply, two other methods of preventing combustion and promoting gasification were tested. The first method consisted of grinding the torrefied pellets before introducing them into the gasifier, which increased the gasification surface area and resulted in stabilising the process and lowering the temperature. However, it also caused an increase of the dust content in the produced gas and led to faster clogging of the cooler. The second method was blending the torrefied pellets with wet sawdust. Consequently the effectiveness of gasification increased and the temperatures inside the gasifier decreased.

Torrefied material may be considered as a good fuel for co-gasification with other feedstock (such as coal with similar properties), but is difficult to handle by itself as it tends to combust rather than gasify due to its low moisture content and high reactivity.

Experimental and Kinetics Studies on Co-Gasification of German Brown Coal and Wheat Straw

Lingmei Zhou, Martin Schurz, Denise Reichel, Guanjun Zhang, TU Bergakademie Freiberg, GERMANY

The continuing development of world economy leads to higher energy consumption. Biomass as a kind of clean and renewable energy source has been increasingly focused, especially in the field of gasification technology. Co-gasification of coal and biomass could be an interesting option with regard to the reduction of CO_2 emissions and the enlargement of feed basis. Huge plant sizes in coal gasification offer advantages in efficiency and costs compared to single biomass gasification. Co-gasification can be realized in these plants with only a few technical adaptions mostly related to fuel feeding. In the present work, the gasification behavior of single and mixed char samples from German brown coal and wheat straw in various ratios was studied. Raw samples (< 2 mm) were pyrolyzed in a high temperature muffle furnace with addition of a constant N_2 flow under atmospheric pressure. The heating rate was 10 K/min and the final temperature was varied between 750 and 1000 ℃. For gasification experiments a small fixed bed reactor equipped with an online GC for monitoring of gas composition was used. The gasification of char samples was done until complete carbon conversion was reached. The results for char gasification at the same temperature like pyrolysis (char preparation) showed the highest reactivity for brown coal char followed by mixture with 10 wt.% and 50 wt.% biomass. The wheat straw char itself possessed the lowest reactivity. There was no synergy effect for experiments at low temperature. However, negative synergy effects were found at high gasification temperature of 900 and 1000 ℃. This occurred probably due to the partially sintered and molten biomass ash, which hindered the reaction. During gasification of 1000 ℃ char at low temperature (800 ℃), no obvious synergy effect at low carbon conversion could be found. Furthermore, the negative synergy effects on gasification of mixed char samples at high carbon conversion was related to the high reactivity of coal leading to a shorter gasification time of coal char. The residual coal ash would be embedded in the spongy structure composed of biomass particles forming at high carbon conversion and hinders the gasification reaction. Three gasification models: the volume reaction model (VRM), the shrinking core model (SCM) and the random pore model (RPM) were applied in this study to fit the experimental data. The method of Least Squares was applied to evaluate these models. Among the three considered models, only random pore model was able to fit most experiments both in low and high temperature range. For gasification of mixed char including 10 wt.% wheat straw the chemical reaction controlled the kinetic up to 900 °C. At higher temperatures pore diffusion became the limiting factor. The temperature, where the limiting step changes was 25 K lower for the 50 wt.% mixture. The apparent activation energy E and the pre-exponential factor A for mixed char samples were lower than the values calculated from the data of single fuels using the rule of mixing. The negative synergy effects in co-gasification experiments showed that the pre-exponential factor had a significant effect.

SESSION 28
Clean Coal and Gas to Fuels: General – 5

Gasoline from Coal and/or Biomass with CO_2 Capture and Storage

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There is renewed interest globally in liquid transportation fuels from biomass and coal. There are two commercially demonstrated routes for converting solids to transportation fuels through gasification. One is the widely known Fischer-Tropsch process (FT). The other is a route through methanol to gasoline (MTG). This paper focusses on the latter. The MTG process produces primarily a finished-grade gasoline, with most of the remainder being propane and butane (LPG). Although MTG systems are much less well known than FT systems, the MTG process was operated on reformed natural gas at commercial scale in New Zealand for about a decade, and several new coal-based MTG projects are in planning, with one demonstration unit already operating in China. In this paper, different coal- or coal/biomass-to-MTG plant design configurations are presented and discussed, including some with capture and storage of byproduct CO_2. Detailed mass, energy and carbon balances are simulated, and fuel-cycle-wide GHG emissions and prospective capital and operating costs are estimated. Some designs with substantial co-production of electric power are also investigated. For these systems, it is found that the marginal efficiency for the extra electricity generation (compared to an MTG plant configuration producing mainly gasoline) is higher than the efficiency for a coal integrated gasification combined cycle (IGCC). Overall economic results are presented for systems that produce primarily liquids and those that co-produce electricity. Economics are presented as a function of assumed world oil price, carbon emission price, and other variables.

STF Technology – Production of High Octane Gasoline from Synthesis Gas on a New Route

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Since 2008, Chemieanlagenbau Chemnitz GmbH (CAC) and TU Bergakademie Freiberg have been performing the joint research project “Production of High Octane Gasoline from Synthesis Gas”. A large test plant was built at the University’s Department of Energy Process Engineering and Chemical Engineering (IEC) to investigate process parameters and to optimize the performance of the newly developed Syngas-To-Fuel technology (STF). It represents a new, highly sophisticated tool to generate transportation fuels from feedstocks which could replace mineral oil. The project is co-financed by the Saxon State Ministry of Science and the Fine Arts (SMWK), represented by Sächsische AufbauBank (SAB), by financial means of the European Regional Development Fund (ERDF).

On the background of decreasing world resources of crude oil, the growing demand for transportation fuels requires other fossil and renewable feedstocks. In addition to the use of coal and biomass the generation of synthetic fuels from natural gas or associated gas is one of the most promising opportunities to increase the energetic and economic benefit. Sophisticated gasification and synthesis technologies allow the non-energetic use of these feedstocks, which are currently used predominantly for heating purposes.

The STF technology which was developed by CAC uses synthesis gases at high pressure. It is based on catalytic processes for an intermediate methanol production from synthesis gas and the synthesis of gasoline from methanol. Special features of the STF technology are the modified reactors which allow an isothermal process with improved catalysts. After synthesis, only a simple destillative post-treatment of the raw gasoline is required to observe the Euro V standard. With these simple post-treatment the produced gasoline is immediately insertable. This technology is in its completeness a novelty in the world.

The installation of the STF test plant at the IEC was successfully finished in June 2010. Several test runs have been carried out in the following months. The feed gas for the STF plant was delivered by the unique HP POX plant operated by the IEC, which generates a specified syngas by autothermal catalytic reforming of natural gas at the required pressure level of up to 70 bar. The IEC and the Department of Technical Chemistry (ITC) support the test runs with experienced operating personnel, scientific assistance and comprehensive laboratory equipment.

The presentation gives an overview of the plant operation, the suitability of the produced gasoline based on the results of motor tests, and strategies for the commercialization of the STF technology. Motor test have been shown, that research octane numbers between 94 and 100 can be reached. The combustion behavior is comparable with Super E10 (RON 95).

Study of Direct Conversion of Syngas to Light Olefins Over Fe Based Carbon Sphere Catalysts

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Light olefins (C_2 to C_4) are extensively used in the chemical industry as building blocks to synthesize a wide range of products such as polymers, solvents, drugs, etc. Compared with or the traditional steam cracking of crude oil or two-step MTO route, the direct conversion of syngas to light olefins via Fischer-Tropsch synthesis (FTO) route, without intermediate steps, sounds a promising solution. So far, many efforts [1,2] have been done to develop the catalysts to promote light olefins selectivity in the FTO reaction synthesis. In the present study, we use a simple and low-cost method to prepare Fe based carbon sphere for FTO reaction. The catalyst shows good mechanical stability and high selectivity for light olefins.

A series of Fe based catalysts were prepared by ion-exchanging iron salt precursor with 0.8% and 5% Fe content into polymer sphere, and then carbonized in flowing N_2 in the range of 500-1000°C. For 5% Fe based catalysts, the XRD patterns of showed that the peaks of Fe_2O_3 and Fe when calcined at 500 °C. With carbonization temperature increasing, the Fe_2O_3 peak weakened and the intensity of Fe peak increased, and the diffraction peak of FeO phase also appeared. When increased to 700 °C, the new peaks of Fe_3C phase occurred besides the sharp Fe diffraction peak. This suggests the oxidized Fe is completely reduced into metallic Fe, and the Fe-C interaction causes the formation of carbide at high temperature [3]. At 1000 °C, the graphite carbon became the dominant phase, due to the carbide nanoparticles further catalyze the formation of graphitic species [3]. The XRD patterns of 0.8% Fe-based catalyst showed the peaks of Fe_2O_3 and Fe_3C were observed when carbonized at 500 °C, and no Fe diffraction peak was observed, indicating the low Fe content favors the dispersion of Fe particles into carbon matrix and the carbide formation.

The surface areas of obtained 5% Fe catalysts significantly increased from 0.02 to 245 m^2/g, and then decreased to 33 m^2/g when calcined at 1000 °C. It is observed from TG-TPD-MS that H_2O, CO and CO_2 were released during the decomposition and carbonization of starting Fe precursor. Therefore, the mesopores and macropores could be formed during the carbonization process and attribute the high surface area of catalyst, while fhe further decrease of surface area might be associated with the coverage of catalyst surface by the excess of graphite carbon.

The catalytic performance of obtained catalysts was evaluated in the 2/1 molar ratio of H_2/CO at space velocity of 4500 ml/g/l at 340°C and 2 Mpa. For 5% Fe catalyst carbonized at 500 °C, almost no CO conversion was observed over the catalyst. For 5% Fe catalyst carbonized at 700°C, CO conversion was about 50%, and CH_4 selectivity was relatively high, and the most of C_2-C_4 is species were paraffins, and ratio of olefins to paraffins was 0.25. For the catalyst carbonized at1000°C, the ratio of olefins to paraffins is only 0.07. For 0.8% Fe catalyst carbonized at 500°C, the CO conversion gradually increased with time on stream and reach about 35%, and the initial ratio of olefins to paraffins could reach more than 3, and slight decreased with time on stream and was still almost 2 after 60h of reaction. This is possibly related to the presence of highly dispersed Fe and iron carbide. T. Galvis et. al. [4] has reported that homogeneously dispersed iron nanoparticles showed high catalytic activity and low olefins selctivities, moreover, Fe_xC_y was found to favor the high selectivity as the active species.

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PDU Scale Demonstration of Substitute Natural Gas Production Using Steam Hydrogasification

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Substituted Natural Gas (SNG) has been identified as an important alternative fuel that can contribute to achieving a number of goals set by the nation related to conventional fuel replacement and emissions reduction in the energy sector. Increased SNG utilization as an alternative fuel will have a significant impact on the nation’s energy consumption and will also result in considerable environmental benefits.

Thermo-chemical process is one of the promising technologies used to produce the syngas which can be utilized to produce several different types of biofuels. Substitute or Renewable Natural Gas (SNG or RNG) is able to be produced from various carbonaceous materials such as coal, biomass and organic wastes via a gasification process. CE-CERT gasification laboratory, University of California Riverside (UCR), has introduced the hydrogasification in the presence of steam to generate a methane rich producer gas from the wet feedstock. The process, called Steam Hydrogasification Reaction (SHR) can produce the SNG in a highly efficient manner.

Producer gas of SHR is primarily consisted of H_2, CH_4, CO, CO_2 and steam. The hydrogen necessary for the SHR is generated internally and is sufficiently recycled back to the SHR process. For the self-sustainable hydrogen supply, Water Gas Shift (WGS) process is followed to convert CO and steam from the producer gas of the SHR to H_2 and CO_2. CO conversion was observed to be approximately 85% via a laboratory scale WGS reactor system using a commercial high temperature shift catalyst. The optimal condition was $350^{o}C$ atmospherically with the space velocity of 4500 hr^{-1}. The process has been scaled up to A Process Demonstration Unit (PDU). A PDU scale bubbling fluidized bed type SHR has been developed, which can process up to 0.1 ton per day of feedstock in dry basis. The PDU produces SNG from co-mingled biosold with biomass, with the more than 15KJ per kg of feed. The final producer gas has 84% of CH_4 content with final separation of CO_2.

SESSION 29
Carbon Management: General - 2

Alternative to Sequestration – Converting CO_2 into Synthetic Gas

David Banitt, Julie Horn, NewCO2Fuels, ISRAEL

Worldwide energy consumption has vastly increased in the last decade and is expected to rise even faster in the years to come.

As more than a quarter of the global energy produced is used for transportation, and more than 90% of the transportation energy comes from petroleum it is vital to develop alternative fuels to ensure a stable future economic outlook regarding transportation fuels.

On the other side of the equation, CO_2 emissions have become a global concern over the last few decades. Atmospheric concentration levels of CO_2 have reached record highs and global CO_2 emissions keep increasing as energy consumption increases globally, especially in developing countries.

NewCO$_2$Fuels (NCF) provides a sustainable and cost effective alternative to Carbon Sequestration by converting the captured CO_2 into a useful product.

NCF is developing an innovative, cost competitive self-sufficient solar based system to produce fuel from renewable sources. The core technology is a solar energy driven, high temperature CO_2 and water dissociation which produces synthetic gas, from which different synthetic fuels can be produced.

The uniqueness of the technology lies in the combination of synthetic fuel production using CO_2 as feedstock while being solar energy driven. The technology has very high efficiency, reaching the level of 40% conversion efficiency making it cost effective. The product is a self-sufficient, flexible integrated solution.

NewCO$_2$Fuels' technology is of great value for coal gasification industry as it recycles the emitted CO_2 from the process into syngas, which is used to enhance the SNG capacity at a competitive cost. In addition, NewCO$_2$Fuels produces pure oxygen as byproduct, which is very valuable for coal gasification projects by reducing operating and capital cost of the oxygen production.

NCF solutions are based on the technology successfully developed in Israel by Professor Jacob Karni and his group at the Weizmann Institute of Science in Israel and proven in laboratory trials. It involves a new method using concentrated solar energy for the dissociation of carbon dioxide (CO_2) to carbon monoxide (CO) and oxygen (O_2). Simultaneously, the same device dissociates water (H_2O) to hydrogen (H_2) and oxygen (O_2). The CO, or the mixture of CO and H2 (called Syngas) can then be used as gaseous fuel (e.g. in power plants), or converted to liquid fuel (e.g. methanol), which has the potential to be stored, transported and used in motor vehicles. The oxygen produced can be used in the combustion of the clean fuel, or elsewhere.

NewCO2Fuels is managed by experienced executives in the high technology and cleantech industries and employs talented engineers working in collaboration with Prof. Karni's team in order to develop and build an economically viable CO_2-to-fuel reactor using solar thermal energy.

Carbon Dioxide Utlization by Catalytic Reactions

Zinfer Rishatovich Ismagilov, Institute of Coal Chemistry and Material Science SB RAS; Svetlana Valerievna Lazareva, Nadezhda Vasl'evna Shikina, Boreskov Institute of Catalysis SB RAS; Tatiana Nikolaevna Teryaeva, Kuzbass State Technical University, RUSSIA

Coal bed methane is a good candidate for utilization of CO_2 produced by coal firing power stations. The main reaction of this process is so called "dry" reforming of methane

$CH_4 + CO_2 = 2H_2 + 2CO$ $(\Delta H^{o}_{298} = +247\ \text{кJ/мol})$

There are at least three ways of extension of this reaction for conversion to high value products.

CH_4 to higher hydrocarbons $CH_4+CO_2 \rightarrow 2CO + 2H_2$
$CH_4 + H_2O \rightarrow CO + 3H_2$
$6CO + 13H_2 \rightarrow C_6H_{12}+H_2O$

CH_4 to methanol $CH_4+CO_2 \rightarrow 2CO + 2H_2$
$CH_4 + H_2O \rightarrow CO + 3H_2$
$CO + 2H_2 \rightarrow CH_3OH$

CH_4 to carbon $CH_4+CO_2 \rightarrow 2CO + 2H_2$
$2CO + 2H_2 \rightarrow 2C + 2H_2O$
$CH_4+CO_2 \rightarrow 2C+2H_2O$

The main limitation of this process is catalyst deactivation. We explored traditional ways of catalyst modification to prevent its deactivation

1. Introduction of alkali or alkali-earth elements to increase basicity of the surface
2. Use of transition metal oxide supports having high oxygen mobility
3. Use of nano-sized active component particles
4. Passivation of active component

Our innovative idea is to use uranium oxide catalysts in reaction of dry reforming. Introduction of U into a Ni containing catalyst significantly decreases carbon yield, substantially increasing catalyst lifetime. Superiority of the mixed catalyst 10Ni-15U-Al_2O_3 is achieved by high resistance of uranium nanoparticles to coke formation.

Uranium oxide particles are not covered by carbon and demonstrate stable catalytic activity.

Introduction of U into 1%Rh/Al_2O_3 catalyst also results in a significant increase of the hydrogen yield. The catalyst activity increase as following 1%Rh/Al_2O_3 < 1%Rh/30%U/Al_2O_3 < 1%Rh/5%U/Al_2O_3 < 1%Rh/15%U/Al_2O_3.

One of the prospective methods of CO_2 utilization is CO_2 reforming with coal. The development of this method can play a significant role in metallurgical coke production and utilization of CO_2 emissions.

$CO_2 + C \rightarrow 2\ CO$
$H_2O + C \rightarrow H_2 + CO$
$CO + H_2 \rightarrow$ liquid fuels + monomers + polycarbonates + chemical products

Our results of study of the reaction of carbon dioxide with fossil coal will be presented. Modification of coal with transition metal additives is a prospective way to control the interaction of CO_2 with coal. The catalytic nature of metal additives into coal require advanced investigations of reaction kinetics, texture and morphology of solid reagents and reaction products.

Towards Industrialization of CO_2 Reforming CH_4 to Syngas Over the Carbonaceous Catalyst

Yongfa Zhang, Guojie Zhang, Yiannian Du, Taiyuan University of Technology, CHINA

There are a great number of coke oven gas and coal seam gas resources in Shanxi province. Processing and comprehensive utilization key and difficult points of coke oven gas and coal seam gas are conversion of the two gases (CH_4 and CO_2) into a valuable synthesis gas ($CH_4+CO_2 \rightarrow CO+H_2$). CO_2 reforming CH_4 to syngas was first reportted in Nature by Ashcroft from the 1990s. Scientists around the world have carried out a lot of research on it since then. Developing a catalyst for CO_2 reforming of CH_4 is a challenge, because they need a very high production rate to make the huge GTL methane reformer as small as possible. Unfortunately, research progress in this field has been slow due to serious coke deposition, high temperature sintering and other defects of the reforming catalysts. Carbon dioxide reforming methane to syngas is recognized as one of the world's challenging current in the field of chemistry and energy research. During the study, we found that carbon materials have better catalytic activity and stability for CH_4-CO_2 reforming. After nearly 10 years of research, our groups have made a systematic study of carbonaceous catalysts characteristic and catalytic properties, the transformation mechanism of CH_4 reforming CO_2 over carbonaceous catalyst, and begin own research and development CO_2 reforming of CH_4 to syngas technology over the carbonaceous catalysts. CH_4, CmHn and CO_2 of the feed gas are efficiently converted into synthesis gas over high temperature carbonaceous catalyst layer. The technology is not only to achieve the atomic level utilization feed gas, but also reduces greenhouse gas emissions. After nearly one year of equipment development and installation, Linfen Tongshida coal chemical group trial run successfully in March 24, 2012. It marks that this innovative technology, CO_2 reforming CH_4 to syngas over the carbonaceous catalyst, achieves industrialization. The technology will generate significantly economic and environmental benefits. It is estimated that it will increase production to annual dimethyl ether of 43,000 tons, which is a \$ 170 million increase in the output value, and reduce CO_2 emissions 77880 tons per year. So we conclude that this industrial technology has a wide market in coal chemical industry. Project technology of CO_2 reforming CH_4 to syngas over the carbonaceous catalyst has a potential environmental and economic benefits and has broad market prospects.

Capturing of CO_2 with Tetraethylenepentamine-Impregnated Industrial Grade Multi-Walled Carbon Nanotubes

Qing Liu, Shudong Zheng, Mengna Tao, Yi He, Yao Shi, Zhejiang University, CHINA

Industrial grade multi-walled carbon nanotubes (I-MWNTs) is a low-cost substitute for commercially available multi-walled carbon nanotubes (MWNTs). In this work, I-MWNTs were functionalized with tetraethylenepentamine (TEPA) for CO_2 capture. The performance of I-MWNTs-TEPA was compared with that of MWNTs-TEPA. It was found that I-MWNTs-TEPA exhibited high CO_2 adsorption capacity similar to MWNTs-TEPA. The adsorption capacity of I-MWNTs-TEPA was in the range of

2.145 to 3.088 mmol/g depending on adsorption temperatures. Both adsorption isotherms of I-MWNTs-TEPA and the isosteric heat of different adsorption capacity were obtained from experiments. H_2O, SO_2 or NO has been found to have no significant impacts on the adsorption capacity of CO_2. I-MWNTs-TEPA was further extruded to form granules (I-MWNTs-TEPA-G) with a specific mold. The adsorption capacity of I-MWNTs-TEPA and I-MWNTs-TEPA-G remained almost the same after 5 cycles of adsorption/regeneration with adsorption conditions of 10 vol % CO_2, 500 ppm SO_2, 500 ppm NO, 100% relative humidity, and a temperature of 313 K. Having advantages such as low-cost, easiness in processing, high adsorption capacity, good poison resistance, and decent performance after recycling, I-MWNTs-TEPA seems to be a promising adsorbent for CO_2 capture from flue gas.

SESSION 30
Combustion: Modelling Studies

Numerical Modeling and Simulation of Hydrogen Sulphide Behavior in Pulverized Coal Combustion

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Nitrogen oxide (NO_x) are among the most important gaseous pollutants released from thermal power plants, and the NO_x emission limits set by local governments have been moving lower year after year in Japan. Therefore, low-NO_x combustion has been stronger. However, hydrogen sulphide (H_2S) concentration in a boiler has a tendency to become higher due to the low-NO_x combustion, and sulfide corrosion of the boiler tube hence has become a severe problem. In this study, numerical model to evaluate H_2S behavior in the pulverized coal combustion was developed. H_2S analysis model consists of four sub-models, namely, sulfur distribution model, sulfur devolatilization model, gaseous reaction model and gas-solid reaction model. The sulfur distribution model classified sulfur in coal which devolatilizes to the gaseous phase and remains the char in pyrolysis process in accordance with the rate of sulfur form, namely, the organic sulfate, the pyritic sulfur and the sulfate sulfur. For the gaseous reaction, two major reactions were selected. Reaction rates of these reactions were calculated by the detailed chemical reaction and the reaction rate database was constructed. In combustion simulation, reaction rate in each numerical cell was determined from the database in accordance with gaseous temperature and mass fraction of each species. Furthermore, numerical simulation was performed for coal combustion test furnace. Results show that the predicted profile of H_2S is qualitatively in good agreement with the experimental result, and the difference of H_2S behavior caused by the difference of coal property can be numerically predicted. H_2S is mainly formed in devolatilization process and H_2S concentration exhibits a peak just downstream the burner. H_2S concentration gradually decreases as the flow moves downstream due to the gaseous reaction and diffusion. The formation and decomposition process of H_2S was also investigated, and dominant process was extracted.

Numerical Investigation of Chemical Reactions Inside Char Particle Macropores

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This work is devoted to the numerical study of char particle oxidation in O_2/CO_2 and O_2/N_2 atmospheres under convective conditions. In particular, the physical phenomena inside the macropores of a porous particle were considered. For this, an idealized geometry was investigated using a CFD approach. Macropores were modeled as a variety of small channels, which are connected together by additional channels in a staggered position. The aim of this work is to better understand the physical phenomena inside chemically reacting char particles, and to improve existing sub-models for char burnout. Such models can be used e.g. for large-scale simulations of entrained-flow reactors.

The processes inside pulverized-coal combustors and gasifiers feature a distinct multi-scale character. This fact necessitates the usage of so-called sub-models to predict the interaction between solid particles and gas phase. The quality of numerical simulations depends directly on the accuracy of the underlying sub-models. However, an analysis of existing burnout sub-models reveals that e.g. the influence of intra-particle phenomena is not well understood (see Edge et al., 2011). It is well-known fact that coal particles after devolatilisation are porous and heterogeneous reactions can occur inside the particle. However, there have been little discussions in the literature about particle resolved CFD-based simulations describing the conversion of porous particles under the influence of an ambient gas flow, where multiple heterogeneous and homogeneous reactions are taken into account.

The numerical model follows the experimental setup published by Bejarano and Levendis (2008). The porous particle is moving at its terminal velocity in hot O_2/N_2 and O_2/CO_2 atmospheres. To solve the Navier-Stokes equations for the flow field coupled with the energy and species conservation equations, a finite volume solver was applied. In addition to the solid carbon the model incorporates six gaseous chemical species (O_2, CO, CO_2, H_2, H_2O and N_2). The reaction mechanism includes the forward and backward water-gas-shift reaction, one reaction for CO combustion and four heterogeneous reactions. The ambient medium is assumed to be nearly dry (Y_{H2O}=0.001). The numerical model is validated carefully against analytical solutions and measurements published in the literature (Bejarano and Levendis, 2008).

The analysis of the numerical data revealed that heterogeneous reactions involving oxygen occur only in a layer close to the particle surface. Inside the particle at T>1000K, no oxygen is present, thus, only the gasification reactions take place. Due to this effect the Stefan flow plays a significant role in mass transport of chemical species inside the porous particle. A comparison with numerical data obtained for a nonpermeable solid particle showed that mainly the reaction rates of gasification reactions are enhanced due to the increased particle surface. Due to the endothermic character of these reactions, the particle-averaged temperature of the porous particle is reduced by approximately 150K in contrast to a nonporous carbon particle.

The Influence of Shape on the Carbon Consumption of Non-Spherical, Reacting Carbon Particles

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Motivated by applications in gasification of coal we numerically investigate the influence of particle shapes on the oxidation dynamics of nonporous char particles using particle resolved numerical simulations. By the modelling of gasifiers so called subgrid models have to be used to describe oxidation of solid particles inside a gasifier, which includes the carbon consumption and heat and mass transfer between solid and gas phases. The standard subgrid models used in the literature for coal gasification (see e.g. [1, [2], [3]]) assume that particles have spherical shape. However, in reality the shape of coal particles is mostly non-spherical. In this work we evaluate numerically the justification of this assumption using detailed CFD-based numerical simulations. In the study a spherical particle was compared with seven different rotational symmetric particles of equal volume corresponding to ellipse, cone, cylinder, disc, rhombus, star, as well as a sphere enlarged with pimples. The temperature of the gas composition, which circulated around the particles, was varied between 1000K-3000K and the relative velocity of particles between 0.1 m/s and 10 m/s. The species compositions which are used correspond to a dry air atmosphere, as well as a low oxygen and water vapor rich atmosphere. For details regarding the numerical setup we refer to [4]. The analysis of the numerical simulations showed that the influence of the particle shape on the carbon consumption depends on the second Damköhler number. Regarding the Damköhler number, two cases can be distinguished. In first case, when the second Damköhler number is less than unity, the carbon consumption is mostly dominated by the reaction rate of heterogeneous reactions at the particle surface. The local specific carbon consumption is independent of the particle shape and constant over the surface. In second case, when the second Damköhler number is higher than unity, the carbon consumption is limited by the mass transfer at the particle interface and therefore a function of the particle shape. In particular, in this regime the local specific carbon consumption fluctuates strongly for the non-spherical particles. On exposed locations (edges, bulges) carbon conversion rates calculated locally can be enhanced by more than 1000% compared to the particle-average carbon consumption. This can be explained by the enhanced mass and heat transfer at these places due to the low boundary layer thickness. Thus, exposed particle locations are eroded much faster than less exposed places, so the particles are rounded with the time. Hence, it can be concluded that the particle shape plays a significant role for the pyrolysis, combustion and beginning of the gasification. For longer residence times, the particles can be regarded as spherical. Based on analysis of numerous simulations we found out a mathematical dependency of carbon consumption rate on particle shapes.

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[3] Hayhurst A.N, *The mass transfer coefficient for oxygen reacting with a carbon particle in a fluidized or packed bed*. Comb. Flame 121, 679–688, 2000.
[4] M. Kestel et al., *Numerical study of the partial oxidation of a coal particle in steam and dry air atmospheres*. IMA J. Appl. Math., 77:32–46, 2012.

3D Numerical Simulation of Gas-Solid Hydrodynamics and Coal Combustion in an Industrial Scale Circulating Fluidized Bed

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In this study, three dimensional numerical simulation of gas and sand particle hydrodynamics along with coal combustion in an industrial scale circulating fluidized bed (CFB) (including riser, cyclone and return leg) was carried out using a commercial code, ANSYS FLUENT. For modeling sand and gas hydrodynamics, Eulerian-Eulerian method (multiphase granular model), was used while for modeling coal particle trajectories, Eulerian- Lagrangian method (discreet phase model, DPM) was used. Also gas phase chemical reactions were solved via the Finite-Rate/Eddy-Dissipation model and particle phase chemical reaction were solved by multiple reaction model. User defined function (UDF) was used to re-inject the sand particles which left the domain via cyclone outlet. Simulation results such as exit gas temperature, sand volume fraction, pressure loop, and mole fraction of combustion products were compared with real data obtained from a 340 MWe CFB boiler located in Yeosu, Korea and showed good agreement.

SESSION 31
Coal Science: General - 6

Experimental Study on Emission of Arsenic during High Arsenic Coal Combustion Process

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Arsenic is one of the toxic trace elements in coal, it greatly harms the environment and the human body. Combustion of coal will accompany arsenic release, so it is necessary to understand the release rule of high-as coal in the process of coal combustion. This paper chose three high arsenic (more than 120ppm) coals which came from the southwestern part of Guizhou province in China. The high temperature combustion experiment was conducted in muffle furnace under the temperature of 800℃, 1000℃, 1200℃ and 1400℃, respectively. The analysis methods in this study include TGA, XRD, XRF, FESM-EDS and ICP-MS. The high-temperature ash (HTA) products were characterized to determine the mineral compositions, chemical compositions, mineral morphology and arsenic content. The research results showed that in the process of coal combustion, the arsenic release rate of LT-K1 coal and JL-CQ coal was 35.8% and 38.8% at the temperature of 800℃, respectively, while arsenic release rate of these two kinds of coal had a bigger increase at the temperature of 1000℃, were 85.6% and 91.1%. The arsenic release rate of LT-D2 coal had a bigger increase at the temperature of 1400℃. The arsenic release rate had a big difference with the temperature increasing, it may owe to the transformations of minerals and mineral phases.

Performance and Flow Pattern of Cyclone in Parallel with Tangential-inlet

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University of Petroleum, CHINA

It is reported that cyclones in parallel usually have lower separation efficiency than an isolated cell because of "cross-talk" in common dust plenum. However, cold test showed that overall efficiency of four identical cyclones working in parallel was significant higher than single cyclone at high inlet velocity. Pressure drop of cell cyclone working in parallel was also higher than identical single cyclone. Simulation for the flow field of cyclone in parallel demonstrated that there were several positive impacts to separation performance for cyclone in parallel such as higher tangential velocity and more stable vortex. Cross talk was negligible when identical cyclone working in parallel.

Study Coal Thermolysis Kinetics Using In-Situ Pyrolytic Time of Flight Mass Spectrometer

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Coal pyrolysis is the initial, accompanying reaction of a number of coal conversion processes such as hydrogenation, combustion and gasification. However, Due to the complextion of coal structures, it's very difficult to describe coal pyrolysis process clearly.Model compounds are often used to give an insight into the structure of coal. Yet the pyrolysis kinetics of single model compound is less representative with that happen in coal pyprolysis process because of the complex chemical situation such as interactions between the different groups and cross-links. The approach used in our work involves observation of coal pyrolysis by a novel time of flight mass spectrometer (TOF) with an in-situ pyrolysis ion source. Typical coals of china were investigated. By means of high sensitivity and instantaneity of our devices, Almost all volatile products were detected include many intermidates and free radicals with short life time and low content. Through product-temperature profile, the different reaction pathway of specific pyrolysis product could be analysised. The experiment resluts show that the releasing behaviour of products with molecular weight from 50 to hundreds Da between different coals are nearly the same. In contrast, the releasing behaviour of H_2O, CO_2, CO have obvious diversity between coals. This resluts indicated that the diversity between coals is essentially the diffenent form of oxygen in different coals. As supplement of direct analysis of coals, the pyrolysis of model compounds were also performed on a TOF system with molecular bean sampling. By the cooling effect of molecular bean, the initial products such as free radicals were clearly detected. The reaction pathway of different model compounds were given.

SESSION 32
Sustainability and Environment: General - 1

The High Efficiency and Near Zero Emission Technologies Based on Coal Utilization

Minfang Han, Suping Peng, China University of Mining and Technology, CHINA

Coal is one of the most abundant and the least expensive energy resources on the earth. Nearly 70% of the electricity in China is generated from coal-based power plants. However, extracting useful energy from burning coal is facing several environmental challenges. Solid oxide fuel cells (SOFCs) can offer an environmentally friendly technology to convert carbon-based fuels into electricity at high efficiencies. In this talk, energy status & development trend based on coal utilization in China are presented. The strategy of near zero emission coal utilization was put forward. The key technologies and processes were developed, which will lead the clean and high efficiency of coal utilization in China.

Solubilisation of Victorian Brown Coal in 'Distillable' DIMCARB

Ying Qi, Tarun Tikkoo, Vince Verheyen, Vijay Ranganathan, Douglas MacFarlane, Alan L Chaffee, Monash University, AUSTRALIA

Victorian (Australia) brown coal is an abundant and cheap energy resource. There is intense interest in identifying new opportunities for its efficient and clean use, for example by solubilisation to produce high quality fuel or chemicals.

Ionic liquids (ILs) have been applied increasingly in recent years to solubilize and recover cellulose, lignin and other components from complex biomass mixtures. Conventional ILs are not distillable and it can be difficult to separate the soluble product from the solvent. However, there is a group of ILs, produced by the association of a secondary amine and CO_2 that are 'distillable' in that they will dissociate back to the respective amine and CO_2 at moderate temperature to facilitate recovery. They can then be re-associated (recycled) by condensation at lower temperature. The simplest form of such ILs, DIMCARB, consists of dimethylamine associated with CO2 at a molar ratio of 2:1. DIMCARB has previously been found to be superior (in terms of solubility) to other ILs in this group for the extraction of a Victorian brown coal.

In this study the extractability of a woody coal sample was compared with a run-of-mine (ROM) sample, both without pretreatment. The wet coal was mixed with DIMCARB at a dry mass ratio of 1 to 20 for 24 hours at room temperature. The soluble product was recovered by centrifuge and acid washed to remove residual DIMCARB. An extraction yield of 25% was achieved for the ROM sample, while for the woody coal the yield was only 10%. The recovered products were characterized by a range of chemical techniques including FTIR and Pyrolysis GC-MS. The lower solubility of the woody coal seems to be associated with a high degree of oxygen containing aromatic components. The nature of this difference and the selectivity of the extraction are discussed.

Influence of Thermal Pretreatment and Acid-Washing On Pyrolysis of Lignite at Low Temperature

Huiling Rong, Cuiping Ye, Xiaohong Li, Jie Feng, Wenying Li, Taiyuan University of Technology; Xiaofen Guo, Ke Liu, NICE, CHINA

The effects of thermal pretreatment and acid-washing on fast pyrolysis behavior of Hulunbeier lignite were investigated in a fixed bed reactor under atmospheric pressure under a high purity flow of nitrogen at lower temperature (500 - 600°C). In comparison with raw coal, the noncovalent bonds of the thermally pretreated coal would be broken at 170-200°C. Pretreating the coal the tar yield raises by about 1 weight percentage point.The yield of pyrolysis water would be decreased by 1 wt%. It was found that the broking of noncovalent bonds led to the hexane-soluble components being increased after thermal pretreatment in N_2 atmospheres. By using de-ash method of HF-HCl, the ash content of the acid-washed lignite could be reduced below 0.6 wt%, the yield of tar from the acid-washed lignite pyrolysis would increase about 2 wt% compared with that of raw coal pyrolysis. This is because metal ions such as Ca^{2+} act as junction points during the process of pyrolysis and inhibit the formation of tar.

SESSION 33
Gasification: General – 6

Advanced Acid Gas Separation Technology for Gasification Markets

Jeffrey W. Kloosterman, Robert Quinn, Fabrice Amy, Jeffrey R. Hufton, Shubhra Bhadra, Ellen M. O’Connell, Air Products and Chemicals; Grant Dunham, Michael Swanson, Energy and Environmental Research Center, USA

Air Products has developed a potentially ground-breaking technology – Sour PSA – to replace the solvent-based AGR systems currently employed to separate sulfur containing species, along with CO_2 and other impurities, from gasifier syngas streams. The Sour PSA technology is based on adsorption processes that utilize pressure swing or temperature swing regeneration methods. The technology has been shown to enable overall plant cost reductions for clean power applications, but also is applicable to broader non CO_2 capture hydrogen and syngas markets, *e.g.* China’s coal to chemicals segment.

The performance of Air Products Sour PSA with feed gas generated from the gasification of lower rank PRB coal has been the focus of recent efforts. An experimental program has been conducted with the Energy and Environmental Research Center (EERC) to characterize the performance of a simple two-bed PSA/TSA system. It was operated with sour syngas generated from EERC’s fluidized bed gasifier utilizing Montana Rosebud PRB coal under oxygen-blown conditions. The results of this testing were used to prepare a techno-economic assessment to predict the benefits of incorporating Sour PSA technology into a base 90% CO_2 capture IGCC power plant design utilizing low rank coal. Additional work has been done to expand this study to look at non-capture and the broader set of hydrogen and syngas based applications. The experimental and techno-economic results as well as applicability to a broader market will be discussed.

Performance of a Small-Scale Injector for Atomization of Coal-Water and Petcoke-Water Slurries

Travis Waind, Kevin Whitty, Pal Toth, University of Utah, USA

The University of Utah operates a 1 ton/day pressurized, slurry-fed, oxygen-blown entrained flow gasifier. Coal or petcoke slurry is introduced into the top of the reactor through an injector, which atomizes the slurry with high-pressure oxygen. An atomizer being developed for this system is a two-stream, coaxial, micro-hole atomizer that functions similar to the airblast design. This atomizer design offers prompt phase contact, with the atomizing gas meeting the liquid approximately 1 mm from the liquid exit orifice. Atomizers of this design are commonly used in slurry-fed combustion and gasification systems. To understand the operation and behavior of these systems, and to help with design of other, larger atomizers, thorough characterization of the spray is needed.

This manuscript describes the characterization of sprays resulting from the atomization of coal-water slurries and petcoke-water slurries. Two solids loadings were explored for both CWS and PCWS. Atomization of water was performed for a baseline. The atomizing gas was air for all conditions, and all tests were performed in atmospheric pressure. Two levels of liquid flow were explored along with three levels of gas flow. Two spray sections were examined: the edge of the spray and a position along the central axis.

As the liquids being evaluated often have very different physical properties, each slurry was analyzed over a range of shear rates (up to 500 s^{-1}) using a viscometer. This provides insight into how these commonly non-Newtonian liquids will respond while undergoing the high shear rates typically associated with this type of atomizer.

The spray was quantitatively characterized using particle shadow velocimetry (PSV), which provides in-line illumination of a portion of the spray paired with imaging equipment. The region captured by PSV was roughly 10.5 mm by 10.5 mm. This allows the detection of drop diameters on the order of 10 micron. This characterization provides drop sizes, a drop size distribution, and a vector field associated with the identified drops. Patternation was also performed, which provides a spatial distribution of the spray.

During gasifier operation, this atomizer design has been shown to offer very stable operation. While the system conditions are different from those existing during spray characterization, this spray characterization offers much into the behavior of fuel suspensions during atomization.

SESSION 34
Clean Coal and Gas to Fuels: General - 6

Process Simulation of Synthesizing Tert-Amyl Methyl Ether with Methanol and C5 Alkenes from High-temperature Fisher-Tropsch Syncrude Oil

Wenying Li, Yanli Wu, Qiang Li, Qun Yi, Jie Feng, Taiyuan University of Technology, CHINA

Fisher-Tropsch syncrude excluding sulfur and nitrogen compound, is clean but abundant in alkenes. The C5-C10 olefin accounted for 25.8% of Fisher-Tropsch syncrude, containing about 7% C5 olefin. Considering tert-amyl methyl ether (TAME) has been extensively used in gasoline antiknock agent with high blending octane number and low blending Reid vapor pressure, etherification of C5 alkenes with methanol to produce TAME is proposed to meet the stringent alkenes specification for motor gasoline without a loss of fuel octane number. Though a 100% selectivity to TAME was achieved, limited to the equilibrium conversion, the maximum conversion ratio of C5 was only 62% under the optimum catalytic properties in the fixed bed. To make full use of raw materials and reduce the difficulty of subsequent product separation, dual-reactors (tubular reactor + the reactive distillation column) in series TAME synthesis process was simulated and optimized to improve C5 alkenes conversion by ASPEN PLUS software. The reactive distillation column here was expected to break the chemical equilibrium limits. The etherification reaction kinetic model on cation exchange resin Amberlyst-35 was adopted. After optimizing analysis, with 9 h^{-1} of liquid hourly space velocity （LHSV） and alcohol to olefin ratio of 1, optimum operating parameters were 343 K reaction temperature and 1 MPa reaction pressure in the tubular reactor; the absolute pressure was 0.35 MPa, reflux mole ratio was 3.5 and bottoms outlet was 28.6 kmol·h^{-1} in the reactive distillation column. Results showed that C5 alkenes conversion ratio reached 62% in the tubular reactor, and 30% in the reactive distillation column. The total conversion of C5 alkenes reached 92%.

Kinetic Study of Gasoline Synthesis from Coal Based Syngas via Methanol and Dimethyl Ether Using Dual Reactor System

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Syngas conversion to gasoline (STG) via methanol and dimethyl ether (DME) is a potential process technology which provides an alternative route to meet the increasing demand for clean motor fuels. Compared with FT synthesis, STG is considered to be more suitable to produce gasoline. There have been some reports introducing the researches on STG or similar processes, but there are few published kinetic descriptions for the STG process because of the complexity of the reaction process. In the present paper, the kinetic study of the STG reaction was preceded in two isothermal integral reactors. The first reactor was used for direct synthesis of DME from coal based syngas containing more than 50% CO, while the second reactor was used to convert the mixture of DME and methanol generated from the first reactor. For direct synthesis of DME taking place in the first reactor, there has been many kinetic studies published, the present study focuses on the kinetics of the second reactor.

A lumping method was used, and a total reaction equation was induced based on the lumps. The kinetic model has five lumps: oxygenates (DME and methanol), light paraffins (methane, ethane, propane and butanes), light olefins (ethane, propylene and butenes), and olefins, paraffins, aromatics in gasoline range. The kinetic experiments were carried out in two isothermal integral reactors installed in series, which contained 6.39 g catalyst for DME synthesis in the first reactor and 5.43 g catalyst for gasoline synthesis in the second reactor. The experiments were performed at 270 ^{o}C for the first reactor, and four different temperatures in a range of 310-360 ^{o}C for the second reactor. The gas hourly space velocity was in a range of 1552-4319 mL•(h^{-1}•g^{-1}), the total pressure inside the reactors was 3.0 MPa for all of the experiments.

To get the parameters of the kinetic model, inlet composition of the second reactor are needed, and obtained based on the experimental results of the independent experiments of direct synthesis of DME from syngas, using multi factor line regression method. The regression results showed that mole fraction y_i for component i and the total mole flow rate N_{2in} agree well in a linear relation with reaction temperature T, total pressure P and gas hourly space velocity GHSV for the first reactor. R^2 for y_{H2}, y_{CO}, y_{CO2}, y_{water}, y_{DME}, y_{MEOH}, $y_{paraffins}$ and N_{2in}, were 0.9972, 0.9890, 0.9473, 0.9364, 0.8799, 0.8732, 0.9384 and 0.9852, respectively. Stoichiometric coefficient of component i was obtained based on the mole flow rates of component i before and after the second reactor. The outlet concentration of the lumped component was calculated using Runge-Kutta method. The residual of experimental results of STG and the calculated results were used as objective function. Genetic Algorithm and Levenberg-Marquardt method were used to determine the parameters of the kinetic model. Finally, statistical analysis and residual error analysis were done to test the calculated results. The statistical results showed that the determination coefficient ρ^2 is larger than 0.90 and sum of mean square to the sum of the mean square of residual F is larger than10$F_{0.05}$, which demonstrates the model is reliable.

Sour Methanation Catalysts and Process Development

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The capital and operating costs of conventional coal to synthetic natural gas (SNG) technology is high because of the process restrictions in using Ni catalysts for methanation. In the process, the H_2/CO ratio of the syngas derived from coal gasification has to be adjusted to over three by water-gas shift (WGS) reaction prior to methanation, and sulfur species in the syngas have to be removed to less than 0.1 ppm by high energy consumption acid gas removal (AGR) process.

Recently, National Institute of Clean-and-Low-Carbon Energy developed a new coal to SNG process in which sulfur resistant Mo-based catalysts are employed for methanation. In the new process, the WGS and methanation reaction are combined into one reactor and the fine desulphurization system is avoided. Thus, the new coal to SNG technology offers obvious advantages on capital cost and heat efficiency comparing conventional process.

SESSION 35
Carbon Management: General – 3

New Enterprises and New Vista - Geological Storage of CO_2 Emitted by Coal Chemical Plants in China

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Deep geological storage of carbon dioxide could offer an essential solution to mitigate greenhouse gas emissions from the continued use of fossil fuels. Currently, CO_2 capture is both costly and energy intensive; it represents about 60% of the cost of the total carbon capture and storage (CCS) chain which is causing a bottleneck in advancement of CCS in China. The authors propose that capturing CO_2 from coal chemical plants where the CO_2 is high purity and relatively cheap to collect, thus offering an early opportunity for industrial-scale full-chain CCS implementation. The total amount of high concentration CO_2 that will be emitted (or is being emitted) by 8 coal chemical factories is 42 million tonnes. If all eight projects could utilize CCS, it would be of great significance for mitigating greenhouse gas emissions in China. Basins which may provide storage sites for captured CO_2 in North China are characterized. Some oil fields are potentially suitable for CO_2 enhanced oil recovery (EOR) and CCS demonstration but all these still require detailed geological characterization. The short distance between the high concentration CO_2 sources and potential storage sites should reduce transport costs and complications. The authors believe these high purity sources coupled with EOR or aquifer storage could offer China an opportunity to lead development in this globally beneficial CCS option.

TC-265: Development of the First Internationally Accepted Standard for Geologic Storage of Carbon Dioxide under Organization of International Standardization (ISO)

Steven M. Carpenter, Advanced Resources International, Inc., USA

The Carbon Capture Utilization & Sequestration (Storage) (CCUS) marketplace is lacking standardization and therefore the ability to allow CCUS projects to be advance as Clean Development Mechanism (CDM) projects. The international effort between the United States and Canada, funded by and the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide (IPAC-CO2 Research Inc.), and managed by CSA Standards, have developed the first internationally recognized Standard for the geologic storage of carbon dioxide Z-741.

The Z-741 Standard has been adopted by the Standards Council of Canada (SCC) and is available to the American National Standards Institute (ANSI). As a direct result of Z-741, the International Standards Organization (ISO) has created a technical committee to advance the development of comprehensive standards that address carbon capture, utilization, and storage. ISO established the Technical Committee TC-265 and the first meeting was held in Paris in June 2012. The objective of the technical committee is to develop and secure a global consensus on a uniform set of rules and criteria that can appropriately, dependably and efficiently applied to CCS projects.

TC-265 has only three short years to develop this framework. Since the kick-off meeting in Paris last summer, participating countries have submitted proposal to lead working groups within the TC-265 committee. The countries reconvened February 4-5, 2013 in Madrid and five working groups were established, scopes of work and individual Secretariats or “conveners” of the working groups were determined. The capture working group is led by Japan, the transportation working group is led by Germany, the storage working group is jointly led by Canada and Japan, the quantification working group is led by China, and the cross-cutting issues working group is led by France.

The presentation will address key issues experienced in the CSA and ISO processes, drawing from experts with full GSC project life cycle knowledge and experience – general interest, operators/industry, regulatory, and consultant/service providers, which represent a balance of stakeholder needs. A progress report of the ISO TC-265 committee as well as implications of the process and participation will be discussed.

MVA Techniques and Application at the Citronelle SECARB Phase III Site, Alabama

Steven Carpenter, George Koperna, Jr., Advanced Resources International, Inc.; Richard Rhudy, Robert Trautz, EPRI; Richard Esposito, Southern Company; Gerald R. Hill, Southern States Energy Board, USA

The Southeast Regional Carbon Sequestration Partnership (SECARB) Anthropogenic Test is a demonstration of the deployment of CO_2 transport and geologic storage and monitoring technologies implemented in conjunction with Southern Company’s Plant Berry 25MW Post-combustion CO_2 Capture Unit. This project is the largest fully-integrated commercial prototype coal-fired carbon capture and storage projects in the USA. The demonstration is approaching the first full year of injection. Two Class V Experimental Injection Well underground injection control (UIC) permits were issued in November 2011 and the project’s injection wells have been installed with one of the two wells being used for injection of CO_2. A robust Monitoring, Verification, and Accounting (MVA) plan has been developed and implemented to monitor and track the CO_2 plume and the associated pressure field.

A maximum of 550 tonnes of CO_2 per day is being captured, transported and injected into a saline geologic formation. The injection target is the lower Cretaceous Paluxy Formation, which occurs at 9,400 feet. Transportation and injection operations will continue for two to three years. Subsurface monitoring will be deployed through 2017 to track plume movement and monitor for leakage and site closure. This paper will discuss the range of MVA techniques deployed at the site, which include surface, shallow, and deep monitoring. Frequency, range of accuracy, and key findings of the MVA program to date will be presented.

From Coal Flue Gas to Fungible Fuels: Demonstration of an Algae Based System for CO_2 Mitigation from Coal Fired Power Plants

Michael Hayes Wilson, Jack Groppo, Andrew J. Placido, Mark Crocker, Eduardo Jimenez, University of Kentucky Center for Applied Energy Research; Aubrey Shea, Czarena Crofcheck, University of Kentucky Biosystems and Agricultural Engineering; Doug Durst, Duke Energy, USA

A pilot-scale vertical photobioreactor (PBR) is currently being operated at Duke Energy’s East Bend Station in Union, KY. The project is a collaborative effort between the University of Kentucky, the Commonwealth of Kentucky’s Department of Energy Development and Independence (KY DEDI) and Duke Energy. The overall goal of this project is to design, operate and evaluate a process capable of utilizing the flue gas from a coal-fired power plant through operation of a continuous microalgae culture, harvesting a sustainable quantity of the algae, and converting harvested algae into value-added products (e.g., biofuels, bio-gas, and/or a nutritional additive for aquaculture/animal feed).

The modular system, designed to be expanded, currently has a total volume of 7000 gallons, which includes 2000 gallons of clear vertical tubing, through which the algae culture is continuously circulated. A slip-stream of the East Bend Station flue gas is educted into the system as CO_2 is consumed. The process is continuously monitored and controlled remotely, with continuous collection of appropriate data. Samples are regularly withdrawn to determine growth rate, which is then correlated with other process data. A portion (15%) of the system culture is regularly harvested and recovered through a batch harvest system, whereby clarified water and nutrients are re-introduced into the system in order to minimize water and nutrient consumption. Harvested biomass is used for evaluation of value-added products. Of particular interest is the production of fungible biofuels such as renewable jet and renewable diesel. Algal lipids, grown off of flue gas, are extracted and upgraded using a catalytic decarboxylation/decarbonylation process. This hydrogen efficient process produces hydrocarbon based liquid transportation fuels that are completely fungible with existing infrastructure.

Ultimate goals of the project are to quantify the CO_2 uptake kinetics, gain a better understanding of the operating costs associated with microalgal cultivation on a large scale, and provide useful data for use in a techno-economic analysis.

Various aspects of PBR and harvesting design, as well as operation, are described along with presentation of current operating data. Results from lipid extraction and upgrading to hydrocarbon based fuels will also be presented.

SESSION 36
Combustion: NO_x Studies

Experimental Study on NO Emission during Coal Char Combustion

Jie Xu, Rui Sun, Lijin-Ma, Hui Liu, Harbin Institute of Technology, CHINA

Coal chars deprived from three different-types coals covering lignite; bituminous and lean coal were prepared in horizontal furnace reactor at 973K, 1173K and 1373K.

During the char combustion, the effects of mixing quartz sand, oxygen concentrations and reactor temperature on the conversion ratio of char-N to NO were investigated. Different ways of heat treatments were adopted to establish the relation of BET surface area and the NO emission. The results show that mixing quartz sand can effectively to minimize the char particles interaction by inhibiting the secondary reaction of char-NO and the particles interaction is weak with the coal rank. As the O_2 concentration increasing, less char-N is converted to NO at 973K and 1173K, but contradictory general trend is observed at 1373K for lignite and bituminous char. As the reactor temperature increasing, less NO is released. The correlation of BET surface area of char and NO emission is observed by comparison chars with different heat treatments and larger BET surface area of char is in favor of less NO formed.

Effects of the Alkali Metals on NO Reduction during Biomass Advanced Reburning

Jiangtao Hao, Ping Lu, Wei Yu, Yufei Zhang, Xiuming Zhu, Nanjing Normal University, CHINA

NO reduction by advanced reburning with biomass including rice husk (RH), saw dust (SD), biomass char (BC) and biomass briquette (BB) were carried out in an entrained flow reactor (EFR). The effects of reaction temperature in the reburning zone (*T*2), biomass species and alkali metal additives (such as Na2CO3, NaOH, NaCl, and KCl, etc.) on NO reduction were analyzed. Furthermore, the migration of alkali metals (Na, K, etc.) during biomass advanced reburning was investigated. The results indicated that NO removal efficiency increases first and decreases later with the increase of *T*2 while *T*2= 850-1150ºC. Different biomass has different performances on NO removal. Additives have positive effects on NO reduction, and NaCl is the most significant additive on NO reduction, followed by NaOH and Na2CO3, and the promoting effect of KCl is the worst. The concentration of additives (NaCl and Na2CO3) has no significant effect on NO reduction in the range of 50-150 μmol/mol. The sodium content in the test biomass does not change obviously during biomass advanced reburning process, however, the potassium content decreases significantly.

Influence of Fly Ash & K/Na Additives on the Thermal DeNOx Process

Wei Yu, Ping Lu, Jiangtao Hao, Yufei Zhang, Xiuming Zhu, Nanjing Normal University, CHINA

Experimental researches focused on the effects of fly ash and K/Na addictives on the thermal DeNOx process were carried out in a drop tube furnace (DTF) at the temperature of 850-1150^{o}C. The effects of reaction temperature (*T*r), water vapor content, K/Na additives (NaCl, KCl, Na_2CO_3) and fly ash on NO reduction were analyzed. The results are as follows: 1) NO removal efficiency increases first and decreases later with the increase of *T*r while *T*r = 850-1150^{o}C. 2) Water vapor can improve the performance of NO reduction and the best NO removal efficiency is 70.5% with the water vapor content of 4% at 950^{o}C. 3) K/Na additives have certain promoting effects on NO reduction of the thermal DeNOx process, in which, the promoting effect of Na_2CO_3 on NO reduction is most obvious, following KCl and NaCl. The concentration of additives has no significant effect on NO reduction in the range of 50-125 ppm. 4) Fly ash with K/Na addictives has a coupled effect on the thermal DeNOx process. On the one hand, adding fly ash will decrease the efficiency of NO reduction; on the other hand adding K/Na addictives will better the performance of NO reduction.

A Study on Absorption of NO in an Aqueous Solution of Sodium Persulfate

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The absorption of nitric oxide (NO) in sodium persulfate solution was investigated in a bubble column reactor. Experiments were carried out to investigate the effects of solution pH, other flue gas components including O_2, CO_2, SO_2 and additives on the NO removal efficiencies at 70 ^{o}C.

For 0.2 M $Na_2S_2O_8$, the removal efficiency of NO increased with the increase in NO inlet concentration. The presence of O_2 also promoted the absorption of NO. When the feed gas both contain NO and O_2, NO could be oxidized by O_2 to form NO_2 in gas phase. Under experimental condition, the NO_2 concentration is low, so NO_2 mainly reacts with NO to N_2O_3. The solubility of N_2O_3 is greater than the solubility of NO and NO_2, so the absorption via N_2O_3 seems to be another route. The presence of O_2 promoted the oxidation of NO and formation of N_2O_3 in the gas phase, resulting in the increase in the NO removal. Then, the concentration of CO_2 has marginal effect on absorption of NO by $Na_2S_2O_8$. When SO_2 is present in the flue gas, the removal efficiencies of NO slightly decrease because of the reaction between persulfate and SO_3^{2-} or HSO_3^{-}. Moreover, the addition of Na_2SO_3 and $FeSO_4$ restrained the conversion of NO. Certainly, the addition of NaCl can also increase the conversion, however, above 0.1M sodium chloride, there has little effect on the conversion of NO by increasing the concentration of NaCl. Besides, we also found that under alkaline conditions the conversion of NO is higher than acidic or neutral condition at 70^{o}C. It could be due to the different mechanisms of NO absorption under acidic and alkaline condition. Under acidic conditions, autocatalytic reaction between H^+ and $S_2O_8^{2-}$ promoted the absorption of NO. Under alkaline conditions, more $SO_4^{\cdot -}$ was converted to $OH^{\cdot}$ (eq.18) with increasing pH. Moreover, $OH^{\cdot}$ is more reactive than $SO_4^{\cdot -}$ and can rapidly react with NO.

On the side, the absorption kinetics of NO into $Na_2S_2O_8$ solutions was also studied in a bubble column reactor. The reaction was found to be 0.5-order (m) for C_{Ai} and 1-order (n) for C_{B0}. And the absorption rate equation can be expressed as:

$$N_A = 2.324 \times 10^{-2} \sqrt{C_{B0} C_{Ai}^{1.5}}$$

It is feasible to use $Na_2S_2O_8$ to remove lean concentration NO in flue gas because of the high absorption rate and low cost of $Na_2S_2O_8$ than other oxidants [30], Moreover, because the presence of SO_2 has slight effect on the removal of NO, the employment of $Na_2S_2O_8$ is suitable for a single scrubber to simultaneously remove NO and SO_2.

SESSION 37
Coal Science: General – 7

Properties of Solidified Fly Ash Suspension Heated at High Temperature

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The paper discusses changes in the properties of solidified fly ash suspensions prepared on the basis of ashes from the combustion of hard coal in fluidized bed boiler and pulverized. Water suspensions of these ashes are used widely in the Polish underground mining as solidifying backfill, but primarily as a means to fill the voids between the rocks in goaf (cavings) of long wall system. This reduces the risk of spontaneous fire, arising as a result of oxidation and self-heating of coal residue, which is especially dangerous phenomenon in a situation of co-existence threats of methane outflow. The proper application of fly ash suspensions allows to fill and isolate the goaf as well as its cooling. However, there are situations when a fire zone will cover areas previously filled, with already solidified suspension. The high temperature in such conditions can have a significant effect on suspensions properties.

To determine the nature and scope of the anticipated changes, solidified samples of suspensions were annealed at temperatures from 400 to 1000°C. The next step was carried out studies and analyzes of selected properties of such suspensions. Among them were structure, leachability of chemical contaminants and mechanical properties of solidified fly ash suspensions.

With the increase of the temperature and the length of heating time, there is more and more pronounced destruction of the samples structure, leading even up to their total destruction. The observed differences in leaching of chemical contaminants are complex matter. Only in some cases, have a homogeneous course. Changes properties of heated samples largely depend on the type of ash.

Critical Evaluation of Mineral Contents in Coal Using Chemical Quantitative Phase Analysis Method

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The method for Chemical Quantitative Phase Analysis (CQPA) of minerals in solids was suggested for sedimentary rocks by Klika et al. in 1986. This method is based on the recalculation of the elemental bulk chemical analysis by optimization procedure using identified minerals and the crystallochemical formula of the same sample. Now, the method has been completely reworked and the calculation possibilities widespread, so that any set of identified minerals can be taken into the calculation. CQPA method enables also the backward calculation of the bulk chemical analysis from mineral contents determined by some other quantitative method. By this way the accuracy of mineral analysis (e.g. X-ray diffraction) can be verified by comparing the calculated chemical analysis of the contents of determined minerals and real bulk chemical analysis. The program CQPA is also modified for quantitative mineral determination of coal. For this calculation except minerals identified in LTA, the crystallochemical formulas, the chemical analysis of LTA and/or HTA and the analyses of CO_2 and species of sulfur (pyritic and sulfate) for whole coal are used.

Experimental Investigation of Factors Governing the Fragmentation of Coal Particles at High-Temperature Pyrolysis

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Knowledge about the particle size distribution is of tremendous practical interest for many coal utilization processes, such as fluidized combustion/gasification, combustion in blast furnaces or fixed bed gasification, since the fragmentation of solid feedstock can strongly impact the flow behaviour of particles, carbon conversion rates and efficiency and further important process characteristics. Unfortunately, the *in-situ* determination of the particle size distribution in industrial-scale furnaces and gasifiers is a non-trivial task due to the extreme process conditions (high temperature, high pressure, reactive gas atmosphere). In order to identify the mechanisms and main factors, which govern the particle behaviour at high-temperature processes of coal utilization, the experimental investigation of the fragmentation of single coal particles, performed under well-definite conditions in laboratory devices, can be helpful. Additionally, such experiments might be used for the determination of customized sets of fundamental data, which are required for the validation of close-to-reality models for the computational simulation of the fragmentation of coal particles at high temperatures.

Motivated by these demands, a systematic experimental and theoretical study of the behaviour of single coal particles under fast pyrolysis conditions was performed. One of the aims was the better understanding of the relationships between the coal properties and the different phenomena of the particle fragmentation, i.e. the fragmentation caused by the thermal shock, by the pressure increase inside the coal particle due to the rapid evaporation of volatiles or by the particle-particle or particle-wall collisions. Using different analytical devices, a comprehensive set of experimental data characterizing the coal fragmentation behaviour was determined. Obtained values were used, in combination with the relevant coal characteristics, in order to establish data-based models for the deeper understanding of the fundamental relationships governing the fragmentation of coal particles.

For a systematic investigation of the influence of coal properties (coal rank, content of moisture, ash and volatile matter, porosity, particle size) and process parameters (temperature, residence time) on the coal particle behavior, measurements on commercial DSC (differential scanning calorimetry) and TG (thermogravimetry) devices were performed. Both devices were used in the drop mode, at which several coal particles placed in a container at room temperature were quickly transferred, using an appropriate feeding system, into the hot zone of the analytical instrument. The number and particle size distribution of the produced fragments was measured *ex situ* using dynamic image analysis. The fragmentation experiments were performed at different temperatures in the range from 800 to 1300°C, under nitrogen atmosphere. It was found that the fragmentation of coal particles is stronger with higher temperature and greater particle size. Below a certain particle size value, which depends on the coal type and temperature, no fragmentation was observed. More than 20 different coals, ranging from lignite to anthracite, were used for these investigations. It is notably, that the strongest fragmentation was observed in case of anthracites and some hard coals with low volatile matter content. Obtained results disagree with the assumption regarding the dominant influence of the devolatilization-driven fragmentation mechanism. In order to examine this aspect more carefully, the influence of varying content of moisture and volatile matter on the fragmentation intensity was investigated. For this purpose, coal samples with different contents of moisture and volatile matter were prepared by fractional drying and by stepwise pyrolysis under mild conditions, respectively.

It is well known, that the coal fragmentation essentially depends on how quick particles were heated up. Higher heating rates lead to stronger thermally-induced stresses in the coal particles, as well as to a faster release of volatiles accompanied by a greater pressure rise inside the particle. For a more detailed and accurate investigation of the effect of heating rate on coal particle fragmentation, we have used the electrothermal evaporation technique in the present study. This method allows the application of heating rates in a very broad range, up to 900 K/sec. Single coal particles were placed in graphite crucibles under argon atmosphere and heated up to a selected temperature. The influence of the heating rate on the particle behavior was characterized using the dynamic image analysis, which was performed by *ex situ* measurements before and after the electrothermal evaporation experiment. We have investigated the effect of coal rank and particle size on the obtained relationships between the particle behavior and heating rate. Obtained results were discussed in terms of the possible mechanisms of coal fragmentation.

Obviously, knowledge about the mechanical characteristics of coals is an essential prerequisite for a complete understanding of phenomena governing the coal particle fragmentation under high-temperature conditions. It is beneficial to investigate fundamental mechanical properties of coals, like the compressive strength and the elastic modulus, since such data might be used both for the empirical correlation analysis and for the validation of computational models described the particle fracture at high temperatures. We have determined these mechanical properties using a uniaxial testing apparatus. Single coal specimens were placed between two steel platens and loaded axially until specimens failed. Recorded stress – strain curves were used to calculate the compressive strength and the elastic modulus of the coal specimen. Obtained values were strongly dependent on the particle size and coal rank. Additionally, it was found that the compressive strength and the elastic modulus were significantly affected by a thermal treatment of the coal specimens. The experimentally determined data were used to establish correlations between the fragmentation intensity and the mechanical properties of coals.

SESSION 38
Sustainability and Environment: General - 2

Physical-Chemical Characteristics and Potential Utilization of Ferroshpere in Hg Oxidation

Jianping Yang, Yongchun Zhao, Junying Zhang, Chuguang Zheng, Huazhong University of Science and Technology, CHINA

Mercury is a trace element of significant concern because of its well-documented food chain transport and bioaccumulation, while the coal-burning power plants are recognized as one of the main anthropogenic sources of mercury emissions to the atmosphere. The mercury in coal mostly enriched in the pyrite and siderite, therefore, the transformation of iron-bearing minerals has a significant effect on the mercury retention during coal combustion. To quantitative assess the influence of the transformation of iron-bearing minerals and the evolution of its lattice parameters on mercury retention and oxidation during coal combustion, six fly ash samples with different origin and characteristics were collected and studied in this manuscript. The fly ash samples with different particle size were separated into three fractions: magnetospheres (ferrosphere), non-magnetic fraction and raw fly ash, while the ferrosphere and non-magnetic fraction were recovered by magnetic separator from the fly ashes. The Vibrating Sample Magnetometer (VSM), Mössbauer spectroscopy, X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to characterize the physical-chemical properties of all the fractions. And also the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was applied to investigate the enrichment of trace elements in ferrosphere. Temperature programmed decomposition (TPD) together with atomic absorption method was applied in order to acquire an understanding of the mode of decomposition of mercury species and content retained in the ferrosphere, non-magnetic components and raw fly ash. Special attention was also paid to the potential utilization in mercury capture and oxidation. The results indicated that different amounts of ferrosphere in fly ash can be extracted, normally accounted for 3-7%. A large percentage of ferrosphere are commonly 50-150μm in size, meanwhile, the BET Surface Area range is between 0.1775 and 0.2775 $m^2 \cdot g^{-1}$. The iron species in ferrosphere is mainly present as Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_3, and Fe^{3+}-glass, while the content of iron-bearing minerals in ferrosphere are different in six fly ash samples with different origin and characteristics. In addition, some trace elements, e.g. Ni, Cu, Mn, Co, V, Cr, et al, are also obvious enriched in ferrosphere. Further, the ferrosphere in fly ash exhibited different catalytic effect on mercury retention and oxidation.

Study on Photocatalytic Conversion of CO_2 into Hydrocarbon Fuels over Cerium Doped Titania Nanoparticles

Zhuo Xiong, Yongchun Zhao, Junying Zhang, Chuguang Zheng, Huazhong University of Science & Technology, CHINA

In recent years, the concentration of CO_2 in atmosphere increases rapidly, which causes inevitable global warming and climate change. One of the most potential routes to control the emission of CO_2 is to transform it into hydrocarbon fuels by photocatalysis, because it not only mitigates emissions but also provides useful chemical products. However, the challenges faced are to increase the conversion efficiency of CO_2 to hydrocarbons and extend the photo-resposive region to the visible light region. In this paper, cerium-doped titania nanoparticles (CTN) were synthesized by sol-gel synthesis (SGS) process and sol-gel auto-igniting synthesis (SAS) process respectively. X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), thermo gravimetric-differential thermal analyzer (TG-DTA), specific surface area and pore size analyzer (BET), UV-Vis diffuse reflectance spectroscopy (UV-Vis) were used to characterize the CTN samples. The photocatalytic reduction of CO_2 was carried out in a $NaHCO_3$ aqueous solution under UV light irradiation. The gas and liquid samples were analyzed qualitatively and quantitatively by GC/FID and ultraviolet-visible spectrophotometer respectively.The effects of synthesis method, doping concentration, irradiation time and reaction temperature were investigated and the reaction mechanism was discussed. It was found that in all cerium doped TiO_2 catalysts, the crystalline form of TiO_2 existed as anatase and the grain sizes of catalysts samples prepared by sol-gel auto-igniting synthesis process (CTN-SAS) were 20-30nm, which is smaller than the samples prepared by sol-gel synthesis process (CTN-SGS) due to the inhibition to agglomeration. Photocatalytic products including CH_3OH, HCHO and CH_4 were detected in all samples and CH_3OH was the primary product. The maxmum yield of CH_3OH was 7.6μmol/g after irradiation for 8h, which was obtained by CTN-SAS and the optimal doping concentration was 0.5wt%. The enhanced photocatalytic activity may owe to the smaller grain sizes and the doping of cerium which can extend the spectral response effectively and slow the recombination of photogenerated electron-hole pairs.The yields of photocatalytic products enhanced with the increasing of irradiation time and reaction temperature. However, the production rates decreased after 5h, which may owe that the intermediate products were not desorbed and diffused from the catalyst surface effectively.

Smart Power Management System for Coal Mining Industry

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A typical Chinese coal mine purchases 93% of its energy in the form of electricity with maximum load around 25 to 50 MW. Industrial average consumption is around 40 KWhr of electricity per ton of coal. Better electricity utilization could have significant impact on coal mining cost. While lots of work has been done to reduce energy consumption at equipment level, a system approach could benefit the mining operation from following perspectives:

1) Upgrading of a power system under smart grid concept to increase robustness & reliability based on a systematic design and optimization methodology at architecture level.
2) Application of unified intelligent compensation device integrated with energy storage to improve overall production efficiency based on a genetic power quality management solution.
3) Engagement of large scale energy storage that integrates peak shaving, energy arbitrage, emergency power, distributed & renewable power integration and the charging of future electric vehicles based on a hybrid storage concept with better economy.

To access the current state and effectiveness of proposed system, a network of monitoring devices are installed at one coal mine to collect real time data, and a demonstration system is underway to be built. Simulation results show achievable electricity savings of 10 to 20% that provides payback in less than 5 years.

Concept of smart power management system will not only integrate existing coal mine power system with distributed & renewable energy generation for multiple applications through advanced technologies and energy storage, it could also be considered as the “first of its kind” smart grid technology application in mining industry. It extends the smart grid research & development from large industrial user perspective which is also one of key interests of grid-company in policy making and standard enforcement for future grid.

A Comparison of the Effects of Coal Production in West Virginia and Shanxi

Qingyun Sun, Jerald Fletcher, Nyakundi Michieka, US-China Energy Center at West Virginia University, USA

The United States (U.S.) and China are the two largest producers and consumers of coal in the world. Shanxi province and the state of West Virginia (WV) are major coal producing regions in the U.S. and China respectively. Coal plays a significant role in these regions‟ economy, political landscape and environment. This paper will perform a comparative economic analysis of coal production and employment patterns between Shanxi province and the state of West Virginia. ARIMA models will be used to forecast coal production and employment for both regions while the ARCH and GARCH(1,1) models will be employed to model and estimate volatility. Results of this analysis should help uncover the challenges and opportunities facing the coal industry in the two regions. Furthermore, Shanxi and WV can work together to address the mutual challenges associated with coal production. In the end, this study will contribute to endeavors that promote energy collaboration and economic development between the two nations.

Trace Element Geochemistry of Some Chinese Coals

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A suite of 305 raw coal samples and 22 washed coal samples were collected from 24 provinces and autonomous regions and 2 municipalities of China in 2000. The run-of-mine samples were primarily collected from the larger coal mines and are believed to represent about 80% of China’s coal production at that time. Detailed chemical analysis of the samples was performed at the U.S. Geological Survey’s laboratories in Denver, CO, USA. The analytical data indicate relatively low to modest concentrations for most trace elements, including potentially hazardous elements. For example, the mean concentration of arsenic in these samples is 4.3 ppm (the mean concentration for arsenic in in-ground U.S. coal samples is 24 ppm); mercury, 0.16 (0.17 for U.S. coals); selenium, 4.1 ppm (2.8 for U.S. coals); lead, 13.9 ppm (11.0 for U.S. coals); thallium 0.34 ppm (1.2 for U.S. coals); beryllium, 1.8 ppm (2.2 for U.S. coals); cadmium, 0.14 ppm (0.47 for U.S. coals); chromium, 21.0 ppm (15.0 for U.S. coals); nickel, 12.5 ppm (14.0 for U.S. coals) and; uranium, 3.1 ppm (2.1 for U.S. coals).

Regional differences are also moderate. For example, Guangxi Autonomous Region in south China had the highest mean arsenic content (23.6 ppm for 5 samples) and Xinjiang Autonomous Region in northwest China had the lowest mean arsenic content (1.6 ppm for 6 samples). The highest concentration was in a coal sample from Guangxi Autonomous Region at 51.8 ppm. Much higher arsenic concentrations have been reported, such as the 35,000 ppm arsenic in a coal from Guizhou Province. However this coal was only used locally and was not intended for power plant use. The highest mean mercury content (other than a single sample from Beijing with 0.55 ppm) was in Guangxi and Jiangsu Province (south eastern China) with 0.35 ppm for 5 and 6 samples, respectively. The highest single value was 0.68 ppm in a sample from Shanxi Province in central China. The highest mean selenium concentration was in the municipality of Chongqing in south-western China with 13.2 ppm in 7 samples. The highest individual value for selenium was in a sample from Henan Province in eastern China at 30.0 ppm.

Correlation coefficients indicate strong correlations between arsenic and thallium (r2=0.85), selenium and molybdenum (r2=0.57), selenium and uranium (r2=0.52), lead and uranium (r2=0.53), mercury and thallium (r2=0.38), chromium and cobalt (r2=0.78), chromium and nickel (r2=0.88), cobalt and nickel (r2=0.87), and molybdenum and uranium (r2=0.81). All of these correlations are consistent with established geochemical principles.

Combined data for the 22 washed (undetermined methods) samples show significant removal for arsenic (34%), lead (29%), thallium (62%), mercury (31%), antimony (45%), manganese (29%), molybdenum (33%), and uranium (30%). These reductions indicate a primary inorganic mode of occurrence for these elements. Selenium exhibited an increase of 17% in the washed coals indicating a primary organic association. Cobalt and nickel exhibited increases in the washed coal of 45% and 32%, respectively, perhaps indicating that they occur in fine particles dispersed in the organic matrix that would then report to the washed coal fraction. Cadmium and chromium showed virtually no change between the raw and washed coals.

For most elements there is little to no variation with coal rank. The notable exception is manganese which has a substantial decrease in concentration from brown coals to bituminous coal to anthracites. This trend likely indicates a predominant organic association in the low-rank coals and progressive release of manganese with rank increase. Antimony shows a similar, but much less pronounced, trend. Selenium, lead, and possible mercury concentration increase with rank, perhaps a result of epigenetic mineralization of the higher rank coals.

In general, the ranges and averages for the potentially hazardous trace elements in this suite of Chinese coals and their behavior during coal cleaning are similar to those of U.S. and world coals.

SESSION 39
Gasification: General – 7

Synergies in Co-Pyrolysis of Lignite and Coal Liquefaction Residues

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The results from TGA experiments at the temperature range of 200~900°C evidently distinguished the different pyrolysis behaviors of lignite and coal liquefaction residues (DCLR); Meanwhile clear synergistic effects could be observed for the mixture. The investigation of co-pyrolysis in a fixed-bed reactor found significant synergies in both pyrolysis product yields and gas product compositions. The tar yields for 80coals: 20DCLR blend determined experimentally higher than the calculated values were 0.826 wt. %, 0.594wt. %, 0.026 wt. % , when the temperature increased by 100℃ from 400 to 600℃, meanwhile the gas yields determined experimentally higher than the calculated values were 0.118wt .%, 0.274 wt. %, and 1.058wt. % when the temperature increased by 100℃ from 600 to 800℃.The yields of CO and CO_2 determined experimentally were obviously higher than the calculated values; the yields of H_2 determined experimentally were obviously lower than the calculated values under the range of temperatures studied. The different synergies occurring at the temperatures 400-600 ℃ and 600-800℃, and the possible mechanisms were described including the interaction between lignite volatiles and DCLR particles. The enhanced devolatilisation of the blend was explained by the transfer of hydrogen from DCLR to coal as well as the promotion of low-temperature thermal decomposition of lignite by exothermic heat released from DCLR pyrolysis during its polycondensation reaction stage, which made gas yields is relatively higher than the calculated values.

Molding a Three-Dimensional Hybrid Entrained-Flow and Fluidized-Bed Mild Coal Gasifier

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The concept of Integrated Mild Gasification Combined Cycle (IMGCC) is being explored to effectively and competitively (a) retrofit existing pulverized coal power plants, (b) utilize low-rank coal (LRC), (c) serve as an alternative to conventional IGCC plant, and (d) incorporate the coal-biomass co-gasification process. The key feature of IMGCC is that it preserves volatiles with high energy density so the size of the piping and the gas cleanup system can be reduced from a fully gasified system. Consequently, since mild gasification is applied, the residence time is shorter than full gasificiation, and the product yield rate will be higher. Therefore, the mild gasifier size will be significantly smaller than a full-blown gasifier. The thermal energy saved from not cracking the heavy volatiles is preserved as chemical energy in the fuel, which partially contributes to the high-efficiency of IMGCC. One of the challenges of making IMGCC work is to design an effective mild-gasifier. The design is based on a new concept of combining the speed of an entrained-flow gasifier to quickly drive out most volatiles with the efficiency of a fluidized bed gasifier by cooking the remaining volatiles out from the chars in a compact space. To help the design process, a preliminary computational model was developed to simulate the reactive thermo-flow behavior in a simplified 2-D gasifier. The objective of this paper is to extend the previous 2-D model to a 3-D simulation model and to further investigate several design options with various changes of operation parameters. The Eulerian-Eulerian multiphase theory has been selected to model mechanisms that happen within primary phase (hot gas) and secondary phase (coal particle). The constitutive equations under the multiphase scheme, which derived from particle kinetic theory, are utilized for calculating the effective shear viscosities, bulk viscosities, and effective thermal conductivities of granular flows to simulate the hydrodynamic and thermal interactions between the solid and gas phases. Multiphase Nativer-Stokes equations and seven global reaction equations with associated species transported equations are implemented to simulate the mild gasification process. The results of this study have provided useful information for understanding the fundamental reactive granular thermo-flow behavior in the gasifier, and this information will be used as an essential guidance to further improve the mild-gaisfer design.

Development of a Higher Concentration Slurry Process Using Low-Rank Coals for the GE Entrained-flow Gasification System

Raul Ayala, Judith Oppenheim, Larry Duke, GE Power & Water, USA; Xijing Bi, GE Global Research – China, CHINA

Low-rank coals are relatively abundant in both China and several other countries and have become candidates as fuel sources for power generation and chemical production. Low-rank coals are characterized for having high moisture contents, typically above 15% and sometimes up to 30%, and in some cases also present high ash contents; these two characteristics may present challenges for making coal syngas at high plant efficiencies expected in future China regulations. Preparation and transport of the slurry feedstock for gasification requires technical expertise and understanding of the nature of coal, the coal chemistry, and how the coal can be prepared to the proper particle size for use in gasification.

GE Power & Water has developed the Extended Slurry Process by which conventional slurry preparation techniques have been improved to produce low-rank coals slurries achieving 5wt% or higher solids concentrations in the slurry, thus improving operating parameters such as plant economics, specific oxygen consumption, specific coal consumption, and syngas production. Moreover, the cost of syngas is reduced by integrating the coal preparation system with the GE gasifier operation so that tailoring of the resulting gas compositions allows for new applications such as substitute natural gas (SNG).

In this paper, experimental results will be presented on the characterization of low-rank coals, particularly those results demonstrating improved rheology (viscosity control at higher concentrations) and higher packing densities (due to better colloidal stability induced by surface chemistry parameters). Methodology using Six-Sigma tools and modeling of variances will introduce the concept of improved process capability and robust design for grinding to specified particle size distributions, addition of surface-active agents, and statistical process control.

SESSION 40
Clean Coal and Gas to Fuels: General – 7

Fast Co-pyrolysis of Coal and Biomass in a Fluidized-Bed Reactor

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The co-pyrolysis of coal/biomass is one of the most promising options for the utilization of renewable fuels and has recently become one of the most desired technologies to be worldwidely developed. Coal/biomass blends were prepared using Yilan subbituminous (YL) and corncob (CB), the ratios of coal in mixtures were varied between 0 and 100wt%. Co-pyrolysis characteristics were investigated in a thermogravimetric analyzer (TGA) from 30 to 700℃with a heating rate of 10°C/min and 40℃/min under the condition of nitrogen atmosphere and a flow of 100mL/min. The residues of co-pyrolysis were less than the calculated. With the increase of heating rate, the residues decreased severely more compared to expected values for all the blending ratios; In the fast pyrolysis fluidized-bed reactor, when the YL blending ratios were less than 60%, the yields of pyrolysis-oil were higher than the expected at the temperature of 600℃, this may be ascribed to the transfer of H/OH in volatiles of biomass to coal.

Ni/Mg-Al Oxide Catalysts for Low-Temperature CO_2 Reforming with CH_4: Effect of Preparation Method on Catalytic Performances

Jie Feng, Xiangdong Feng, Jieying Jing, Xiaohong Li, Wenying Li, Taiyuan University of Technology, CHINA

To develop an environmental friendly reaction and fully utilize the greenhouse gas, CO_2 reforming of CH_4 (CRM) is an attractive process but challenging subject for chemical application. In the CRM reaction, carbon deposition which made the catalysts deactivated is a critical issue that is thermodynamically favored at reaction conditions. The high reaction temperature (>700°C) was widely used because it was beneficial to CH_4 and CO_2 conversion and retarded coke formation. However, a lower temperature operation could give rise to decreasing energy costs. And an economical moderate degree of CH_4/CO_2 conversion could be provided by a facile on-site recycling of educts. Nevertheless, there are a few studies of the CRM reaction about 500°C. The low reaction temperature may cause more serious coke formation than the high temperature which make the catalyst easy deactivation in the CRM reaction.

In this contribution, we compared the Ni/Mg-Al oxide catalysts prepared by co-precipitation with mechanical mixed method to elucidate the effects of the preparation method as well as CO_2 adsorption ability on activity and stability of catalysts in CRM reaction. The activity measurements of these catalysts were conducted at the reaction condition of 500°C, 1atm, GHSV of 24000 $mL/g_{cat}·h$, the molar ratio of CH_4 to CO_2 is 1:1, and no inert components. The Ni/Mg-Al oxide catalysts prepared by co-precipitation had the high CH_4 conversion approach to equilibrium conversion for 25 h without deactivation due to the high CO_2 adsorption ability and well nickel dispersion.

Structure and Hydrogen Storage Properties of the Mg-C Composites Prepared by Mechanical Milling and Heat Treatment

Tonghuan Zhang, Shixue Zhou, Naifei Wang, Weixian Ran, Haipeng Chen, Qianqian Zhang, Shandong University of Science and Technology, CHINA

In this paper, the caking property of bituminous coal was used to bind the nano-magnesium particles which were prepared for hydrogen storage by reactive ball milling. The effects of heat treatment temperature and atmosphere on the microstructure and phase composition were investigated. Results show that when the material gets heat treated at 550ºC under argon atmosphere, the nano-magnesium particles could be effectively bound by the bituminous coal in the material. However, the carbon could react with some Mg, and Mg_2C_3 was generated. When 1.0 MPa of H_2 was introduced at 550 ºC, the magnesium was well protected from generating Mg_2C_3 and the powders were well bound. The Mg-C hydrogen storage material showed a hydrogen capacity of 3.8 wt.%. Besides magnesium, the carbon can also store some hydrogen according to the FTIR analysis.

Solid-State Synthesis of Calcium Carbide

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A process for the preparation of calcium carbide pellets of high purity and density is described. Calcium carbide was synthesized by conventional and microwave heating of micron-sized calcium oxide and graphite particles in argon atmospheres between 1500-1800°C and a pressure of 1000 psi, with no subsequent purification. In addition to variations in temperature, heating rates where varied from 45ºC/min to 4ºC/min. The effects of the processing techniques on the final density, microstructure properties and percent purity of the resulting products were characterized. Calcium carbide pellets (CaC_2 II tetragonal structure) with yield percent above 80% was prepared. The density and degree of purity of the product were affected by reaction temperature and time, particle size of starting materials and the dimension of the sample container. The main impurities were calcium oxide, unreacted calcium and free carbon. Additionally, the data obtained from reactions performed in the microwave furnace suggest that graphite was determined to be not only an excellent microwave absorbing material but also a reductant, preventing the oxidation of calcium carbide.

SESSION 41
Carbon Management: General - 4

Synthesis of Solid Amine Sorbents from Fly Ash for CO_2 Capture

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A novel method for the synthesis of solid amine sorbents integrated into alumina extraction from fly ash (FA) has been developed in order to reduce the sorbent production cost and improve its sorption performance. A supernatant solution of silicate species extracted from fly ash by alkali solution and CO_2-philic polyethylenimine (PEI) were used as precursors to synthesize PEI-WCB solid amine sorbent for low temperature CO_2 capture. The PEI-WCB samples were prepared by a wet gel impregnation method. The effects of sorption temperature and PEI loading amount on CO_2 sorption capacity were measured. The CO_2 sorption capacity and the regenerability of PEI-WCB were evaluated by using thermogravimetric analyzer (TGA). The best PEI-WCB sorbent gives a high sorption capacity of 139.8 mg-CO_2/g-sorbent. This CO_2 sorption capacity is higher than those of previously published literatures for sorbent obtained from fly ash because this method loads more amine into the pores of support material. Comparing with the sorbents, which have the similar sorption capacity, the preparation cost of PEI-WCB is significantly reduced. and more importantly, the solution of silicate, a low value by-product derived from industrial waste via Al extraction from fly ash, was directly used as raw material for high performance PEI-WCB solid amine sorbent synthesis. The results indicate that the PEI-WCB synthesized by this environmental friendly and cost effective method has potential application for low temperature CO_2 capture in terms of its outstanding features such as high capture capacity, fast sorption/desorption rate, infinite regenerability, no corrosion and cost-effective.

Effect of $NaNO_3$ on the CO_2 Capture Activity of MgO-$CaCO_3$-$NaNO_3$ Sorbent

Xinfang Yang, Lifeng Zhao, Yunhan Xiao, Chinese Academy of Sciences, CHINA

The previous research has indicated the potential of the $CaCO_3$-promoted MgO-based sorbent for CO_2 capture at 250-500^{o}C. The activity tests of the MgO-$CaCO_3$ sorbent prepared by the co-precipitation of $Mg(NO_3)_2$, $Ca(NO_3)_2$ and Na_2CO_3 has indicated the high CO_2 absorption capacity. However, the MgO-$CaCO_3$ sorbent directly derived from the calcination of the natural dolomite shows poor CO_2 absorption capacity. Comparing the preparation techniques of the co-precipitation method and the direct calcination of dolomite, the introducing of $NaNO_3$ during the co-precipitation process is inferred to have an important effect on the MgO-$CaCO_3$ sorbent activity. Besides, the absorption capacity of the prepared sorbent by different researchers or different techniques differs largely, and the different amount of $NaNO_3$ in the sorbent is inferred to be a reason. In this paper, the activity tests of the prepared MgO-$CaCO_3$-$NaNO_3$ sorbent by the co-precipitation of $Mg(NO_3)_2$, $Ca(NO_3)_2$ and Na_2CO_3 with different amount of $NaNO_3$ remaining in the sorbent and the modified dolomite with different proportion of $NaNO_3$ introducing into the dolomite have been investigated. The activation temperature at which $MgCO_3$ decomposes without $CaCO_3$ decomposition is critical to the sorbent activity, and the activation temperature of the modified dolomite with $NaNO_3$ producing MgO-$CaCO_3$ sorbent has been optimized, with the consideration of the activation atmosphere in N_2 or air. The results have indicated that the introducing of appropriate amount of $NaNO_3$ has an obvious effect on lowering the activation temperature of the double salts of $MgCO_3$-$CaCO_3$-$NaNO_3$, and increase the CO_2 absorption capacity of the obtained MgO-$CaCO_3$-$NaNO_3$ sorbent. The affecting mechanism of $NaNO_3$ has been analyzed, based on the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of the sorbent during the activation process, and the X-ray diffraction (XRD) characterization of the sorbent before and after activation process.

The Effect of Doping CeO_2 for CO_2 Capture of Calcium-Based Sorbent at High Temperature

Xiaotong Liu, Xiaoxun Ma, Junfei Shi, Northwest University; Shisen Xu, Chen Li,
China Huaneng Group Clean Energy Technology Research Institute Co., Ltd, CHINA

The fossil fuel power plant has been regarded as the chief culprit for the increasing concentration of CO_2 in our atmosphere. In order to avoid the harm done by the greenhouse effect, it becomes emergency to capture the CO_2 from flue gas of power plant. However, the current separation methods could not be conducted until the high temperature flue gas is cooled below 100℃. With the advantages of wide sources, low cost, easy preparation and regeneration, CaO becomes the suitable absorbent for CO_2 at high temperature.

In this study, aiming at the sintering problem of CaO through multiple carbonation and calcination, a kind of modified calcium-based absorbent was studied to capture CO_2 from flue gas at high temperature by doping CeO_2. The TGA was used to estimate the adsorption capacity of absorbents with different doping ratios of CeO2 at 700℃ in the 30vol% CO_2 atmosphere. Ca/Ce(8:2), with the largest surface area(50.90m2/g), had the best performance in all doped absorbents. In the carbonation/calcination cycling experiments, the adsorption capacity of Ca/Ce(8:2) only dropped a little with the increase of cycle number and kept well cycling stability (86.1%) after 20 cycles. The BET data, SEM and XRD images demonstrated that the appropriate doping ratio of CeO_2 could structure a strong framework to obstruct the contact between CaO particles. The mesoporous were kept in good condition and sintering was almost prevented after multiple cycles at high temperature. And the optimal calcination condition for Ca/Ce(8:2) was studied. Ca/Ce(8:2) would be an anticipated high temperature absorbent for capture CO2.

Theoretical Screening of Solid Sorbents for CO_2 Capture Applications

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DOE/NETL; Keling Zhang, Xiaohong Shari Li, David King, Pacific Northwest
National Laboratory, USA

It is generally accepted that current technologies for capturing CO_2 are still too energy intensive. Hence, there is a critical need for development of new materials that can capture CO_2 with acceptable energy costs. Accordingly, solid sorbents have been proposed to be used for CO_2 capture applications through a reversible chemical transformation. By combining thermodynamic database mining with first principles density functional theory and phonon lattice dynamics calculations, a theoretical screening methodology to identify the most promising CO_2 sorbent candidates from the vast array of possible solid materials has been proposed and validated. The calculated thermodynamic properties of different classes of solid materials versus temperature and pressure changes were further used to evaluate the equilibrium properties for the CO_2 adsorption/desorption cycles. According to the requirements imposed by the pre- and post- combustion technologies and based on our calculated thermodynamic properties for the CO_2 capture reactions by the solids of interest, we were able to screen only those solid materials for which lower capture energy costs are expected at the desired pressure and temperature conditions. These CO_2 sorbent candidates were further considered for experimental validations. After introducing this methodology, in this presentation, we will report that by mixing two kinds of materials to form a new sorbent could fit the desired operating conditions. As an example, the Li-Si-O system is fully investigated. With different ratio of Li_2O and SiO_2, a series of lithium silicates (Li_2O, Li_8SiO_6, Li_4SiO_4, $Li_6Si_2O_7$, Li_2SiO_3, $Li_2Si_2O_5$, and $Li_2Si_3O_7$, and SiO_2) can be obtained. By calculating thermodynamic properties of the reactions of CO_2 captured by these lithium silicates, we found that with increasing the ratio of Li_2O/SiO_2, the CO_2 capture turnover temperature of the corresponding lithium silicate increases. Therefore, by adjusting the mixing ratio of two or more solids to form a new sorbent, it is possible to move the turnover temperature window of the mixed sorbent for capture-release CO_2 into the desired operating conditions and to provide a way for designing and engineering the optimal sorbent materials. Our theoretical investigations on $CaCO_3$-promoted and M_2CO_3 (M=Na, K)-promoted MgO sorbents revealed that the sorption processes take place through formation of the double carbonates ($M_2Mg(CO_3)_2$ (M=Na, K), $CaMg(CO_3)_2$) with better reaction kinetics over pure MgO, which are in good agreement with the experimental results that the Na_2CO_3-promoted MgO sorbent has high reactivity and capacity towards CO_2 sorption and can be easily regenerated either through pressure or temperature swing process.

SESSION 42
Combustion: Ash and Mercury

A Study of Slagging and Fouling: Current Theory and Experimental Characterisation of Deposits

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This paper will present an extensive review of current theory and practical considerations affecting fouling and slagging, as well as an experimental study on the characterisation of ash deposits collected from a pulverised lignite-fired 150t/h steam industrial boiler. With the depletion of high-rank coals and petroleum, the use of low-rank coal such as Victorian brown coal, rich in moisture and alkali and alkaline earth metals (Na, K, Ca and Mg), has been receiving increased attention in the energy and mining industries. The low-rank brown coal has large reserves in both Australia and China, and also other parts of the world. It is estimated that fouling and slagging related issues cost the global utility industry several billion dollars annually due to reduced heat transfer and equipment maintenance. In particular, brown coal or lignite may have increased tendencies for fouling due to its higher sodium content than bituminous coals.

The analysis on ash deposits was conducted on samples collected at various locations in the industrial boiler using X-ray Diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy as well as a computer controlled scanning electron microscope (CCSEM). This serves to identify the roles of different chemicals in slagging and fouling. The results demonstrated the dependency of certain chemicals to initiate a primary deposit on boiler surfaces including walls of the combustion zone and superheater tubes that is highly sticky having the capability to trap fine ash particulates. The nature of these chemicals was conditional upon the location within the boiler.

Numerical Study on Ash Deposition of Blending Coal in a Drop Tube Furnace

Chung-Hwan Jeon, Byung-hwa Lee, Min-Young Hwang, Seoung-Mo Kim, Sang-In
Kim, Ke-Ju An, Pusan Clean Coal Center, Pusan National University, KOREA

Slagging tendency for four coals (Moolarben, Bera-multi, Berau, Tanito) include blends, under constant environmental condition have been investigated to clarify the ash deposition mechanism in drop tube furnace. Also, the modeling for ash deposition based on critical viscosity temperature obtained by TMA has been developed and validated with experimental results. Besides measuring the weight of the deposits, a detailed characterization of the coals, fly ashes and deposits has been performed using ASTM procedures and SEM. Experimented parameters are used to represent the deposition behavior: capture efficiency (CE) is a measure of the intrinsic tendency of the particles to form a deposit, which is useful both to characterize the experimental method and to determine the influence of some mechanisms relevant to deposition phenomena. The results show that ash behavior of the blends is expected to be more complex. It seems alkali species from Indonesian coals may combine with Quartz grains of Moolarben coal to form sticky aluminosilicates particles which eventually grow. Further examination ash particles of blend samples as well as deposit samples may clarify the mechanisms of clinker formation in boiler.

Fine Particulate Matter Formation during Co-Firing Lignite with Semi-Char in 25KW Down Fired Furnace

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The upgrading of low-rank lignite to high-rank solid fuels, besides some vapor-phase by-products, has received renewed attention due to the increasing energy utilization efficiency and decreasing pollutants emissions. After most moisture and part of volatile removed from the parent lignite, the fine particulate matter (PM2.5) formation of the upgrading fuels might dramatically reduce in contrast to that of original lignite combustion, which is the main objective of this work. In this work, one kind of semi-char fuels derived from a typical kind of lignite was co-fired with its parent coal by five different blending mass fractions (0%; 20%; 40%; 60%; 100%). The experiments were operated on 25kW Tsinghua self-sustained, one-dimensional down fire furnace. The derived semi-char was supplied by NICE by a low-temperature pyrolysis process. Comparing to parent lignite, the moisture content of semi-char fuel is decreased from 22.5% to 6.0%, while the volatile content is decreased from 30.1% to 19.0% all on air received basis. Ultrafine particles (aerodynamic diameter smaller than 100nm) and fine particles (aerodynamic diameter smaller than 10 um) concentrations were measured and sampled by both SMPS and ELPI, respectively. The results indicate the amounts of $PM_{0.1}$ and $PM_{0.1\text{-}1}$ are quite similar between different blending fraction of semi-chars. But the amount of $PM_{1\text{-}10}$ obvious differs between different semi-char fraction during the co-firing. These results illustrate the distinct formation mechanisms between different particle size ranges during coal combustion process. The detailed mechanisms are discussed in this work and compared to already published works. As a summary, the upgraded lignite (here called semi-char) combustion will produce less fine particulate matters (PM_{10}) rather than parent lignite which encourages power plants to burn semi-char in order to reach the government's emission standards.

SESSION 43
Coal Science: General - 8

Analysis of Low Temperature Oxidation of Coal to Understand the Self-Ignition Mechanism of Coal

Kouichi Miura, Hiroyasu Fujitsuka, Ryuichi Ashida, Kyoto University, JAPAN

High self-ignition tendency of low rank coals has been making their transportation and storage extremely difficult. It has been requested to develop a method for suppressing the self-ignition tendency to utilize the lower rank coals more effectively. Effective self-ignition suppression method, however, has not been developed yet, mainly because the self-ignition mechanism of coal has still not been clarified. It is believed that the aliphatic carbons moieties mainly contribute to the low temperature oxidation of coal. They are first oxidized to form peroxides, then further oxidized to aldehydes, carboxyls, esters, anhydrides, and finally converted to H_2O and CO_2. However, the mechanism of the low temperature oxidation is too complex and few quantitative works have been performed to relate the low temperature oxidation to the self-ignition of coal.

Then the purposes of this study are to examine the mechanism in more detail and to formulate the rate of the low temperature oxidation of coal. To do so, weight change, gas formation rates, and heat generation rates were measured respectively by using a sensitive thermobalance, a micro gas chromatograph, and a differential scanning calorimeter (DSC) during the oxidation of several coals below 300 °C at several constant heating rates of 2 to 10 K/min. Furthermore, the fate of the functional groups on the coal surface was also observed by using an in-situ FT-IR spectrometer. The thermogravimetric and gas analyses at the initial stage of low temperature oxidation showed that oxygen was adsorbed onto the coal with simultaneous production of CO_2, H_2O and little amount of CO. In-situ FT-IR measurement clearly showed that the aliphatic carbons were first oxidized to form carboxyl groups at 180 to 240 °C, further oxidized to form esters at 240 to 280 °C, and then converted to anhydrides at 280 to 300 °C. Oxidation of coal main body started over 300 °C producing only CO_2, H_2O and CO. The oxidation rate of the aliphatic carbons, for example, was 100 times larger than the oxidation rate of the coal main body when compared at 200 °C for a specified coal. Based on the information of the oxidation kinetics and the heat generation rate estimated by the DSC measurement, the adiabatic temperature rising profiles were successfully calculated to estimate the self-ignition tendencies of several coals.

Controlled Separation of ≥ 300°C Fractions from Low Temperature Coal Tar Based On Selective Reactions

Ming Sun, Xiaoxun Ma, Pengpeng Du, Jing Chen, Northwest University, CHINA

The separation of low temperature coal tar is an important key to the identification and utilization of coal tar. But the core issues lie in the separation method and its theory of high boiling fractions from low temperature coal tar which restrict the processing, utilization and composition research of coal tar all the time.

According to the basic characteristics of low temperature coal tar, with ≥300°C fractions in atmospheric distillation from low temperature coal tar as research object, the purpose of this study was to investigate the controlled separation of ≥300°C fractions by the methods of selective reaction of benzaldehyde with phenolic compounds and polycyclic aromatic hydrocarbons (PAHs) in ≥300°C fractions, and gradient separation of reaction products by different polar solvents. After reaction, residual oil-1 (toluene soluble), residual oil-2(toluene insoluble and tetrahydrofuran soluble) and residual solid (tetrahydrofuran insoluble) were collected and analyzed by gas chromatography-mass spectroscopy (GC-MS) and a thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR), respectively. GC-MS analysis of residual oil-1 showed that it contained free alkanes, phenanthrenes, anthracenes, benzo[e]pyrene, perylenes, etc. The TG-FTIR results showed that the pyrolysis process of >300°C fraction(184 to 384°C, 384 to 555°C), residual oil-2(93°C to 212°C, 212 °C to 415°C, 212 °C to 415°C), residual solid(73°C to 236°C, 236°C to 285°C, 285°C to 518°C, 518°C to 595°C) are mainly divided into 2, 3, 4 stages. Absorption peaks of the bands at 680-900cm^{-1} are attributed to Mono- and di-substituted benzene rings in >300°C fraction are stronger than residual solid-2 and residual solid. In the pyrolysis process of >300°C fraction, CO has no significant absorbency for infrared at 2060-2240cm^{-1}, but there are obvious absorption peaks in residual oil-2. Based on gel permeation chromatography (GPC) analysis the residual oil-2 (<13KDa), polymers were generated and the carbonization yields (residual oil-1 char is 31%, residual oil-2 char is 48%, residual solid char is 57%) were increased by polymerization reaction. The FTIR results showed that the band at 1227cm^{-1} and 1025cm^{-1} are C-O and C-O vibration, respectively, and the band at 871 cm^{-1} is C-C backbone stretching vibration [*v*(C-COO)] in residual solid. Polymerization reaction of benzaldehyde and compounds with carboxyl, short-chain fatty and ester group in >300 ◦C fraction generates polymers and fixes these compounds.

Investigation of Drying Kinetics of Lignites under Isothermal Condition

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Lignite as a very important fuel has attracted extensive attention due to its rich reserves. However the high moisture content reduces the energy density and causes problems in storage and transport. Drying treatment is necessary before combustion and gasification processes. In this research, Yunnan and Neimeng lignites were dried by thermo-gravimetric method to study the drying kinetics. Different mathematical models were used to simulate drying curves and Page model is better to describe isothermal drying process. An empirical equation was proposed to simulate drying rate curves. The effective moisture diffusivity and activation energy were determined with a diffusion model. An equation expressing the effect of temperature on the drying characteristics was obtained.

SESSION 44
Sustainability and Environment: General – 3

Optimal CO_2 Abatement Pathways with Induced Technological Progress for Chinese Coal-Fired Power Industry

Aijun Li, Huazhong University of Science & Technology; Zheng Li, Tsinghua University, CHINA

During 2009 UN Climate Change Conference in Copenhagen, Chinese government promised that carbon dioxide emissions per unit of GDP should be reduced by 40%～45% from 2005 to 2020. And this indicator of carbon intensity reduction has been set as Chinese national mid-term planning target. As well known, energy related CO_2 emissions contribute over 80% of total CO_2 emissions in China. From the view of macroeconomics, a lot of factors will affect energy consumption for a region or a country. It has been extensively accepted that energy consumption is affected by economic level, economic structure, energy structure, energy efficiency and technological progress. In our previous studies, all these factors will be considered by applying a hybrid energy model, which is combined top-down computable general equilibrium model (i.e., CGE model) with bottom-up energy engineering model. And this hybrid energy model (i.e., Chinese energy CGE model) initially has been constructed to analyze Chinese industrial energy-saving potential in our previous research. Besides, main energy economic indicators (i.e., energy intensity, CO_2 emissions per unit of GDP, total energy consumption, and total energy-related CO_2 emissions) by 2030 during Chinese urbanization also have been analyzed. Since coal will still dominate Chinese primary energy consumption within a long future, coal consumption and its related SO_2, NO_x and CO_2 emissions in Chinese coal-fired power industry by 2030 have been forecasted as further research. By considering the ecological assessment, emergy analysis has been combined into the hybrid energy model in order to understand the ecological impacts of energy efficiency improvement for coal utilization by 2020 in China. Particularly, the ecological impacts of developing energy-saving related technologies in Chinese coal-fired power industry have been estimated.

Based on these existing researches, the cost-abatement function is built for Chinese coal-fired power industry by 2050 in this study, and the abatement amount of CO_2 emissions with induced technological progress is optimized. Thus by applying the above hybrid energy model, this study analyzes the optimal CO_2 abatement pathways of low-carbon development for Chinese coal-fired power industry. Firstly, main indicators of coal-fired power generation in China by 2050 are forecasted. Then whether CCS technology will be introduced to China from 2020 differentiates the entire simulation analysis into two studied cases. In the first studied case, the optimal CO_2 abatement pathways of indirect CO_2 emissions mitigation without CCS technology introduction are estimated. The abatement amount of CO_2 emissions in this study is assumed to be as the difference of CO_2 emissions amount between the technological levels of the studied scenario and baseline scenario. The base scenario is set according to the technological level of 2005 China. In the second studied case, the optimal CO_2 abatement pathways of direct carbon removals with CCS technology introduction from 2020 are also evaluated. Especially, oxy-fuel CCS technology has been regarded as a potential commercialized option in this study. Particularly, learning-by-doing based knowledge accumulation is considered under a cost-effectiveness criterion. Finally, the impacts of technological progress on the optimal timing of CO_2 emissions abatement are analyzed for the planning of developing advanced coal-fired power technologies in China.

Forecasting Future Coal Production from Surface Mining in Central Appalachia

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This study created a spatially explicit grid cell model of the central Appalachia region of the United States to predict where coal surface-mine production is likely to occur in this region in the near future. Based upon time series econometric models, we used historical, county-level production data to predict future high, medium, and low levels of production. Next, we combined GIS spatial analysis and a Random Forest predictive model to match spatially explicit data to the econometric projections.

Predictor variables for the grid cell model include distance to existing coal-fired power plants, distance to railroads, distance to intermodal transportation facilities, distance to inland ports, human population density, coal geology type, and sulfur percentage of the coal. In addition to the predictor variables we also integrated spatial data sets as exclusions or areas where surface coal mining could not occur. Areas excluded from modeled potential future mining activities include permanent conservation lands and areas with existing land uses that are not conducive to mining activities (urban and developed lands, water). In all, 57,185 square kilometers (km^2) throughout the study area (9.6%) were excluded due to land use restrictions, while 14,366 km^2 of the study area were excluded due to presence of conservation lands (2.4%).

The machine learning algorithm Random Forest was used to produce a probability score for each of the one km^2 grid cells within each central Appalachian county that contained coal production data. With this model, the coal geology type and the sulfur content of the coal reserves were found to be the most important predictive variables for the spatial model.

In order to map future potential surface mining activities on a landscape scale, we used results from the probabilistic Random Forest model of surface mine potential along with county-level estimates of future coal mining production for the years 2015, 2025, and 2035. County-scale surface coal production estimates, in short tons, were translated into estimates of surface area impacted by developing a production to unit area relationship using existing recent permit data and production data from Kentucky and West Virginia. We found the highest concentrations of high probability areas are found in eastern Kentucky, southern West Virginia, and Alabama, with smaller high probability areas scattered across western Kentucky, Ohio, southwestern Virginia, and Pennsylvania.

SESSION 45
Gasification: General – 8

Three Dimensional Computational Fluid Dynamics Simulation for Parametric Study on Gasification Performance in an One-stage Entrained Bed Gasifier

Sang Shin Park, Hyo Jae Jeong, Jungho Hwang, Yonsei University, KOREA

Three-dimensional computational fluid dynamics (CFD) modeling on gasification performance in an one-stage entrained bed coal gasifier (Korea SCGP gasifier) was performed for parametric studies with various O2/coal ratios (0.1, 0.3, 0.5, 0.7, 0.9, and 1.1) and steam/coal ratios (0.01, 0.05, 0.1, 0.15, and 0.2) using a commercial code, ANSYS FLUENT. The CFD modeling was conducted by solving steady-state Navier–Stokes equations with the Eulerian–Lagrangian method. Chemical reactions were solved via the Finite-Rate/Eddy-Dissipation Model for gas phase. Illinois #6 coal and design coal for the Korea SCGP gasifier were used for validation of our model and parametric study, respectively. In order to verify our CFD analysis results, actual operating data were compared with our results. Optimal conditions of O2/coal ratio and steam/coal ratio for the Korea SCGP gasifier using design coal were obtained as 0.7 and 0.05, respectively. Carbon conversion efficiencies, cold gas efficiencies, exit temperature and species mole fractions were also calculated by the modeling.

A TG-FTIR Study of Low Rank Coals

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Four Chinese low-rank coals were investigated, characterized by high moisture content, relatively low ash, low sulfur and high chemical reactivity. These low-rank coals are known for their favorable characteristics making them interesting candidates to be pyrolyzed for the production of coal oil. However, little so far is known about these low rank coal’s macromolecular structures or the reactions occurring during pyrolysis. Hence, this study was conducted to obtain information of the structure and consequently the pyrolysis reactions occurring, as a function of heating rate, end temperature and type of low-rank coal.

Firstly, the low rank coals were characterized by ultimate analysis, XRD, FTIR and Raman spectroscopy to gain more insight in the molecular structure of the coal species under investigation. Secondly, the TG-FTIR technique was implemented, to investigate the reactions occurring during the pyrolysis of low rank coals. The obtained FTIR spectra provide information about the evolution of functional groups during pyrolysis as a function of heating rate, pyrolysis temperature and type of low rank coal and will permit to choose the optimal parameters for coal pyrolysis for the production of oil and/or chemicals.

Synergistic Effects during Fast Co-Pyrolysis of Corncob–Lignite Blends Effect on Char Oxidation Reactivity

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Increasing concerns regarding pollution from coal use has been a driver for research into new and clean energy solutions, especially in China. Recently, interest in co-utilization of coal and biomass has been growing significantly, as the use of renewable biomass resources when co-fired with coal directly reduces fossil-based CO_2 emissions. Regardless of the gasification technology of interest, devolatilisation is an important aspect to the overall conversion process, as it plays a significant role in the amount and nature of the char that must be gasified. There is some evidence in the literature [1-8] of synergistic effects from co-gasification of coals and biomass materials; this work is part of a wider study investigating possible synergies arising from co-pyrolysis of coal/biomass blends.

Previous work by the authors, a lignite and a corncob used as sample, has investigated possible synergistic effects on products distribution from devolatilisation. A modified two-stage fixed-bed reactor with three quartz reactor tubes was used to observe and resolve the products distribution of synergistic effect on the fast pyrolysis of corncob/lignite blends over the temperature range 500-900°C. Three series contrast experiments were performed to investigate possible mechanisms of interactions between volatiles and carbon matrices, as well as the interactions among volatiles from different fuels. In addition, the distribution of products was also measured to investigate the effect of synergy on the reactivity of chars made from the co-pyrolysis of corncob/lignite blends.

The aim of this current work is to investigate possible synergistic effects of co-pyrolysis on the oxidation reactivity of chars. Char reactivity in air was determined using a STA 409C thermogravimetric analyzer at 450°C, and the inorganic compositions and chemical structure of chars were measured by ICP-AES and Raman spectroscopy, respectively. The results show that the reactivity of chars made from the corncob–lignite blends during co-pyrolysis is higher than that of the mixture of chars prepared separately, and that this is related to impacts of co-pyrolysis on char chemical structure as well as the migration of alkali and alkaline earth metal (AAEM) and other catalytic species between the char matrices.

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Effects of Inherent Moisture Contents on Lignite Conversion in the Absence and Presence of Steam as Reaction Atmosphere

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This study is to investigate the influence of inherent moisture contents on Shengli lignite conversion using different particle sizes with and without steam as reaction atmosphere. A drop tube quartz reactor was used for conducting all the experiments. For the large coal particle sizes (0.9-2mm) in the inert gas atmosphere, the increase in moisture contents in coal did not always see the increase in coal conversion at 900^{o}C, for which the fast ―escape‖ of moisture before inner area of coal particles reached the gasification temperature should be the main reason. For the small coal particle sizes (less than 0.075mm), the heat could immediately transfer into the inner particles and initiated the reaction between coal and the inherent steam, thus resulting in the increasing coal conversion and also more production of light gases. In the presence of steam for the reaction atmosphere, decreasing char yields with increasing inherent moisture content for large coal particle size was found as the transferring speed of inherent steam inside the coal particles was getting slow, compared to the case when the reaction atmosphere was ultra pure nitrogen. Furthermore, the reactivity of chars from pyrolysis was apparently different from that of chars from gasification, partially owing to the change in char structure caused by char-steam reactions.

SESSION 46
Clean Coal and Gas to Fuels: General – 8

Electrochemical Capture of CO_2 and Instant Conversion into Syngas

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Climate change caused by global warming is one of the greatest challenges to the future of human society. Manmade CO_2 through the use of fossil energy is thought to be the major source of the global warming. In an effort to mitigate the global warming and climate change, stabilization of atmospheric CO_2 concentration is the best near-term realistic solution. The current mainstream technical approach to achieving that goal is to limit the emission of CO_2 from the existing and new large-scale fossil-fueled power plants by capturing CO_2 at point-sources and geologically storing it. Three industrial combustion processes have so far been developed as the carbon removal point sources: pre-combustion, post-combustion and oxy-combustion. Significant technical progress has been made over the past decades, but the major challenge to a commercial deployment of these technologies remains to be the high energy penalty associated with CO_2 capture, compression and storage (CCS) that appreciably lowers the overall plant efficiency and ultimately increases the cost-of-electricity produced.

An appealing alternative to geologic storage of the captured CO_2 is to have CO_2 recycled back to fuel form. The significance of this technological development is enormous: it rebalances the carbon cycle in our ecosystem and therefore enables a sustainable energy future. With renewables as the energy input to the conversion, the making of synthetic fuels from CO_2 can be carbon-neutral or even carbon-negative.

In this presentation, we report two new types of high-flux electrochemical separation membranes that can selectively and efficiently capture CO_2 from a source of flue gas or fuel gas. A new concept that combines these new high-temperature CO_2-capture membranes and conventional high-temperature solid oxide electrolysis (SOE) cells is also proposed and evaluated with the aim to develop an integrated reactor capable of capturing and converting CO_2 into syngas in one single step. Such a unified system has a great potential to be cost effective and energy efficient for the ultimate synthesis of artificial fuels with zero carbon emission.

Crack Formation Characteristic of “Ball Structure” Carbonized Briquette

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To improve the mechanical strength of anthracite carbonized briquette, a spheroidizer has been developed to control the shrinkage and crack formation of briquette in carbonization process. In this paper, the effect of spheroidizer on the mechanical strength and crack formation characteristic of “ball structure” carbonized briquette were studied. The results indicate that the addition of spheroidizer could improve the internal structure and mechanical strength of carbonized briquette.

The size of spheroid produced by carbonization has a certain influence on the mechanical strength, which indicates that the creak formation and the mechanical strength of products could be controlled through adjusting the size of spheroid. In the spheroidizing carbonization process, the shrinking stress section of briquette was non-uniform and cambered. Moreover, the shrinkage of sphere has always taken spheroidizer as center and the shrinkage between spheres is also in progress, which can fully disperse the shrinking stress of briquette and restrain the crack formation.

Role of the Ti, Mn, and Cu Promoters on the Structure, Reduction, and Catalytic Behavior of Iron-Based Fischer–Tropsch Catalysts

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Ti, Mn and Cu effect on the structure and surface area, reduction and carburization of Fischer–Tropsch Fe-based catalyst. The catalysts were prepared by co-precipitation and impregnation method and characterized by X-ray diffraction technique. Fe2O3 precursors initially reduce to Fe3O4 and then to metallic Fe (reduced by H2) or to a mixture of FexC (x=2.5 or 3, reduced by CO). BET surface characterization shows that addition of Ti increases the surface area of precipitated oxide precursors by inhibiting sintering during calcination. Though Ti does not reduce to active FTS structures, instead, lead to the dispersing of active components or active sites of the catalyst during activation and reaction in H2/CO synthesis gas, leading to lower FTS rates but better FT reaction stability than on Ti free precursors. Cu increases the reduction rate of Fe2O3 to Fe3O4 by providing H2 dissociation sites. Research on catalyst activating by H2-TPR indicates that Cu/Fe atomic ratios are achieved at intermediate. The catalytic tests (P = 2.3 MPa,H2/CO =1.5, GHSV=3000 h-1) indicate that with content change of Cu, significant changes in CO conversion and hydrocarbon selectivity are observed, Cu increases CH4 in FTS products, but has less thing to do with CO2 selectivity during FTS reactions on catalysts based on Fe oxide precursors. By the H2-TPR characterization result on Mn promoted catalyst, the addition of Mn doesn’t changed the reduction temperature, but according to the catalytic tests, Mn addition would increase the CO conversion during the reaction, and have an optimized intermediate Fe/Mn ratio.

Study on Shrinkage Characteristic of Briquette during the Pyrolysis Process

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This thesis regards large size briquette as the research object. The shrinkage characteristic of briquette and effects heating rate and reaction temperature on shrinkage during pyrolysis process was studied with the measure equipment of contraction and mass loss under atmospheric pressure. The results indicated that with the increase of carbonization temperature, the briquette volume shrinkage was increased gradually, while the reaction time was decreased. The increase of heating rate led to the increase of shrinkage rates and the decrease of final shrinkage. The pyrolysis process of briquette includes depolymerization stage, polycondensation stage and crack formation stage.

SESSION 47
Gasification: General – 10

Co-Pyrolysis Behavior of Saw Dust, Straw and Shenfu Bituminous Coal in Fixed Bed Reactor

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Co-pyrolysis behavior of two kind of biomass and Shenfu bituminous coal were studied in a fixed bed reactor under nitrogen atmosphere. The pyrolysis temperature was 700℃with a heating rate of 5℃/min. Saw dust and straw were blended with coal as 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0(wt), respectively. Gas, tar components were analyzed by a gas chromatograph and a gas chromatography-mass spectrometry respectively. The results showed that the gas volume yields in co-pyrolysis process were higher than the calculated values. In the heating process, gas released at 250℃ and gas volume achieved maximum at 300-400℃, which were mainly pyrolyzed by biomass. Compared with Shenfu bituminous coal, saw dust and straw produced more CO_2 and H_2 in the co-pyrolysis process, which promoted methyl free radical convert to CH_4 and made some char gasified in the process. Tar yield increased with the increasing biomass ratio. Alkanes in tar were increased in co-pyrolysis process. Compared with the char yield in biomass pyrolysis and coal pyrolysis process, the char yields in co-pyrolysis were lower slightly. With the increasing biomass ratio, char yield had a greater degree of deviation. The SEM showed that the differences between co-pyrolysis char and their parents chars were not much. These variations can't be explained by simple additive behavior, it showed some interaction between biomass and coal existed, which may due to the secondary reactions.

Effect of Mineral Content and Composition on Catalytic Coal Gasification Characteristics

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The catalytic activity of K_2CO_3 in steam gasification of coal has been known for a long time. However, the potassium reacts with the mineral containing silicon and aluminum leading to catalyst deactivation and incomplete recovery of catalyst from gasification ashes. Moreover, the added catalyst can be a source for agglomeration due to the formation of low-melting minerals with the calcium and iron in coal ash. Chinese Wangjiata coal with 14% ash which poor in Si, Al and rich in Ca, Fe was selected to investigate the influence of mineral matter on gasification reactivity, agglomeration and catalyst recovery through demineralization and addition of clay.

In case of Wangjiata raw coal, the gasification rate increases with the increase of catalyst loading. The catalyst loading saturation level is about 15%. Demineralized coal with about 2% ash has higher gasification reactivity compared with raw coal. The carbon conversion is over 99% at catalyst loading of 8%. However, with the addition of 5% clay to coal impregnated 10%K_2CO_3, the carbon conversion decreases from 96% to 90%. The higher the content of mineral in coal, the larger the amount of K_2CO_3 must be added to increase the reactivity.

In term of agglomeration, the degree of agglomeration increases severely with the increase of impregnated amount of K_2CO_3. At a catalyst loading of 10%, the minimum sintering temperature of ashes decreases from higher than 800℃ to 650℃ compared with in the absence of K_2CO_3. The minimum sintering temperature increases to 760℃ with the addition of 5% clay mineral, suggesting that the clay mineral is effective to reduce the agglomeration.

The reaction between minerals and catalysts is also important for the recycling of the catalyst. The catalyst water washing recovery of raw coal gasification residue is 65.8%. For the demineralized coal, the recovery of water soluble potassium salts is 86.0%. The amount of water soluble potassium decreases to 52.7% with the addition of 5% clay. The results of XRD measurement conform that catalyst reacted with ash mineral to form water insoluble potassium compounds, such as $KAlSiO_4$ and $K (Si_3Al) O_8$, which should be recovered by digestion with calcium hydroxide.

This study demonstrated that not only ash composition but also content of the ash affect gasification reactivity, agglomeration and catalyst recovery. Coals rich in Ca and Fe can applicability in catalytic coal gasification through adding little amount of clay. This technique can lead to a sensible and effective utilization of the coal resource in catalytic coal gasification process.

Characteristics of Soot Formed by Rapid Pyrolysis of Solid Carbonaceous Materials

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Rapid pyrolysis of several types of solid carbonaceous materials (lignite, bituminous coal, and petroleum coke) was conducted in a drop-tube furnace at elevated temperatures under ambient pressure. Special attention was paid to the dependence of the yield and gasification reactivity of soot on fuel type. Solid products, soot and char, were sufficiently separated by liquid-suspension gravity separation. SEM-EDX was employed to study the morphology of soot and char. Further studies of the soot particle nanostructure were also conducted using a HRTEM imaging technique. The gasification reactivity of solid product with CO_2 was determined by temperature-programmed gasification using thermogravimetric analyzer.

The yield of product gas is much lower than the volatile matter of raw material, which is attributed to the formation of soot by secondary reaction of primary volatile matters. The relation between the soot yield and O/C molar ratio presents a volcano-type curve. Soot yield of bituminous coal is nearly half of the volatiles yield, while that of lignite and petroleum cokes is merely several percents of the input quantity. Soot aggregates consist of roughly spherical particles of 50-500 nm in diameter and are mainly composed of carbon element, which is completely different from the properties of char. The gasification reactivity of soot produced from coal is lower than that of coal char. However, the reactivity of soot from petroleum coke is higher than that of the corresponding char. The difference in gasification reactivity of soots was clearly observed. Soot from lignite pyrolysis is most reactive, while that from petroleum coke displays the lowest reactivity. Meanwhile, different curvature and length of graphene layers were found to develop in soot particles. A relationship between nanostructure and soot reactivity is established.

Effect of Temperature and Pressure on Brown Coal Pyrolysis in a Drop Tube Reactor

Stephan Siegl, Denise Reichel, Steffen Krzack, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

Thermochemical processes like gasification, pyrolysis, combustion and hydrogenation play an important role in energetic and non-energetic applications of coal worldwide. Since this fact, knowledge about thermochemical conversion behaviour of various coals is needed for development of new technologies as well as optimisation of existing processes and plant dimensioning. Process simulation tools are often used for prediction of conversion behaviour including material and energy balances. Therefor it is absolutely necessary to have consistent data for implementation and also validation of these process models.

Pyrolysis has an exceptional position within the thermochemical processes due to its relevance as a single process for char and tar/oil generation as well as a pre-step in other thermochemical processes like gasification. Furthermore, it is possible to draw conclusions about coal structure if pyrolysis behaviour is known. But the pyrolysis process of coal is a complex process composed of a multitude of parallel reactions, which are partly dependant on each other. Due to this fact various parameters, related to process and feedstock, have an influence on pyrolysis. In general, it is hard to find consistent and complete data sets for coal pyrolysis behaviour. Less data are available in the literature especially for the pressure influence.

To obtain experimental data on coal pyrolysis a new drop tube reactor was built in the framework of the research project "German Center for Energy Resources" installed in Freiberg, Germany in the beginning of 2010. The reactor with an inner diameter of 20 mm and a heated length of 2.5 m can be operated at pressures up to 100 bar and temperatures up to 800 °C under different gas atmospheres like argon, hydrogen, methane, carbon dioxide, steam and mixtures of them. One of the primary goals is the improvement of knowledge of the product yields of char, gas, tar/oil and reaction water during coal pyrolysis. Furthermore, the evaluation of the reaction mechanisms and the structural information of coal and its products before, during and after thermochemical conversation processes is absolutely necessary for understanding the decomposition of coal in detail. Particularly with regard to pyrolysis as a pre-step for gasification processes, experiments with a German brown coal (Region: Lusatia, particle size: 63…200 µm) were carried out at varying pressures (up to 60 bar) and different temperatures (500 and 800°C) at adapted volume flow of argon to obtain similar gas residence times and approximately similar particle residence times within the heated zone. The knowledge of the residence times is necessary for the evaluation of the results. Different approaches for calculations of the particle residence time were used and real gas behaviour was assumed.

Influence of the Hydrothermal Dewatering on the Physicochemical Characteristics of Chinese Low-Rank Coals

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Three typical brown coals with different coal ranks in China were upgraded by hydrothermal dewatering at different temperatures. The influences on the physicochemical characteristics, including composition, micro-morphology, pore structure, chemical structure, and chemical reactivities of pyrolysis, gasification and combustion were investigated. It was found that the upgrading process significantly decreased the coals' inherent moisture and oxygen content, and increased their calorific value and fixed carbon content. The upgraded products exhibited compositions comparable with those of high rank coal. From microcosmic aspect, the upgrading process broke the coal particle to pieces, increased coals' hardness and brittleness; pore distribution of upgraded coal developed to the microporous region, and the surface area and volume increased at first but then decreased as the treatment temperature increased; the unstable components in the coal decreased, and stable components increased; oxygen functional groups were reduced and destroyed, and unsaturated side chains decreased; the apparent aromaticity increased, suggesting the low-rank coals were upgraded to high-rank coals. From macrocosmic aspect, the thermo-gravimetric curves of pyrolysis, gasification and combustion were delayed toward the high-temperature region, closing to Da Tong bituminous coal. Compared with raw brown coals, the upgraded coals exhibited weak chemical reactivities similar to bituminous coal. Further more, the changes in physicochemical characteristics became more notable when 2 treatment temperature increased from 250 °C to 300 °C or the rank of raw brown coal was lower. For upgrading brown coal process, hydrothermal dewatering method could be considered as an effective dewatering and upgrading process.

SESSION 48
Combustion: Oxy-Combustion & Chemical Looping – 1

Update of Alstom's Oxy-Combustion Development for Steam Power Plants

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Since the combustion of fossil fuels plays a key role in the global emissions of CO_2, new technologies are required to enable the power industry to continue meeting the global demand for electric power, while controlling emissions of CO_2. Alstom is developing a portfolio of solutions to address CO_2 emissions reduction and to support power plant owners in anticipation of emerging regulations. Among these solutions is oxy-combustion technology, which is one of the most advanced and promising CO_2 capture technologies. Alstom is convinced that this robust clean power solution will be able to supply competitive electricity for the future low carbon systems. This technology also offers operational flexibility options to address grids sustainability, which becomes more critical with the increased share of renewables and related intermitting power generation.

Alstom is a leader in the evaluation and commercialization of oxy-combustion with efforts addressing all major components and their design and integrated operation. This paper focuses on oxy-combustion and will provide a comprehensive updated overview of Alstom's development and commercialization of oxy-combustion technology for CO_2 capture from coal-fired power plants.

This paper will highlight key findings from several years of comprehensive testing at Alstom's 15 MW_{th} Boiler Simulation Facility in Windsor, CT under our joint US Department of Energy development program and at the 30 MW_{th} Vattenfall Schwarze Pumpe oxy pilot plant. The most recent results of the advanced oxy-boiler and GPU systems testing at the Boiler Simulation Facility will be discussed. Additionally, updated oxy-combustion power plant systems integration and optimization results will be discussed and economic evaluations of the cost of electricity for coal power generation with CO_2 capture compared to other power generation options will be presented. . An update will also be provide on the White Rose project, which is an advanced 400 MW power plant applying oxy technology for CO_2 capture and storage. The new plant will be built at the Drax power station in North Yorkshire, UK. The project partners are Alstom, Drax Power, British Oxygen Company, and the National Grid. This project has been selected under UK's Carbon Capture and Storage Commercialisation Programme for the FEED (Front End Engineering and Design) study.

Ignition and Combustion Characteristics of Wet Victorian Brown Coal in Oxy-Firing and Air-Firing Conditions

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Oxy-fuel combustion is a promising technology for carbon capture in coal-fired power plant and has demonstrated distinct combustion characteristics, such as ignition delay, heat and mass transfer and decrease in flame stability. Victorian brown coal condenses a lot of moisture while being burnt in the furnace. Current drying technology for Victorian brown coal is via the extraction hot gas from the boiler to entrain this wet pulverized coal into the furnace. In oxy-fuel combustion technology, while the flue gas is continually being recycled, the steam content in the furnace will exponentially increase and resulted in the inefficient drying. To fully utilize wet Victorian brown coal in oxy-fuel technology, understanding on the moisture effect and steam on the combustion behaviour is a must. This paper presents an experimental and theoretical study of wet Loy Yang brown coal combustion in air-fired and oxy-fuel fired in a laboratory scale laminar entrained flow reactor coupled with a flat flame burner. The combustion environment was generated by burning mixture of C_2H_4, air, O_2 and CO_2 in the flat flame to produce oxygen concentration ranging from 21%-31%vol. The combustion environment was insulated in a transparent cylindrical quartz reactor, allowed the coal particle combustion to be observed individually via high-speed cinematography and optical in-situ diagnostics equipment, such as high speed infrared pyrometer.

Based on the experimental data, the ignition was observed to be delayed in O_2/CO_2 atmospheres as well as wet coal. Small differences in the ignition between air and O_2/CO_2 can be accounted for the differences in the physical properties in N_2 or CO_2. In the case of wet coal combustion, this was due to additional time required to dry the additional moisture in the coal sphere. Consequently, the steam condensed during the heating-up period will also dilute the volatile released during the thermal decomposition stage and reduced its flammability, resulting in the further delayed ignition. High speed photography evidences showed the increasing volatile cloud size in wet coal combustion, which explained the volatile gas was swept away from the particle surface. As volatile was ignited further away from the surface, the heat transfer back to the particle was minimized and resulting in lower particle surface temperature. This evidence was further supported that the longer flame was observed in wet coal combustion. Theoretical study was also presented in this paper using a single kinetic rate devolatilization model to predict the thermal decomposition rate of brown coal and the use of kinetic-diffusion single film model. All the results were aligned with the experimental data.

It was also shown that this worse combustion behavior can be offset by increasing oxygen volume fraction in the background gases from 21% to 31% in oxy-fuel combustion, while burning wet coal will require higher oxygen mass fraction to achieve the similar combustion behavior as to that in conventional air combustion. This was expected as increasing oxygen concentration will increased the char surface temperature, char burning rate and resulted in shorter burnout time.

Chemical Looping Combustion of Methane over Bimetallic Fe_2O_3 – CUO Oxides with Higher Amounts of Fe Oxide

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This paper contains the results of research work on chemical looping combustion. The significant advantage of a chemical looping combustion technology is that, a concentrated CO_2 stream can be obtained after water condensation without any energy penalty for CO_2 separation. The objective of this work was to prepare supported bimetallic Fe-Cu oxygen carriers with higher amount of Fe oxide, and to evaluate the performance of these for the CLC process with methane/air. Multi-cycle thermo-gravimetric analysis (TGA) tests were conducted at temperature range of 750 and 950 °C with oxygen carriers utilizing both concentrated and diluted CH_4 as a fuel. The oxygen transport capacity was calculated and reactions rates stabilities were evaluated. Acknowledgement: The research was financed by the Polish Ministry of Higher Education and Science, project No. 685/N-USA/2010/0 and the research work was conducted at U.S. Department of Energy/National Energy Technology Laboratory.

Development, Scale-Up and Process Modeling of Copper-Based Chemical Looping with Oxygen Uncoupling (CLOU)

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Chemical looping with oxygen uncoupling (CLOU) is a form of chemical looping combustion (CLC) well-suited for processing solid fuels such as coal. With CLOU, the thermodynamics of the oxygen carrier are such that the equilibrium partial pressure of oxygen at combustion temperatures is in the range 0.01 to 0.10 atm. In the air reactor (incoming partial pressure 0.21 atm), the carrier is oxidized. In the fuel reactor where the partial pressure of oxygen is very low, oxygen is spontaneously released ("uncoupled") as gaseous O_2. The oxygen readily reacts with char and volatiles, enabling much more rapid consumption of coal than is possible by conventional CLC, which requires that the coal be gasified either in-situ or in a separate upstream gasifier. Only a few metal complexes based on copper, manganese, cobalt or iron-manganese display CLOU behavior. Copper, cycling between cuprous (Cu_2O) and cupric (CuO) oxides and loaded onto inert material at concentrations to 60 wt%, has displayed good physical resiliency and is promising for CLOU systems both because of its fast oxidation and reduction kinetics and because the low heat of reaction allows both the air and fuel reactors to operate exothermically. In this paper, research on copper-based CLOU at the University of Utah is presented. Several different types of copper-based oxygen carriers are compared in terms of both reactivity and physical performance in a lab-scale fluidized bed reactor. A process model for a dual fluidized-bed system that combines thermodynamics, experimentally-determined reaction kinetics and heat flow is presented, and results for a variety of conditions and scales shown. Finally, the design and construction of a 200 kW chemical looping process development unit (PDU) at the University of Utah is presented, and practical challenges of scaling up chemical looping technology is discussed.

Pore Structures Change of Different Particle Size of Pulverized Coal Combustion in an O_2/CO_2 Atmosphere

Baojun Yi, Liqi Zhang, Zhihui Mao, Fang Huang, Chuguang Zheng, Huazhong University of Science and Technology, CHINA

Oxy-fuel combustion is one of the most potential technologies for carbon capture and storage. This paper studies the pore structure characteristic of pulverized coal combustion in an O_2/CO_2 atmosphere. The pore structure of pulverized coal can be changed by the variation of particle size. And also that will remarkably affect the combustion characteristic. To study pore structure variation of pulverized coal in O_2/CO_2 atmosphere, the influence of particle size was considered. Different particle sizes of pulverized coal were being prepared and some of them be made to char. Although the char is composed of a large number of micro-pores, the trend of pore structures change is consistent with the raw coal. It can be speculated that the pore structure can be affected by devolatilization process and reactions of volatile matter, but those not altered the affection of the particle size. Contrast of the O_2/CO_2

atmosphere and the air atmosphere can be found out. The influence of particle size on pulverized coal combustion in an air atmosphere is larger than in an O_2/CO_2 atmosphere. However, there is different from the result obtained from the char. Further explanation of the entire combustion process was affected by the particle size. Isothermal combustion experiments were taken at 900 ℃ in both air and O_2/CO_2 atmospheres. The pore structure changes of various carbon conversion stages were analyzed. The carbon conversion rate in the air atmosphere is higher than in the O_2/CO_2 atmosphere at the same time. Pulverized coal combust in an O_2/CO_2 atmosphere developed more micro-pores than in an air condition at the initial stage (less than 50% carbon conversion rate), and the consequent specific surface area and the specific volume are greater too. On the contrary, the surface area growth during the combustion reaction in the O_2/CO_2 atmosphere is less than in the air atmosphere at the late stage (the carbon conversion ratios larger than 50%). There is not difficult to get the result that pore structure change of the pulverized coal combustion under O_2/CO_2 condition is quite different from the air condition. Most of the reason is char-CO_2 gasification was occurring under an O_2/CO_2 atmosphere, the reaction at the initial stage is easy to form a large number of micro-pores. But due to the CO_2 have a great heat capacity and kinematic viscosity, resulting in combustion products is not easy to be released. They do, however, greatly affect the subsequent reaction. Until the reaction rate reduces to less combustion products, abundant specific surface area can be significantly accelerated the reaction speed, following micro-pores of expansion and the char burns out. The present results might have important implications for understanding the variation of pore structure on pulverized coal combustion in an O_2/CO_2 environment.

Combustion of Carbonaceous Material in High Temperature of the Oxidizer with Low Oxygen Concentration

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The moderate or intense low oxygen dilution (MILD) combustion is a technology that has a great potential to increase the thermal efficiency and reduce the pollutant emissions. High reactants temperatures and a strong recirculation of combustion products are the main characteristics of this technique. The recirculation leads to a low oxygen concentration in the primary reaction zone. Several fuels have been burned under MILD conditions in numerous investigations; however, there are some fundamental issues that require further attention and consideration. Even more, when a complex material as coal is used as a fuel. In this case, some topics that require to be addressed are related to NO_x formation mechanisms and the chemical evolution of coal particles during its combustion.

The aim of this study was to improve the understanding of phenomena that occur when a carbonaceous material is burned in a high temperature environment with a low oxygen concentration. Those features emulate MILD conditions for coal combustion. The experiments were carried out in a natural gas premix burner, and the flame was stabilized over a ceramic material (honeycomb type). Argon was injected parallelly around the premixed flame to avoid the air diffusion into the reaction zone. The equivalence ratio (Φ) was fixed at 0.65 (excluding the contribution of the coal) to guarantee flame stability and oxygen excess in the combustion products. Sub-bituminous coal was used as a fuel in two different presentations; the first one was pulverized with particle size in the range of 75-150 µm, and the second one was a carbonaceous fragment (2.0 g). In each case, the sample was suspended over the flame with a height of 2.5 cm above the burner surface. In this zone, the oxygen concentration was 8.0 % v/v and the temperature was 1173 K. The standard gases released during coal combustion were measured using a water cooling sampling probe and analyzers. When a single fragment of coal was burned, OH* and CH* chemiluminescence profiles were measured by means of an ICCD camera. In this way, was possible to see clearly the main zone of reactions.

For the two coal presentations studied, the ignition of the carbonaceous material started with a flaming ignition of the volatile material. Pulverized coal was burned in lower residence time than the single coal fragment. It can be explained for the formation of a uniform layer of ash around the coal fragment. A detailed and quantitative evolution profiles for CO, CO_2, O_2, NO and NO_2 were determined. From CO, CO_2 and NO_x concentration profiles were possible to see that nitrogen release has similar tendency than carbon release in the earlier stages of combustion. However, carbon was released faster than nitrogen during this stage. Additionally, during char oxidation, NO and CO_2 have showed similar evolution profiles. The information obtained in this investigation can be used for the study of reaction mechanisms of coal combustion under high temperature oxidizer and low oxygen concentration.

SESSION 49
Coal Science: General – 9

An Integrated Process of Coal Pyrolysis with Methane Steam Reforming for Improving Tar Yield

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In this work, a new process to integrate coal pyrolysis with steam reforming of methane (SRM) (CP-SRM) was put forward for improving tar yield and quality. The effects of pyrolysis temperature (550-750 ^{o}C) and pyrolysis atmosphere (H_2, N_2, SRM) on tar yield and tar composition were investigated with a Chinese lignite and industrial catalyst (Ni/Al_2O_3). The results show that the tar yield in integrated process, obviously higher than that in H_2 or N_2 pyrolysis at the same temperature, increases with the pyrolysis temperature to 650 ^{o}C and then decreases. Below 650 ^{o}C, low conversion of methane on the catalyst leads to weak effect on the tar yield; but too high temperature also leads to lower tar and char yield because of coal gasification taking place. The tar yield in the integrated process at 650 ^{o}C is about 1.57 times and 1.44 times as those in N_2 and H_2 pyrolysis, respectively. To better understand the integrated process, tars from lignite pyrolysis under N_2, H_2, CH_4, H_2O and integrated process at 650 ^{o}C were investigated by simulated distillation, GC and GC-MS to compare the quality of tar and analyze the changes of tar composition. Tar is divided into six parts according to the temperature: light oil (below 170 ^{o}C), phenol oil (170-210 ^{o}C), naphthalene oil (210-230 ^{o}C), wash oil (230-300 ^{o}C), anthracene oil (300-360 ^{o}C) and asphaltene (>360 ^{o}C). The results show that the tar from integrated process has the highest phenol oil and naphthalene oil yield; the tar under CH_4 atmosphere has the highest light oil yield with the least tar yield, and the highest asphaltene yield is from the tar under N_2. By GC and GC-MS analysis, about 134 organics can be identified and the major products of all kind of tar are phenol, naphthalene and their alkyl-substituted homologs from C1 to C4. Phenols content in the tar from the integrated process is 4.53% and 8.78% higher than that from N_2 and H_2 pyrolysis, respectively. Lower phenol in the tar from H_2 pyrolysis than that from N_2 pyrolysis implies the possible reaction between hydrogen free radicals and phenolic hydroxyl to produce water. However, high content of C1 to C3 alkyl-substituted homologs of phenol in the tar from integrated process suggests radicals such as $\cdot CH_3$, $\cdot CH_2$, $\cdot CH$, $\cdot H$ produced from SRM process contributes to the increase of phenol content. The similar phenomenon appeared in naphthalene and its alkyl-substituted homologs. The content of alkene in tar from different atmospheres have the order as $N_2>CH_4>H_2O>$CP-SRM$>H_2$, while the alkane content is in the order of CP-SRM$>CH_4>H_2>N_2>H_2O$. The change of alkene to alkane can attribute to the activated hydrogen produced during steam reforming of methane and H_2 pyrolysis. The formation of activated free radical in SRM and the integrated process with lignite pyrolysis should contribute to the increase of tar yield of CP-MSR process.

Catalytic Performance of Chars as Catalyst for Reforming Pyrolytic Tars from Shengli Lignite Pyrolysis

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This study is to examine the in situ catalytic reforming of the coal tar derived from the pyrolysis of Shengli brown coal at slow an d fast heating rates in a fluidized-bed/fixed-bed quartz reactor. The catalysts (chars) were produced from pyrolysis of brown coal with and without the subsequent activation by steam. Besides the tar yields obtained from each experiment, the chemical composit ions of tar were further analyzed using GC-MS. It was found that the yields and compositions of tars from the slow and fast heatin g rates significantly varied. In the presence of catalysts (especially the activated char), the tar production dropped while the propor tion of large aromatic ring system in tar also significantly changed. The tar yields were generally decreasing with increasing reaction temperatures from 700 to 900 ℃, but the increase in temperature changed the tar chemical compositions differently between slow and fast heating rates.

Studies on Physical and Chemical Properties of Liquid Products in the Extraction of Coals with Supercritical Carbon Dioxide/NMP Mixed Solvent

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A novel coal conversion process was proposed: the method combined the high efficiency of extraction of coals with CS_2/ NMP and the high diffusibility, separation and environmental friendliness of supercritical carbon dioxide ($SCCO_2$) extraction. Coal samples of 10 g were exhaustively extracted with $SCCO_2$/NMP mixed solvent (1:1 by volume) in a high-pressure vessel made of stainless steel with internal volume of 1 liter and inner diameter of 87.8 mm. Physical and chemical properties of the liquid products in the extraction of coals with $SCCO_2$/NMP mixed solvent were studied in this paper. The analysis of the low molecular weight compounds in the liquid products by GC-MS shows that the main types of the low molecular weight compounds in the liquid products are aromatic compounds and alkanes. Increases in temperature and pressure enhance types and alkanes' ratio in low rank coal's extract. Pressure plays less important role in the types of bituminous coals' extract. But enhancement in temperature increases the ratio of alkanes. Functional group and crystallite size of extracts was analyzed. Result shows that mixed solvent have strong selectivity for hydroxy rich matter and oxygen-containing substance such as grease, phenols, and ketones. With the addition of $SCCO_2$, the extraction of hydroxy rich matter is enhanced while the aliphatic matter in extracts decreases. Crystallite structure in extracts is found similar with raw coals, but their graphitization degrees are lower.

Effects of Pyrolysis Conditions on Swelling and Sphericity Properties of Chinese Coals

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For the development of dense phase transport gasification technology, Three Chinese coals: Lignite (YN), sub-bituminous (SD) and bituminous (NM) coals were pyrolyzed in a pressurized drop-tube furnace under 1273K with pressures from 0.1 to 2.0 MPa. A digital image particle analyzer was used to obtain both swelling ratio and sphericity simultaneously. The effects of coal rank, particle size, temperature, pressure and drying pretreatment on char morphology were studied. The particle sphericity was increased after pyrolysis, because of the softening. With the increase of coal rank, the swelling ratio and sphericity were both increased. SD sub-bituminous and NM bituminous swelled obviously, and YN lignite underwent an obvious shrinkage. Finer coal particles resulted in higher swelling and roundness for all three coals. With the pressure increased the swelling ratio of NM and SD coals were increased first then decreased with the summit at about 1.0 MPa. The swelling of coal particles with diameter more than 160 μm lead to rupture and finer particles were formed. But with the increase of pyrolysis pressure, the fragmentation was reduced. With the increase of pyrolysis temperature, the swelling ratios of NM coal were decreased.

The effect of moisture in coal was also investigated, the swelling ratios of dried NM coal were higher than the coal with moisture, and the ratio increased with a higher pyrolysis temperature, which is also contrary to the untreated raw coals. Drying treatment before pyrolysis could change the heating rates of coal particles in the PDTF, so the morphology of chars were significantly influenced.

Catalyst Development for Rate Enhanced Acid Gas (CO_2) Scrubbing

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The removal of carbon dioxide from gas streams is a commercially well-known process dating back to the 1930's. This process plays a vital role in the economics of enhanced oil recovery, enhanced gas recovery, natural gas acid gas capture, and post-combustion carbon capture (PCC) alike. PCC contains the largest potential market share of ~ $6 billion where the most common methods utilized for carbon capture and sequestration (CCS) are amine based absorbents in aqueous solvents. This process uses ~ 25% of the power generated which correlates to an 85% increase in the levelized cost of electricity compared to a non-CO_2 capture case. UK-CAER is developing a catalyst capable of reducing these large energy demands through enhanced rates of carbon capture. This catalyst technology is applicable to all the industries described above and would provide a competitive advantage in their respective markets.

A family of catalyst has been developed that are water, air, and thermally stable as well as soluble under conditions conducive to carbon capture. This new family of catalyst show significant improvement in mass transfer over un-catalyzed solutions. For example, a rate enhancement of > 30% is observed in 30 wt% MEA solutions. Further experiments have shown the broad applicability of the developed solvents in various CO_2 capture solvents. This allows for the utilization of solvents and/or solvent blends that will reduce operational cost downstream without having a prohibitive capital cost.

SESSION 50
Sustainability and Environment: General – 4

Effect of O_2 Content during Calcination of $V_2O_5-WO_3/TiO_2$ Catalyst on Selective Catalytic Reduction Activity of NO by NH_3

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Vanadium-titanium based catalyst has been widely used for abatement of NOx from flue gas, i.e. selective catalytic reduction (SCR) of NOx by NH3. Although this catalyst has been produced on a large-scale, fundamental research on calcination atmosphere is very little in the literature. Since calcination atmosphere, especially O2 content, may influence nature of the active components and thus the activity, this work presents a systematic study in this aspect with the aids of activity test, XPS, FTIR and NH3-TPO and NH3-TPD. The catalysts in this work are termed according to the O2 content during calcination, such as 47O or 10O. Results indicate that a higher O2 content during calcination has a positive effect on the SCR activity but little effect on the mechanical strength. O2 content during calcination does not influence the form of tungsten, which is WO3 in all the catalysts. Vanadium in all the catalysts is in two forms, V5+ and V4+. V5+ content in the fresh catalyst increases with an increase in O2 concentration during calcination but that in the used catalyst is reverse, indicating transformation of V5+ to V4+ for 47O catalyst and transformation of V4+ to V5+ for 0O catalyst. A higher O2 content during calcination yields a catalyst of a stronger acidity and stable NH3 adsorption. Excessive oxidation of NH3 is also inhibited with increasing O2 content during calcination. These two aspects may account for the higher SCR activity of 47O.

Characterization of Sulfation Behavior of Indian Limestones for Sulfur Capture

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Sulfur dioxide capture from coal combustion is becoming a requirement in India to meet the emission regulations. Circulating Fluidized bed combustors (CFBC) have received considerable attention from utilities worldwide because of their ability to capture SO_2 limestones. Limestone attrition in the circulating fluidized bed combustor has been of significant interest primarily because of its influence on sorbent performance.

In the current study, five limestone samples from various parts of India that are currently being used in power plants were characterized for sulfur capture. These limestones were marked, Sorbent A, Sorbent B, Sorbent C, Sorbent D, and Sorbent E, for confidentiality reasons. They were characterized based on their porosity and pore size distribution, surface area, chemical composition analysis, petrographic characteristics, and SO_2 capture performance in a Thermogravimetric Analyzer (TGA). The calcium carbonate content of these limestones varied between 70 and 95 wt. %. Three size fractions, -20 to +25 (-850μm to +710μm), -80 to +100 (-180μm to +150μm) and -200 to +270 (-70μm to +53μm) US mesh, were used to determine the sulfation behavior in a TGA. Some limestones were found to be more sensitive towards sulfation on reduction of particle size compared to others. For example, the -20 to +25 mesh sample of Sorbent C required 17.7 g of stone per g of sulfur captured whereas the -200 to +270 mesh sample required only 5.7 g of stone per g of sulfur captured. On the other hand, the -20 to +25 mesh sample of Sorbent D required 7.6 g of stone per g of sulfur captured while the -200 to +270 mesh sample required 6.3 g per g of sulfur captured.

Hot stage microscopy data clearly revealed that Sorbent D, the most particle size insensitive limestone, developed a network of Thermally Induced Fractures (TIFs) that provided easier access to internal surface area compared to the rest of the limestones that did not develop TIFs. BET surface area of the raw limestone did not correlate well with the stone requirement of the limestones studied. Regardless of the calcium carbonate content, limestones that developed TIFs were found to have higher calcium utilization efficiency and were also observed to be insensitive to the particle size during sulfation. Thus smaller particle size was not a requirement to maximize sulfur capture.

SESSION 51
Gasification: General – 9

Downdraft Steam-Plasma Gasification of Coal: 1D Kinetic Model and Results

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The description is presented for 1D kinetic model designed to estimate the reduction zone volume of a downdraft gasifier. The equilibrium approach in gas-phase is used to determine the maximum value of temperature in a gasifier and initial conditions for modeling. Two main heterogeneous reactions of H2O and CO2 with fixed carbon are considered. The diffusion mass transfer limits rate of these reactions and penetration of gaseous reactants trough pores. The model validation for low temperatures is performed using experimental data along with homogeneous and random pore models. The calculation results are also presented for gas composition, temperature, fixed carbon conversion in the reactor reduction zone for steam-plasma gasification of coal. Several calculations were conducted varying the following parameters: oxidant flow rate, energy content of plasma and size of coal particles. The gas-phase composition at the end of the reduction zone and equilibrium composition of gasification products were compared.

Preliminary Characteristic of Coal Gasification by-product from Pilot Plants Based on Fluidized Bed Reactors

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Coal gasification technology in reactors with circulating fluidized bed is being developed as an alternative to gasification in entrained flow reactors. To the advantages of fluidized bed reactors can be include lower capital and operating costs as well as reliability, at a relatively low temperature of the process. Research and development in this field, are conducted also in Poland, in the framework of the project "Development of coal gasification technology for highly effective production of fuels and energy", which is funded by the National Research and Development Centre. Researches are based, inter alia, on two pilot plants built and / or upgraded by the Institute for Chemical Processing of Coal in Zabrze, Poland, and the Technical University of Czestochowa.

In the first period of the pilot plants work, a few kinds of hard coal and lignite gasification by-products were produced, and the initial diagnosis of their properties is the subject of this paper. Two groups of materials have been the subject of analysis. The first one contains inter alia fly ash and bottom ash of granulation similar to fly and bottom ash produced in fluidized bed boilers. In the second installation by-product in the form of char is produced. It can not be considered as waste because of the significant content of unburned carbon. One of the possible directions of utilization is a thermal treatment such as combustion, in result which real waste could be produced.

The conducted study included identification of the basic properties of the gasification by-products, including grain composition, chemical composition, leachability of chemical contaminants, as well as studies of the microstructure using SEM.

Common Active Sites Assumption of Coal Char Gasification in the Mixture of H_2O and CO_2

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The mechanisms of char gasification in the mixture of H_2O and CO_2 are not clear and some problems are yet to be solved. Langmuir-Hinshelwood (L-H) model of char gasification in the mixture of H_2O and CO_2 is one of these problems. Two controversial mechanisms have been presented by many researchers: common active sites assumption or separate active sites assumption. In this paper, experiments were carried out at atmospheric pressure using a modified thermogravimetric analyzer (TGA) system at various reactant partial pressures and within a temperature range of 1173 K-1273 K. The kinetic parameters of L-H model were determined from pure H_2O and CO_2 gasification (N_2 as diluent). In order to validate the two controversial mechanisms, the char gasification experiments in the mixture of H_2O and CO_2 are conducted, and the experimental data are compared with the predictions of the two controversial L-H models. It was found that the L-H model based on common active sites assumption can fit the experimental data very well, which means that the common active sites mechanisms are applicable.

Study on Solutions to Resistance to Slagging of the Easy Slagging Wangjiata Type Coal

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Agglomeration in fluidized bed gasification system is considered as a primary operational problem.Wangjiata type coal with lower content of silicon, aluminum and higher content of calcium, iron in ash, was easy to slagging. And additional alkali catalyst could react with coal minerals to generate low temperature eutectic in certain process condition and reaction atmosphere, which lowered the ash fusion point of coal to cause slagging in furnace, and affected the continuous and stable operation of reactor. The sintering characteristics of coal ash are studied as one of methods for judging slagging behavior. In view of the easy slagging characteristics of Wangjiata type coal at low temperature, The purpose of this study was primarily to investigate the effect of coal blending, demineralization, and additives adding, for example alumina, silica, kaolin, diatomite, clay and calcium oxide, etc., to sintering characteristics, with the view to understand their effect on the ash slagging characteristics. Combined with XRD, SEM-EDX analysis to research mineral change features in the coal ash, and the mechanism of inhabitation slagging tendency was obtained. FactSage simulation was used to analyse equilibrium conditions for reactions occurring between different mineral components, as well as provide insight into mineral transformation and slag formation. A series of experiments and analyses results showed, adding materials rich in aluminium and blending different coals were testified as one of the efficient methods to solving the slagging. However, gasification activity of coal was reduced, carbon conversion and the catalyst recovery were lowered by adding materials rich in alumina to coals. According to this, coal blending was one of the efficient and economical methods to solving the slagging. Using coal blending to obtain lower iron, calcium content, and higher silicon, aluminum content of to inhibit the slagging tendency of Wangjiata type at a lower level. The phase diagram calculated with thermodynamic program FactSage could be used for type selection and optimization of coal blending, and for prediction of coal blending effect, thus to guide coal preparation, coal blending.

Sulfide Capturing Techniques for Advanced Fuel Conversion Process by Silica-Supported Sorbents

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Since industrial revolution, carbon dioxide (CO_2) concentration in the atmosphere has risen from 280ppm to 400ppm recently. International Energy Agency (IEA) warns the entire world that more and more serious greenhouse effects will lead to unavoidable crisis in our ecosystems, if people don't take effective measures to reduce air pollutant emissions. Some clean coal schemes have been proposed by IEA, which include developing renewable energy, improving energy efficiency in existing power plants, and executing carbon capture and storage (CCS). Energy Technology Perspective 2010 (ETP 2010) reported that if the reduction of half amount of greenhouse gas is expected before 2050, CCS technology should contribute up to 20% of all the carbon abatement scenarios. Institute of Nuclear Energy Research (INER) has involved in R&D on clean coal technologies since 2005, which include coal/biomass gasification, hot/warm gas clean-up, and CO_2 capturing techniques. Among hot/warm gas clean-up techniques, it is divided into particulate filtration and sulfur removal. In this paper, sulfur removal at medium-high temperature with simulated syngas environment will be discussed. Compared to traditional scrubbing methods, the advantages of increasing operational temperature in clean-up process are improving energy efficiency and reducing pollutant emission. In our study, silica-supported sorbents, which are composed of Zn, Cu, Mn or Fe metal oxide, are synthesized by incipient wetness impregnation method. The precursor solution was poured on silica supporters, dried and calcinated accordingly. The physical properties of sorbents were analyzed by X-ray diffractometer (XRD) and inductively coupled plasma atomic emission spectrometry (ICP-AES). XRD patterns showed that there was specific crystalline phase for every kind of sorbent, for example, _-Fe2O3 phase for iron-based sorbents. ICP-AES results indicated that the composition of metal oxide was close to the theoretical value, in other words, 20 wt%. For sulfur-capturing tests, sorbents were introduced into specific simulated syngas environment in a fixed-bed reactor. The analysis showed that zinc-based sorbents exhibited the best performance, in which breakthrough time was about 39 minutes, and sulfur capacity was 6.86 g-S/100g sorbent. For parametric discussion, it was found that sulfur capacity kept the same while space velocity was controlled between 8000-12000 mL/g.hr. For space velocity reaching 20000 mL/g.hr, the breakthrough time declined to 11 minutes, and sulfur capacity was 4.83 g-S/100g sorbent. For chemical stability evaluation, zinc-based sorbents were experienced for 10 cycles of desulfurization-regeneration reaction. It showed that sulfur-removal capability dropped to 60% of the initial performance at the final cycle. It will be promising to apply this kind of sorbents to advanced fuel conversion processes, and in order to achieve this objective, more related tests will be conducted continuously in the future.

SESSION 52
Clean Coal and Gas to Fuels: General – 9

Experiments Study on Coal Tar Pyrolysis in Thermal Plasma

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The pyrolysis of coal tar in thermal plasma provides a direct and cleaner route for producing acetylene with low hazardous emission, since the ultra-high temperatures and concentrated active species in thermal plasma can easily decompose solid/liquid/gas feedstock into smaller molecules. Experiments were carried out in a lab-scale plasma test platform to investigate the effects of key operating conditions including the plasma atmosphere, coal tar feeding method, and coal tar specific enthalpy on the performance of coal tar pyrolysis. The results demonstrated that coal tar can be rapidly cracked to acetylene, methane, carbon monoxide, and other light gases in the thermal plasma reactor. The higher specific input power of coal tar leads to higher coal tar conversion and acetylene yield. The increased hydrogen concentration in plasma working gas enhances the coal tar conversion, and correspondingly raises the yields of acetylene. More than 70% coal tar conversions and 25% acetylene yields can be obtained in the experiments. In addition, the mixing efficiency of coal tar and plasma jet is the key to guarantee the coal tar conversion and yield of light gases, which also has direct influence on the coking phenomenon during the reactions.

The Effect of Coal Pyrolysis Temperature on the Gas Evolution

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Compared with coal pyrolysis in inert gas atmosphere, the coal pyrolysis in reductive gas atmosphere could enhance the quantity and quality of tar, but the structure information of tar evolving from varied hydrogen atmosphere was little known. the effect of hydrogen added in atmosphere on the characteristics of tar composition was investigated in fluidized bed, The coal was fed to the fluidized-bed reactor through a screw feeder continuously, GC and GC-MS were employed to analyze the tar obtained under different conditions, the results demonstrated the distribution of tarry component was sensitive to the reactive atmosphere and temperature, especially to hydrogen concentration in atmosphere, the main components of tar (distillate below 300℃)were light aromatic hydrocarbons such as PCX, BTX, naphthalene. 1H NMR and 13C NMR analysis of tar represented that tar originated from hydrogen coal pyrolysis was mainly composed of substitutes attached aromatic rings. The yield of gas components increased monotonously with the temperature arising. The maximum tar yield was in the temperature range of 550-600℃. The mechanism analysis of coal pyrolysis in hydrogen atmosphere indicated that the increase in low hydrocarbon component of tar was probably attributed to the free radical reaction between the radicals of hydrogen and coal.

The Catalytic Effect of CaO and Fe_2O_3 on Reducing PAHs Release During Coal Pyrolysis

Chun Zhang, Guanglong Li, Lunjing Yan, Changlong Liu, Fan Li, Taiyuan University of Technology, CHINA

In order to reduce the emission of the 16 PAHs which are on the Environmental Protection Agency (EPA) Priority Controlled Pollutant List from coal pyrolysis, the catalytic cracking method of PAHs in the pyrolysis products is proposed to control their to the environment pollution. In this study, the PY(Pyro-probe CDS5250)-GC-MS is used to investigate the catalytic effect of CaO and Fe_2O_3 on the 16 PAHs from Pingshuo coal pyrolysis under different catalytic temperature and catalyst particle size. The results demonstrate that catalytic cracking effect of Fe_2O_3 on the16 PAHs is better than that of CaO but their catalytic temperature corresponding to the maximum PAHs cracking rate are different. The PAHs cracking rate is up to 60.59% for Fe_2O_3 at 600^{o}C and is 52.88% at 700^{o}C for CaO. The catalytic temperature and particle size of the catalysts have significant effect on PAHs cracking rate and CaO will lose the capability of decreasing 16 PAHs when the temperature is higher than 900^{o}C. The possible cracking process of 16 PAHs is proposed by elaborate analyzing the cracking effect of the two catalysts on 16 different species PAHs and comparing the composition difference of the pyrolysis products before and after the catalytic cracking. Moreover, it is deduced that the catalytic cracking of 16 PAHs by Fe_2O_3 can promote the forming of phenols.

CO_2 Reforming of CH_4 over Ni Catalyst Prepared from MgAl Layered Double Hydrotalcite by Two-Steps Method

Haoquan Hu, Mingguang Song, Lijun Jin, Chan Dong, Dalian University of Technology, CHINA

Hydrotalcite-type material as the Ni catalyst precursor has aroused more and more attention because high dispersion of metal species and stable particles on the surface may be obtained.

In this paper, Ni catalyst for CO_2 reforming of CH_4 was prepared from MgAl layered double hydroxides (LDHs) by two-steps. After LDHs were first synthesized through rapid precipitation combined with microwave assisted hydrothermal crystallization, the obtained sol was mixed with nickel nitrate solution for substitution of Mg^{2+} with Ni^{2+} under stirring. The prepared Ni catalysts were characterized by XRD, ICP, SEM, CO_2-TPD and used as the catalysts for CO_2 reforming of methane. The results showed that the LDHs synthesized by microwave assisted hydrothermal crystallization have well-formed crystallites with larger and similarly narrow range of diameters. The characterizations by ICP, XRD, SEM-Energy dispersive X-ray spectrometer indicated that the outside Mg^{2+} in the hydrotalcite-like structure is partially replaced by Ni^{2+} through ion-exchanging. The derived Ni catalysts exhibit well-dispersed nickel phases upon reduction and high and comparative stable activity for CO_2 reforming of CH_4 compared with the co-precipitation catalyst. When the Ni based catalyst was further doped with Ce or La, the basicity get strengthened, and the catalyst showed a better resistance to carbon deposition with little decrease of activity.

Sulfur Removal and Release Behaviors of Sulfur-Containing Model Compounds during Pyrolysis Under Inert Atmosphere

Fenrong Liu, Lili Xie, Mei Xue, Ruisheng Hu, Huiqing Guo, Inner Mongolia University; Haoquan Hu, Dalian University of Technology, CHINA

In this study, sulfur containing model compounds, tetradecyl mercaptan, dibutyl sulfide, phenylsulfide, 2-methyl thiophene, benzothiophene and dibenzothiophene, were selected to investigate their sulfur removal and release behaviors during pyrolysis under inert atmosphere by thermo-gravimetric analyzer with mass spectrometer (TG-MS) and pyrolysis connected with gas chromatogram (Py-GC). It is found that the order of sulfur removal is tetradecyl mercaptan > dibutyl sulfide > 2-methyl thiophene > benzo thiophene > phenylsulfide > dibenzothiophene. Except for phenylsulfide, this rule is contrary to the decomposition temperature order of the sulfur functional groups. SO_2 evolution was detected by MS and GC for all those model compounds; COS evolution was also detected except for phenylsulfide and dibenzothiophene; While H_2S evolution was measured only for tetradecyl mercaptan, dibutyl sulfide and 2-methyl thiophene. However SO_2 content is much higher than H_2S and COS in pyrolysis gas for each model compound, this may be caused by that indigenous hydrogen is much less than indigenous oxygen under inert atmosphere, when active carbon used to carrier. Thus most of sulfur radicals can connect with indigenous oxygen and release in the form of SO_2. For phenyl sulfide, benzothiophene and dibenzothiophene, as their indigenous hydrogen is not enough to react with sulfur radicals, therefore no H_2S was measured during pyrolysis under inert atmosphere, while SO_2 was measured and its content is very high in pyrolysis gas.

SESSION 53
Gasification: General – 11

Synergies in Co-Gasification with Mixtures of H_2O and CO_2

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The purpose of this study was to determine the gasification reactivity of a coal char under mixtures of steam and CO_2 and to determine whether there is any synergistic effect when mixtures of CO_2 and steam are used for gasification. The coal was first pyrolized under Ar at 4 different temperatures (800-1100^{o}C in 100^{o}C increments). These 4 different chars were then gasified at their devolatilization conditions under 5 different environments spanning from pure CO_2 to pure H_2O in 20 vol-% increments. Repeated experimental data from 20 TGA experiments suggested that the conversion rate within 800^{o}C was faster for mixtures of CO_2 and H_2O than either of the two pure gases, adding CO_2 alongside steam leads to enhanced char reactivity which is superior to the sum of the individual reactivity obtained respectively with H_2O and CO_2. This result was dependent on the pyrolysis temperatures, at the other temperatures, H_2O gasification proceeded the most rapidly, and decreased as the volume fraction of CO_2 increased. Plots linearity simulated by Shrinking un-reacted core model after 800^{o}C are much better than that before 800^{o}C, the gasification mechanism before and after 800^{o}C are different. Synergies were not observed in case of demineralized coal gasification with CO_2/H_2O mixture at 750^{o}C and 800^{o}C, which means the synergy has an obvious dependency on mineral matter. The catalytic effect of AAEM was the critical factor that leads to the synergy.

Computational Fluid Dynamics Simulation of Coal Gasification in a Circulating Fluidized Bed Gasifier

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Gasification is an attractive technology for clean and efficient utilization of solid fuels such as coal and biomass to produce synthesis gas, which can be used in the Integrated Gasification Combined Cycles (IGCC) to produce electricity with much higher efficiency than traditional power generation technologies, or used as petrochemical materials to synthesize other fuels and chemicals. Computational fluid dynamics has become an attractive approach to understanding the gasification processes, and providing detailed information for the design, analysis, and optimization of gasifiers. In this study, a numerical model based on the Eulerian-Eulerian multiphase framework was developed to simulate the coal gasification in a circulating fluidized bed gasifier. The gas phase was modeled with k-ε turbulence model and the solid phases were modeled with kinetic theory of granular flow. Coal drying, pyrolysis, char gasification, and gas phase reactions were included, and the overall gasification rate was determined by combining rates of chemical kinetics, diffusion in heterogeneous reactions or turbulent mixing in homogeneous reactions. The model was employed to predict gasification process of a circulating fluidized bed coal gasifier, and profiles of gas and solid volume fractions, velocities, temperatures, and gas composition were obtained. Comparisons between computational and experimental data showed good agreement in terms of the calculated exit gas composition. Furthermore, the influence of air/coal and steam/coal ratios on the gasification process was studied, and the simulation results were compared with experimental data. It reveals that the numerical model of multiphase reactive flow is applicable to simulate the coal gasification in circulating fluidized beds, thus it facilitates our understanding of coal gasification processes.

Mineral Matter Behavior during Co-Gasification of Coal and Biomass

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With ongoing development of gasification technologies, mineral matter related issues in gasification process have caused growing attention. The paper mainly focuses on inorganic matter transitions, ash melting behavior, and also slag corrosion of refractory materials under gasification-like conditions. These are associated with numerous parameters, e.g. temperature, pressure, atmosphere, blending ratio of coal and biomass, ash content of feedstock, and others.

Temperature treatment experiments under oxidizing conditions with subsequent XRD and HT-XRD (high-temperature XRD) analyses under reducing and oxidizing conditions at temperatures of up to 1100 °C have been carried out. The findings have been compared with results of thermo-chemical calculations by FactSage™. TOM-AC (Thermo Optical Measurement with Atmosphere Control) experiments have been used to investigate the slag infiltration under reducing atmosphere with a maximum temperature of 1600 ℃. Infiltrated ceramics were analyzed by SEM-EDX to reveal the extent of slag infiltration and corrosion mechanisms.

Even at top temperature (1600 °C), some unmelted phases (mainly CaO, MgO) were calculated. In TOM-AC it was found that the pure coal ash only formed local melts and thus did not infiltrate into the refractory. Also blended ash with low biomass addition ratio (9:1) did not infiltrate refractory ceramics to a great extent (partly due to higher viscosity). In contrast, blended ash of Rhenisch lignite (HKN) and wheat straw (WS) with a mixing ratio of 1:1 totally infiltrated into the ceramic already at 1400 ℃. Additionally, strong volatilization occurred around 1600 ℃. The high SiO_2 content in WS and high CaO content in HKN lead to substantial formation of calcium silicates in the blended ash. These are known to melt at comparably low temperatures. Pure WS ash formed a flat droplet on the refractory surface, yet infiltrated only little into the ceramic body. Also here, this might partially be due to its high viscosity.

Syngas Combustion in Ash Layer Remained on Coal Surface during Gasification

Xi Lin, Zhenyu Liu, Qingya Liu, Beijing University of Chemical Technology, CHINA

Gasification of coal of large sizes, such as those in fixed-bed or underground coal gasification (UCG) proceeds generally in the presence of an ash layer remained on the coal surface. It is well recognized that the ash layer constitutes a mass transfer barrier that reduces diffusion rate of gases, such as O_2 from the bulk gas phase to the coal surface and syngas from the coal surface to the bulk gas phase. In principle it is possible that some of the O_2 diffused in the ash layer reacts with syngas (combustion) before it reaches the coal surface for gasification. This combustion may generate hot spots in the ash layer that leads to local ash melting and results in more resistance for mass transfer of gases. This behavior would be more serious for UCG where rejection of ash from the coal surface is difficult to be controlled. This combustion behavior, however, has not been understood clearly. The aim of this work is to study significance of the ash layer on combustion of syngas.

The experiments were conducted in a tube reactor using a cylindrical coal sample that was sealed in an corundum mould with only one end exposing to the gas phase to allow one-dimensional gasification. A gas stream with a low O_2 concentration (1% O_2 in N_2) was used to better monitoring the gasification process. The gas products were analyzed online by a gas chromatography and the ash at different depth was analyzed by SEM and XRD to indentify sign of hot spots.

It is found that the CO concentration is initially high but decreases to zero over time, indicating an increase in syngas combustion with an increase in ash layer thickness. For gasification at a nominal temperature of 1300 ^{o}C local ash melting is observed by SEM for a coal sample with an ash deformation temperature of 1460 ^{o}C, indicating also syngas combustion in the ash layer. The observation of Ca_2SiO_4 in ash close to the coal surface and the absence of Ca_2SiO_4 in ash away from the coal surface further supports the presence of hot spots in ash, because Ca_2SiO_4 was reported to disappear at temperatures higher than 1400 ^{o}C. Detailed procedure and more discussion will be given in the presentation.

Sintering Characteristics of Fly Ash from Lignite Gasification in Fluidized Bed

Xin Yang, Jiejie Huang, Huibin Fang, Yitian Fang, Yang Wang, Junguo Li, Chinese Academy of Sciences, CHINA

In order to effectively re-gasify the fly ashes from fluidized bed gasifier, an integrated coal gasification system—fluidized bed combined with entrained flow was proposed. Therefore, sintering properties of fly ashes need to be elucidated to provide guidelines for stable operations in the new gasifier. Under temperatures approaching the deformation temperature (DT), the sintering properties of fly ashes were tested by manual disintegration and classification method. Then the quantitative deduction of minerals in the fly ash was analyzed by Rietveld based XRD analysis in order to understand their sintering behavior. Results show that significant changes in the disintegration strength and shrinkage level were observed when the temperature was approaching DT, due to the formation of molten phases. A large amount of fluxing crystalline (gehlenite, pyrrhotite, troilite, and Fe alumnosilicate) was transformed, which was in agreement with the test of pilot-scale pressured fluidized bed-entrained bed integrated gasification in which the lignite fly ash is quite sensitive to the variation of operation temperature approaching the DT. The contents of glass phase first decreased and then increased, which indicated that sintering behaviors of fly ash were mainly controlled by crystallization of amorphous phases at first, following by the transformation of crystalline, and then by the formation and fusion of low melting point eutectic matrix with temperature elevating.

The Effect of Cooling Rates on Crystallization Characteristics of Coal Slag

Xuan Weiwei, Zhang Jiansheng, Tsinghua University, CHINA

It is acknowledged that the occurrence of crystallization in molten slag in liquid drain out gasifier can have an impact on the viscosity, which is critical for the good operation of gasifier. In this study, the crystallization characteristics of coal slag in continuous cooling period were investigated by Differential Scanning Calorimetry (DSC).Two kinds of ashes with different chemical composition were prepared in a muffle furnace according to the Chinese national standard. After heated above their flow temperature and melting for 10 minutes, the samples were cooled down at different cooling rates and the resultants morphology were observed by Scanning Electron Microscope (SEM).Through the combination of the TGA and DSC curves, the crystallization peaks of coal slag were identified. It indicates that both the components of sample and the cooling rate can influence the crystallization temperature and phases. A continuous cooling transformation diagram(CCT) of each ash was constructed from which the critical cooling rate can be determined. Two methods, Kissinger and Friedman were used to calculate the activation energy of crystallization and both can reflect the reactivity.

SESSION 54
Combustion: Oxy-Combustion & Chemical Looping - 2

Devolatilization of US and Chinese Coals Under Oxy-Combustion Conditions

Xiaohong Huang, Zhao-Hui Liu, Chu-Guang Zheng, Huazhong University of Science and Technology, CHINA; Shengteng Hu, Babcock & Wilcox Research Center, USA

Under China and the United States (U.S.) Clean Energy Research Center (CERC) collaboration initiative aimed to accelerate the development of clean energy technologies, Huazhong University of Science and Technology (HUST) and Babcock & Wilcox (B&W) Power Generation Group, Inc. are jointly investigating the fundamental burnout process of coals from both countries under oxy-coal combustion conditions. Oxy-coal combustion is a viable technology for carbon dioxide (CO_2) emissions control from coal-fired power plants. In the oxy-fuel combustion, the mixture of pure O_2 and recycle flue gas is used as oxidizer instead of air to generate CO_2 concentrated product gas. Devolatilization characteristics of coals under oxy-coal combustion conditions can affect the ignition behavior, coal burnout, pollutant emissions.

In this paper, we will report newly devolatilizaiton experimental results from coals of various ranks under simulated oxy- and air-combustion conditions. The tests are conducted on a flat flame assisted entrained flow reactor. The reactor used a modified McKenna flat-flame burner to provide high-temperature burnt gas, which rapidly heated the injected coal particles and acted as the coal oxidation medium. The particle heating rate was 10^5~10^6 K/s, and the H_2O content were kept at 16%, which all simulate those in the industry furnace. N_2 and CO_2 diluent gases are used for the simulation of air- and oxy-combustion conditions, respectively. Char samples are collected at different residence times through an oil-cooled sampling probe and a cyclone. Their apparent volatile yields are determined by the ash tracer technique.

Rank-dependent high temperature volatile factors ($Q=VM*/VM$) for oxy- and air-combustion conditions are derived from the experimental results. The CPD model is modified to simulate the devolatilization process of coals under oxy-coal combustion condition. The effects of physical properties of CO_2 and CO_2-char gasification on devolatilization process were considered. Sensitivity analyses are conducted to evaluate action mechanism of high concentration CO_2 on devolatilization process.

Char Burnout of U.S. and Chinese Coals Under Oxy-Combustion Conditions

Shengteng Hu, Babcock & Wilcox Research Center; Alan N. Sayre, Babcock & Wilcox Power Generation Group, Inc., USA; Xiaohong Huang, Zhao-Hui Liu, Huazhong University of Science and Technology, CHINA

Under the United States (U.S.) and China Clean Energy Research Center (CERC) collaboration initiative aimed to accelerate the development of clean energy technologies, Babcock & Wilcox (B&W) Power Generation Group, Inc. and Huazhong University of Science and Technology (HUST) are jointly investigating the fundamental reaction kinetics of coals from both countries under oxy-coal combustion conditions. Oxy-coal combustion is a viable technology for carbon dioxide (CO_2) emissions control from coal-fired power plants. It produces a concentrated CO_2 stream by way of burning coal with oxygen instead of air. Since combustion of fuel with pure oxygen results in very high flame temperatures, flue gas recycling is applied to control the temperature and provide adequate gas flow over the heat absorption surfaces.

In this paper, we will report newly acquired char burnout experimental results from coals of various ranks under simulated oxy- and air-firing conditions. The tests are conducted on a flat flame assisted entrained flow reactor facility. The facility is capable of simulating staged combustion by supplying different gas mixtures to its inner primary oxidant zone and outer secondary oxidant zone of the McKenna flat-flame burner mounted on top of an electrically heated furnace. N_2 and CO_2 diluent gases are used for the simulation of air- and oxy-firing conditions, respectively. Char samples at different residence times are collected from the reaction zone and their extents of burnout are determined by the ash tracer technique.

Rank-dependent kinetic rate parameters for both the oxidation and gasification reactions are derived from the experimental results. The optimization program, PGSL, is used to obtain the optimized reaction rate parameters by way of seeking the minimum value of the error function (error between predicted and measured results) while adjusting the corresponding rate parameters systematically. Sensitivity analyses of the optimized parameters are conducted to evaluate the quality of the optimization results.

We will also include all of the previous test data in this paper for completeness. The combined data set covers the typical ranks of coal in both China and the U.S.

Redox Kinetics of Oxygen Carriers for Chemical Looping

Marek Sciazko, Ewelina Ksepko, Institute for Chemical Processing of Coal, POLAND

This paper contains results of research work on chemical looping combustion (CLC). The CLC is found to be one of most promising combustion technologies, of which main advantage is based on production of concentrated CO_2 stream, that is obtained after water condensation without any energy penalty for CO_2 separation. The objective of this work was to study kinetics of both reduction and oxidation reactions for Fe_2O_3-CuO/Al_2O_3 and Fe_2O_3/TiO_2 oxygen carriers. Based on our previous CLC research results, the most promising oxygen carriers were selected for the analysis. Tests have been performed at isothermal conditions (600-950 ^{0}C) in multiply redox cycles using thermo-gravimetric analyzer (Netzsch STA 409 PG Luxx). For reduction 3% of H_2 in Ar, and for oxidation cycle air was used. Energy of activation and the pre-exponential factor was determined, also reaction model was selected.

Acknowledgement: This research was financed by the Polish Ministry of Higher Education and Science within frame of State Subsidy Project No. 11.13.003.005.

Effects of Steam on Coal Pyrolysis and Char Combustion in the Presence of CO_2

Dunxi Yu, Wenyu Sun, Minghou Xu, Huazhong University of Science and Technology, CHINA

In oxy-fuel combustion with wet flue gas recycle, the presence of steam is expected to impact both coal pyrolysis and char combustion. However, little work has been done to address such issues. The present work selects two typical Chinese utility coals with a narrow size distribution. Coal pyrolysis and char combustion experiments in the presence of steam are carried out on a well-designed thermogravimetric reactor. Weigh loss with time is recorded online. The effects of steam on coal pyrolysis and char combustion are investigated. Mathematical modeling is made to help interpret the obtained data. The data show that steam affects coal pyrolysis at the later stage, and char combustion is significantly enhanced in the presence of steam. Increasing steam concentration is observed to promote both coal pyrolysis and char combustion. Carbon gasification with steam seems to play an important role, which is evidenced by modeling work. The results presented provide new insights into the role of steam in oxy-coal combustion.

Experimental and Modelling Investigation of the Pilot-Scale Oxy-Fuel Combustion of Victorian Brown Coal

Lian Zhang, Jian Zhang, Xiaojiang Wu, Monash University, AUSTRALIA; Jianwen Zhang, Shanghai Boiler Works Co Ltd, CHINA; Yoshihiko Ninomiya, Chubu University, JAPAN

Victorian brown coal is the single largest source contributing to the power generation in Victoria, Australia. Due to the presence of abundant moisture, *i.e.* up to 70 wt%, Victorian brown coal exhibits a greenhouse gas emission rate as high as ~1300 kg-CO_2/MWh-electricity sent out in the existing air-fired power plant, relative to ~900 kg-CO_2/MWh for the Australian black coal. Oxy-fuel combustion is a cost-effective option to deliver a CO_2-rich gas stream that is ready for direct CO_2 sequestration, when compared with the post-combustion capture, *e.g.* amine absorption for CO_2 recovery. As the youngest lignite in the world, Victorian brown coal is supposed to possess a variety of distinct characteristics during the oxy-fuel combustion, which are to varying extents linked with the abundant moisture within the coal matrix. On the one hand, the abundant moisture is believed to enhance coal volatile ignition delay, due to the required evaporation of it at the initial heating step for coal particles. On the other hand, once being evaporated, the steam possesses a larger specific heat capacity than nitrogen and oxygen. Its presence in the furnace thus promotes the radiative heat transfer from coal flame to flue gas, and consequently to the water in the heat exchange tubes. The use of recirculated flue gas (RFG) in place of air could further complicate these two issues, considering that CO_2 also has a large specific heat capacity that is comparable to steam, whilst the adjustable oxygen concentration in the furnace is in favor of shortening the ignition time of coal particle, either dry or wet. In light of this, it is of great interest for us to investigate the oxy-fuel combustion of Victorian brown coal particularly on a pilot scale.

Oxy-fuel combustion of Victorian brown coal is being carried out in a 3MW pilot-scale boiler to clarify its distinct combustion characteristics. The residual moisture in brown coal plays a critical role on the ignition delay and expansion of the flame length as well, which subsequently affects flame stability, heat-transfer in furnace and even the stability of the feeding of the pulverized coal. Through a preliminary test in the pilot-scale plant, a variety of essential data for the combustion of Victorian brown coal under the oxy-fuel mode have been obtained, which are useful for the future design and optimisation of an industrial-scale oxy-fuel system and burner for Victorian brown coal. Apart from experimental investigation, the computational fluid dynamic (CFD) modeling have also carried out to confirm the remarkable influence of moisture on the combustion of this distinct low-rank coal in both air and oxy-fuel mode. As has been confirmed, 3MW pilot-scale oxyfuel combustion of Victorian brown coal has been successfully, leading to the production of 80% CO_2 at the 5% air ingress in the system. The moisture in brown coal plays a crucial role on coal ignition delay and the flame stability. Upon the pilot-scale tests, the valuable data for the oxy-fuel plant and burner design for Victorian brown coal are being gained, including coal oxidation rate, heat flux and distribution in the furnace, pollutant emission, and its ash fouling and slagging propensities.

Flameless Pressurized Oxy-Coal: The Top of Power Cost Competition for CCS, and the Best Cost Option Along the Transition to Near-Zero Emission

Massimo P. Malavasi, SVP R&D, ITEA Spa; Giancarlo Benelli, Nicola Rossi, Danila Cumbo, Alessio Bardi, ENEL Ingegneria e Ricerca, ITALY

The availability of a cost competitive CCS technology is mandatory to coal fired power industry, to avoid the crowding of power production around a single source/single technology, NG and turbogas combined cycle. ITEA-ENEL conceived flameless pressurized Oxy-combustion for coal since 2006, and have been developing process and technology engineering, to fully exploit technology potential. FPOC distinguish itself for several capabilities, favourably impacting cost profile, like “flexible fuel” extended to low ranking coals, “velox” with constant control logic from standby (5-7%) to full load, on top of the highest efficiency (35%) among CCS technologies and the best overall emission profile (ashes transformed into vitrified slags). ITEA-ENEL 350 MWe power plant engineering study is concluded. Economics, based on commercial figures, are now available and represented. The study teaches FPOC is highly innovative, and it calls for solution from OEM designed around the new technology. Numerous improvement looks at hand, further launching FPOC at the top of the competition. The case of FPOC solutions, along the transition to near zero emission situation, is here examined; and relevant economics are presented.

POSTER SESSION 1
GASIFICATION

Characteristics of Solid Materials Sampled at Several Points during Operation of the 3T/d Entrained Coal Gasifier

Bongjin Jung, Nayeon Lee, Chan Lee, The University of Suwon; Yongseung Yoon, Institute for Advanced Engineering; Daesung Kim, Korea Westernpower Co., KOREA

To meet the strict environmental regulations and maintain higher efficiency, IGCC(Integrated Gasification Combined Cycle) technology can be considered as the alternative to conventional pulverized coal power plant. In Korea IGCC research works have been mainly carried out by IAE(Institute for Advanced Engineering) and KEPRI(Korea Electric Power Research Institute) et al. since 1992. The Korea Westernpower Company is now constructing the 300 MW-sized IGCC plant using coal at Taean which is located in the southwestern region of Korea by 2015. As one part of the R&D program for the development of IGCC process, in this study, gasification test of Indonesia Kideco subbituminous coal was carried out under the operating conditions of 8 bar and 1450 ^oC in the 3T/d bench scale entrained coal gasifier operating by IAE. So this paper mainly described some characteristics of solid materials sampled at several points of gasification system to get engineering informations for developing technologies of coal gasifier. Basic physical and chemical properties of the Kideco coal and ash samples were analyzed. This coal has high volatile matter and low ash contents in the proximate analysis. And sulfur content is very low compared to other coals generally used in power plants. Melting of this coal ash measured by heating microscope was started from about 1,000^{o}C and it was completely melted around 1320^{o}C with increasing temperature. Also some characteristics (that is, carbon content, XRD analysis, component analysis, shape and cross section analysis by SEM/EDX, heavy metal components in slag and extracted water from slag etc.) of slag discharged from bottom section of the bench scale coal gasifier were investigated. In addition ultimate analyses and particle size distribution of solid materials sampled from several points of gasifier system were carried out to investigate the thermal behavior of solid samples formed during the operation of gasifier.

ACKNOWLEDGMENT
This work was supported by the Development of 300MW class Korean IGCC demonstration plant technology of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy. (*No. 2011951010001C*)

Comparison of Ash Fusibility Behavior in Thermal System using Coal and Solid Waste Fuels

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Free flow of molten solid fuel ashes from taphole is especially important in the successful operation of coals and solid wastes utilization equipments, such as the slagging gasifier, the cyclone combustor, the direct melting furnace of solid waste, the incineration ash melting furnace etc.. Melting behavior of their ash materials can be characterized mainly by fusion temperature and viscosity of sample to evaluate the suitability of easy tapping of molten solid ashes in the above devices. Measurement of ash fusion temperature is described by several temperatures relating to stages of deformation of cone or cylindrical-shaped ash samples on heating using analytical euipment. This test is generally based on the use of shrinkage levels for an ash sample during heating. Viscosity of any molten ash through melting temperature range is also useful for characterization of melting behavior of sample. In this study two kinds of coal ashes and three kinds of solid waste incineration ashes were chosen for measuring fusion temperature and viscosity of ash samples. Using heating microscope for determination of ash fusion temperature, melting temperature range of sample can be easily measured, but determination of very easy slag tapping temperature corrsponding the 8 Ns/m^2(80 poise) in the viscosity test is still uncertain without further other informations. In the case of viscosity test of ash sample, it is one of the good guidelines for determination of slag tapping temperature, but experimental work is very hard and time-consuming job. So continuous study for getting good correlation between viscosity and heating microscope tests are needed

Acknowledgement: This work was supported by the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (*No.20123010100010*)

The Effect of Flux on Ash Fusibility of High-Calcium Shanxin Coal

Jie Xu, Guangsuo Yu, Feng Zhao, Xia Liu, Qinghua Guo, Fuchen Wang, East China University of Science and Technology, CHINA

The primary aim of this study is to understand the effect of flux on the fusibility of high-calcium Shanxin coal ash. The different oxides, Al_2O_3, TiO_2, Na_2O, K_2O, MgO and SiO_2, are separately added into high-calcium Shanxin coal ash to prepare the coal samples. Experiments are conducted to inspect the effect of different oxides on ash fusion temperature (AFT) variation. The FactSage 6.2 software is used to predict the proportion of solid phase and the mineral phase formed as a function of the composition and temperature. The changes of AFT caused by the addition of flux have been studied by mechanism analysis. The results show that the AFTs of coal samples decrease with the increase of Al_2O_3, TiO_2, Na_2O, K_2O and SiO_2 and then increases. However the AFT always increases with MgO in the whole content range. And SiO_2 is the most effective in lower the AFT. The binary and ternary phase diagrams are plotted by FactSage, illustrating optimum value of adding flux and the AFT variations. The simulation results of FactSage 6.2 software are consistent with the AFT experimental values, which indicates that the software is reliable and effective in the application of AFT prediction.

Comparison of Fouling and Sintering Characteristics of Coal Ash with Several Fouling Factors at Reduction Environment

Hueon Namkung, Dong-ha Jang, Tae-Jin Kang, Dong-Ju Kim, Hyung-Taek Kim, Ajou University, SOUTH KOREA

One of the major operating problems in the gasification and combustion systems is the ash deposition phenomenon. The deposition of ash typically reduces the heat transfer rate in the heat exchange part and hence the performance or efficiency. Ash fouling can cause as much as a 60% decrease of the heat transfer when operated over long times. The ash deposition phenomenon is related with mineral components of coal. In general, alkaline earth and alkali minerals influence on the growth of ash particle size. When alkaline earth and alkali minerals exist with acid minerals, they decline the melting temperature of inherent melting temperature of minerals. Finally, they make the ash particles sintered together. The sintering characteristic is generally verified by measuring the changes in the physical dimension of sample through dilatometer analysis. The dilatometer analysis is generally a very accurate method for measuring the shrinkage and sintering temperature. Measuring temperature of ash samples in dilatometer was from atmosphere condition to 1000 ^{o}C, because low temperature ash fouling occurred below 1000^{o}C. The temperature of dilatometer including ash samples, whose heating rate was set with 5 ^{o}C /min, steadily increased with Ar gas purge. Nine ash samples were analyzed by dilatometer. Their sintering characteristics were different and showed some relationship. Many of coal ash samples had sintering temperature and shrinkage. However, some of coal ash samples did not have the sintering temperature and shrinkage. The coal ash samples, which do not possess the sintering temperature and shrinkage, include a little ratio of Fe, Mg and Ca components. Sintering temperature decreases with increasing Fe, Mg and Ca ratio. And shrinkage of coal ash samples increases with increasing Fe, Mg and Ca ratio. When the ash particles sinter, activation energy for agglomeration increases with shrinkage. Several known factors of the fouling phenomenon were evaluated to compare to the effect of ash deposition tendency.

Kinetic Model of Coal-Char Gasification with Steam at Elevated Pressure

Qixuan Yan, Jiejie Huang, Yitian Fang, Jiantao Zhao, Chinese Academy of Sciences, CHINA

The kinetics of three different ranks of typical Chinese coal chars gasification with steam was investigated at higher pressure (up to 2.0 MPa) in a pressurized fixed bed differential (PFBD) reactor. The results show that the global nth-order rate equation including the only item of steam partial pressure is not appropriate for the gasification in which the total system pressure changes. Thus, in this work, a modified nth-order rate equation was proposed, to be applied for three types of coal-chars including the independent variables (T, y_{H2O}, P_{total}). It is indicated that the effect of steam molar fraction gasification rate is greater than that of the total system pressure. For the three types of coal-chars, the correlation exponent with respect to steam molar fraction decreases with the increase of carbon conversion; however, the carbon conversion has little influence on the correlation exponent with respect to the total system pressure. In addition, as the coal rank increases, the correlation exponent with respect to steam molar fraction and the correlation exponent with the total system pressure increase slightly.

Mild Pyrolysis Behavior and Kinetics Study of Low Rank Coal

Lijuan Gao, Xianglong Zhao, Zhuowu Men, Yi Guo, Ke Liu, NICE, CHINA

As coal is a complex mixture of organic macromolecules and inorganic materials, the properties such as coal metamorphism, petrology, etc., play an important role in coal devolatilization. The literatures usually studied pyrolysis as the initial phase in coal conversion processes, so they conducted pyrolysis test at high temperature or at rapid heating rate in order to evaluate the kinetic data and to establish reliable models for the complex reaction scheme. For Low Rank Coal (LRC) upgrading, the LRC is pyrolyzed under mild conditions to obtain pyro-oil and high-BTU upgraded coal which can be transported easily and used for gasification or other process. The research on coal pyrolysis at mild conditions is still limited in literatures.

Pyrolysis experiments have been carried out in a thermogravimetric analyzer coupled with FTIR system obtain transient pyrolysis conversion data; the primary gas species (CO, CO_2, CH_4, and H_2O) from coal mild pyrolysis are analyzed quantitatively. The gas compositions were different at different temperatures; so different species should have distinct kinetics. A mathematical model for devolatilization of coal particle, involving coal properties, and by coupling of intrinsic kinetics of coal pyrolysis with internal and external heat transfer has been developed; the comparison between model calculations and experimental data shows that the model can predict the pyrolysis of coal particle well.

Co-Gasification of Coal-Biomass Blended Char with CO_2 at Temperatures of 900-1100˚C

Hyo Jae Jeong, Sang Shin Park, Jungho Hwang, Yonsei University, KOREA

Co-gasified biomass and coal can be considered a potential fuel base for gasification and offers the advantage of a reduction in CO_2 emissions. In addition, use of biomass could contribute to a reduction in fossil fuel dependency. In this study, a mixture of coal and biomass was placed in a lab-scale tube furnace and co-pyrolyzed to be transformed to a char under nitrogen atmosphere. Three mass ratios of coal and biomass, 4:1, 1:1, and 1:4, were tested, and then each char was co-gasified with CO_2 after the furnace was isothermally maintained. Three isothermal conditions of 900, 1000, and 1100 °C were tested. In every test the carbon conversion ratio was calculated from the CO concentration measured at the exit of the furnace. The reactivity of char was improved with an increasing amount of biomass owing to the catalytic effect of the alkaline minerals included in the biomass. In addition, reactive synergy was observed with the biomass blended char and increased with the amount of biomass utilized. The volume reaction model (VRM), shrinking core model (SCM), and random pore model (RPM) were used to interpret the carbon conversion data. The overall fitting extent of the RPM was slightly better than that of the VRM and SCM, thus the RPM was adopted to derive reaction rate constants. For each coal-biomass ratio in the mixture, the activation energy and pre-exponential factor were determined using the Arrhenius equation.

A Numerical Study on Coal-Biomass Co-Gasification According to Steam/Fuel Ratio

Jung-Hoon Lee, Hyo Jae Jeong, Sang Shin Park, Jungho Hwang, Yonsei University, KOREA

Co-gasified biomass and coal can be considered a potential fuel base for gasification and offers the advantage of a reduction in CO_2 emissions. In addition, use of biomass could contribute to a reduction in fossil fuel dependency. In this study, a mixture of woody biomass and coal was gasified with air and steam to discuss the molar ratio of H_2, CH_4, CO and CO_2 in the product gas. In addition, the effect of the mixtures with varying ratio of steam/fuel in a wide range on co-gasification behavior was investigated taking into account the gasification behavior of each feedstock.

A comprehensive three-dimensional simulation model was developed for co-gasifiers. The co-gasifier was numerically modeled by simultaneously solving the rate equations for chemical reactions of the solid and gas phases for coal and biomass. Three-dimensional computational fluid dynamics (CFD) modeling on gasification performance in an one-stage entrained bed coal and biomass co-gasifier was performed for parametric studies with various steam/fuel ratios (0.008, 0.016, 0.025, 0.033, 0.042, 0.05, 0.058, 0.066, 0.075) using a commercial code, ANSYS FLUENT 14. The CFD modeling was conducted by solving steady-state Navier–Stokes equations with the Eulerian–Lagrangian method. Chemical reactions were solved via the Finite-Rate/Eddy-Dissipation Model for gas phase. Optimal conditions of steam/fuel ratio for this study gasifier using design coal and biomass were obtained as 0.058. Carbon conversion efficiencies, cold gas efficiencies, exit temperature and species mole fractions were also calculated by CFD modeling.

Co-Gasification of Petcoke with Coal at High Temperatures

Liwei Ren, Jianli Yang, Chinese Academy of Sciences; Feng Gao, Taiyuan University of Technology, CHINA

Petcoke, as a byproduct of petroleum refinery process, can be used as feedstock for gasification due to its high carbon content and high calorific value. However, its low gasification reactivity and low ash content may restrict its application to some gasifiers. In this work, co-gasification reactivity of petcoke and coal under CO_2 atmosphere were investigated in a drop-in-fixed-bed reactor in temperature range of 1200-1400 ^oC. Produced CO was monitored continually using an online mass spectrometry to calculate the dynamic gasification rate. The characteristics of coals and petcokes were analyzed by scanning electron microscopy and X-ray diffraction. It is found that the petcoke has a much lower reactivity than that of coals, especially the low rank coals. The complete gasification time of petcoke is 10 times more than that of low rank coal at 1200 ^oC. The low reactivity of petcoke is related to the low mineral content, compact carbon structure and high degree of graphitization. Fortunately, the reactivity of petcoke can be improved by co-gasification with coals or by loading their ashes in the temperature range of 1200-1400 ^oC. The Fe_2O_3 and CaO can improve the reactivity of petcoke significantly at temperature of 1400 ^oC. The synergistic effect during co-gasification of petcoke and coal is closely related to the composition of mineral matter in coal. The high content of active components such as Ca and Fe in coal or ash is beneficial for co-gasification. Some coals, however, are lack of these active components (which limit the catalytic effect) and with high Si and Al content (which may retard the gasification reaction).

The Brin Process for Separation of Oxygen from Air

Evan Granite, Elliot Roth, Michael Hajduk, Karen Uffalussy, DOE/NETL, USA

The separation of oxygen from air has been studied and practiced with different degrees of success since the late 19th century for various industrial applications. Recent concerns with greenhouse gas emissions has inspired ideas of using oxygen instead of air to burn fossil fuels, specifically coal, for generation of electricity. By using oxygen instead of air, the exit flue gas stream would be nearly ready for sequestration or enhanced oil recovery with very little clean up or separation processes. In addition, coal gasification processes use large quantities of oxygen, and would benefit from cheaper methods of oxygen manufacture. Today the commercial method to produce large amounts of oxygen is by cryogenic separation, but this process is thought to be too expensive for economical use in coal-fired power plants. Chemical separation of oxygen from air may be an attractive alternative to cryogenic separation. The Brin Process uses barium oxide (BaO) to react with oxygen in air, and was the first commercial process to separate oxygen from air. This process was used for approximately twenty years before cryogenic separation was introduced.

The Brin Process employs the reversible reaction between a barium oxide sorbent and oxygen gas (from air) to form barium peroxide. Either a temperature or pressure swing can be used for reversing the reaction (regenerating the barium oxide sorbent for reuse). The reaction was first discovered by the French chemists Joseph-Louis Gay-Lussac and Louis-Jacques Thénard in 1811. A drive for a better understanding in chemical processes for oxygen separation has inspired other researchers to reinvestigate the Brin Process. This poster/paper reviews the Brin Process and the recent research into improving the technique.

The Co-Pyrolysis of Sawdust and Bituminous Coal Using Thermogravimetric Analysis (TGA) and Concentration Measurements of the Evolved Species

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A sample consisting of woody biomass and bituminous coal was pyrolyzed in a lab-scale furnace with a nitrogen atmosphere until the furnace wall temperature reached 900°C at 10°C/min. Five blending ratios(BRs) of biomass-coal were tested. For each BR, the mass loss of the sample and mole fractions of the gaseous species evolved from the sample were measured using a thermogravimetric analyzer (TGA) and a real time gas analyzer (GA), respectively. In order to evaluate the synergistic effect of the co-pyrolysis of the biomass-coal blend on product yield, the cold gas efficiency (CGE) obtained from experimental data was compared with that obtained using an additive model. The TGA results revealed the action of a synergistic effect at temperatures between 450 and 500°C, compared to between 450 and 600°C with the GA method, for all pyrolyzed gases, and especially between 350 and 650°C for H2. The maximum CGE was 0.37 at the BR of 0.75, while the maximum ratio between the experimental CGE and the calculated CGE was 1.52 at the BR of 0.25. In addition, kinetics analysis of co-pyrolysis was conducted and it was found that the activation energies of BRs at the temperature of 390 to 450°C can be predictable using the additive method.

Overview of Oxygen Generator Materials

Evan Granite, Elliot Roth, Michael Hajduk, Karen Uffalussy, DOE/NETL, USA

Chemical oxygen generators or “oxygen candles” have been used to generate oxygen in places where a compact oxygen generator is needed or other means of generating oxygen is impractical. Typical applications for chemical oxygen generators are emergency oxygen systems in airplanes, submarines, space craft and mine rescue equipment. These generators usually consist of an alkali metal chlorate or perchlorate, a small amount of metal oxide as a catalyst, and a metal as a fuel. Sodium and potassium chlorates are examples of typical alkali earth metal chlorates used in oxygen generators. The reaction reduces the metal chlorate to a metal chloride, and is initiated by raising the temperature above a critical point. The oxygen generator reaction is usually exothermic and self-sustaining giving off a steady flow of oxygen. The decomposition temperature of these chlorates varies depending on the catalyst used such as cobalt oxide or manganese oxide.

The production of oxygen is very important to a vast amount of industrial and chemical processes. Recently burning of fossil fuels in oxygen instead of air has been suggested as a way to produce an exit flue stream that is mostly CO_2, which could be sequestered or captured easily to reduce CO_2 emissions. Although oxygen generators do not generate oxygen by the separation of air, the study of these materials and mechanisms could provide useful insights into chemical separation of air for combustion of fossil fuels or other commercial uses.

Biomimetic Separation of Oxygen from Air

Evan Granite, Elliot Roth, Michael Hajduk, Karen Uffalussy, DOE/NETL, USA

Biomimicry is the process of imitating models and systems found in nature to solve complex human problems like the separation of oxygen from air. Through respiration and oxygen carriers in the blood, animals are easily able to separate oxygen from air and release it to different parts of the body. Oxygen carriers found in nature have been evolving for over a billion years. Iron and copper are the reactive centers for these oxygen carriers, which can be significantly different even within the same organism.

Hemoglobin (Hb) is an oxygen carrier found in red blood cells of mammals and other animals. The primary function of hemoglobin is to bind with oxygen that is diffused into the bloodstream from the lungs, transport it and release it to tissues throughout the body. Myoglobin is similar to hemoglobin and is abundant in muscle. Myoglobin is found in large quantities in diving animals, and its function has been attributed to O_2 storage. The study of hemoglobin has been an ongoing area of research for many years in the medical field for the development of artificial blood to reduce the need for blood transfusions. Hemoglobin has also been studied for oxygen-selective membranes to produce oxygen-enriched air, and as an oxygen transporter in artificial gills.

In this poster the structure, mechanisms, and characteristics of hemoglobin and myoglobin in the uptake, transport, and release of oxygen will be examined. Current research in artificial blood and artificial gills will also be studied. By studying different oxygen separation systems found in nature, we may be able to mimic these processes to produce a novel air separation material for oxygen separation, or improve current industrial air separation processes. This study may provide useful insight for a more economical separation of oxygen from air, which would be useful for economical oxyfuel combustion of coal.

Magnetic Separation of Oxygen from Air

Evan Granite, Elliot Roth, Michael Hajduk, Karen Uffalussy, DOE/NETL, USA

The most widely used method for the production of pure oxygen today is the Cryogenic process. Cryogenic separation takes advantage of the fact that oxygen condenses at 77K, but nitrogen and other components of air remain gaseous, allowing them to be separated. Cryogenic plants are capable of producing oxygen of the highest purity, but the distillation process requires so much energy that it needs to be carried out on a very large scale to be economical. As a result, new methods for the production of pure oxygen or oxygen enriched air are being investigated. One novel

technique is the use of a magnetic field gradient to change the trajectories of oxygen and nitrogen in a flowing air stream.
High-gradient magnetic separation (HGMS) is possible because oxygen is paramagnetic and nitrogen is diamagnetic; molecular oxygen has a magnetic susceptibility that is both several orders of magnitude higher than that of molecular nitrogen and in the opposite direction. A magnetizing force produced by a magnetic field gradient can therefore attract oxygen molecules but not nitrogen. This poster/paper examines this phenomenon and how it is being utilized in novel oxygen separation processes.

Simulation of High Ash Content Coal Gasification on Circulating Fluidized Bed to Produce Fuel Gas for Ceramic Kilns

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The Brazilian Coal Association (BCA) and the U.S. Department of Energy's National Energy Technology Laboratory (NETL) signed a Memorandum of Understanding (MOU) that reflects a mutual interest of the parts to pursue collaborative work to advance the technical, environmental, and cost performance of fossil energy technologies including gasification. The Brazilian coal is a specific coal that has high, non-cleanable ash content. One of the possible applications for this fuel is produce fuel gas through the circulating fluidized bed (CFB) technology. To verify the behavior of Brazilian coal in a gasification system at atmospheric pressure, 2D simulations were performed with different conditions where air has been used as oxidizing agent. The tests were done using a Brazilian bituminous coal seam called "Bonito", which is situated at Criciúma, Santa Catarina state and focus on fuel gas product to be used in ceramic kilns on this region. The Two-Fluid Method was used to describe governing equations. Temperature, air flow rates, steam and feeding position were the main parameters varied in this study. The software C3M was used to provide the reaction constants through the C3M's default kinetics. The results from C3M were incorporated in a Computational Fluid Dynamics (CFD) code the Multiphase Flow with Interphase Exchanges (MFIX), developed at NETL. In this work the CFD simulation utilized the default models in MFIX, namely the Syamlal-O'Brien correlation for the gas -solid drag force. The model takes accounts nine gas species, which are O_2, CO, CO_2, CH_4, H_2, H_2O, N_2, Tar and soot, and four pseudo-species of solids, that are Fixed Carbon, Volatile Matter, Moisture and Ash. The results indicated that the gasification process using a CFB technology can be very useful to produce fuel gas from Brazilian coal and showed values of high heating value near the minimum standard for those kilns which shows optimization is needed. In addition 3D simulations were performed to help on verification of 2D simulation and scaling up.

Reactivity of Brazilian Coals in CO_2 Atmosphere

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Coal gasification has emerged as a clean and effective way for the production of gas which can be used for power or heat generation or as a synthesis precursor. The main characteristic of Brazilian coal is the high ash content and one of the possible applications is produce fuel gas through the gasification. A good way to verify this possibility is understand the coal and char reactivity that can be used to indicate which coals are more appropriated for this process beyond to improve the gasifier design and efficiency. Reactivity experiments of four Brazilian seams coal and their respective chars were carried out in a TGA at atmospheric pressure where nitrogen was used to perform the coal pyrolysis step and CO_2 to verify the coal-chars reactivity. The effect of coal particle size (0.075mm, 0.10mm, 0.25mm) and temperature (850, 950 and 1050ºC) were investigated and the experiment results were used to generate the curves of reactivity and conversion versus time. Beyond that the activation energy and pre-exponential coefficient were determined using Arrhenius equation for the five coal-chars. These data are important to indicate which sample needs lower energy to promote the gasification process considering the Boudouard reaction. The results indicated a high influence of the temperature in the reactivity and conversion of the chars for the different coal samples. The same wasn't verified to particle size where the curves presented similar behavior in the range tested. The results showed a high reactivity of the Brazilian coal and point out the gasification as a useful process to fuel gas production and to heat generation.

Cold Flow Test of Coal Pyrolysis with a Solid Heat Carrier

Shuxian Liu, Xianglong Zhao, Zhuowu Men, Li Weng, Ke Liu, NICE; Minshu Zhan, Guogang Sun, China University of Petroleum-Beijing, CHINA

A cold model experimental apparatus was set up to study the mixing and flow behaviors of lignite and a solid heat carrier in a novel coal pyrolysis process. Lump coal and 3 mm heat carriers were mixed, and the effects on mixing homogeneity by conical type and baffle plate mixing internals and heat carrier-to-coal mass flow ratios as well as the mixture flow pattern were investigated. The experimental results showed that a cross-sectional mixing homogeneity of 85% was achieved with two or more sets of conical mixing internals. A similar homogeneity was achieved with the baffle plate mixing internals. The homogeneity improved with increasing the ceramic ball to coal mass flow ratio. A continuous, steady and homogeneous solid mixture flow was finally achieved with the combination of conical structures and angle bars.

Gasification Reactivities of Chars Derived from Different Lignites

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The purpose of this work is to investigate the gasification reactivities of chars derived from three lignites (XD, ZD and YX lignites). Interest is focused on their differences with different lignites. Gasification experiment was carried out in a tubular fixed-bed reactor using steam as a reactant gas. It was found that the reactivities of three lignites behaved quite differently, and XD lignite gasified very fast at a low temperature of 750 °C, whereas YX lignite did slowly. Mineral components present in lignite played an important role in the char gasification. X-ray Absorption Near Edge Structure (XANE) analysis confirmed that XD lignite was enriched with carboxylic calcium. The influences of mineral components on the char gasification were investigated by leaching different mineral components. It was observed that the organically associated alkali and alkaline earth metals (AAEMs), particularly calcium, had a strong catalytic activity for char gasification; the existence of water-soluble chlorine in ZD coal somewhat lowered the char reactivity; the clay minerals also only slightly influenced the char reactivity.

POSTER SESSION 2
COMBUSTION

Status and Evaluation of the Various Methods of Renewable Fuel Co-Firing in Korean Pulverized Coal Power Plants

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In Korea, recently, co-firing of renewable fuel becomes more and more important for securing fuel flexibility and RECs (Renewable energy certificate) in pulverized coal firing boilers. There are several methods for co-firing and each method has different applicable co-firing ratios, capital costs and effects to CO_2 reduction. In this study, Four methods of the co-firing were considered: (1) Co-firing of the solid renewable fuel using existing coal mills, (2) Co-firing of the fuel using extra mills, (3) Co-firing using extra mills and biomass burners (or a burner) and (4) Co-firing of the gas fuel produced from a gasification unit for the renewable solid fuel. We analyzed the technical (qualitatively) and economic feasibility (quantitatively) of each co-firing methods for a commercial-scale pulverized coal power plant, and preliminary results of the analysis are presented. In addition, status of co-firing renewable fuel in pulverized coal power plant in Korea and its perspective are briefly discussed.

Numerical Approaches to Retrofit of a Conventional Pulverized Coal Burner to an Oxy-Firing Burner

Taeyoung Chae, Won Yang, Korea Institute of Industrial Technology;
Changkook Ryu, Sungkyunkwan University, SOUTH KOREA

This study is aimed to provide basic information for retrofit of a conventional air firing pulverized coal burner to an oxy-firing burner which can be operated in both air and oxygen condition. Computational fluid dynamics (CFD) was utilized to determine main design conditions of the oxy-firing burner such as oxygen concentrations, dehumidification and adjustment of the flowrate and swirl in the primary and secondary oxidizer streams. A 30 MWth scale conventional burner was simulated in a virtual furnace for various air- and oxy-firing conditions, and the simulation results were analyzed and discussed in the sense of combustion stability and thermal matching for air- and oxy-firing conditions. In addition, effects of direct oxygen injection were investigated for various burner configurations such as locations of the oxygen lancing nozzles and shapes of the nozzles. Through the simulation, mixing of the oxygen and oxidizer through the swirling flows was found to be the most important parameter for optimizing positive effects of the oxygen injection to combustion stability.

A Study on NO_x Reduction Characteristics through Syngas Reburning in a Pilot Scale Pulverized Coal Combustion System

Seuk Cheun Choi, Taeyoung Chae, Jae Wook Lee, Kie Seop Kang, Won Yang, Korea Institute of Industrial Technology, SOUTH KOREA

Utilization of renewable fuels in coal-firing power generation system has been important issues related to meet RPS (renewable portfolio standard) in Korea. In addition, NOx control in a boiler becomes important for reducing maintenance cost for SCR (selective catalytic reactor) and for coping with regulations on pollutant emission. This study is aimed to investigate NOx reduction characteristics through co-firing of syngas, usually produced from a gasification system for waste and/or biomass. Single gas species (CO, H_2 and CH_4) in the syngas was co-fired in a pilot-scale (80 kWth) down-fired pulverized coal combustion system and effects of each species to the NOx reduction were investigated for various stoichiometric ratios (co-firing ratios) in the reburning zone. Various mixtures of the gas species were also co-fired in the furnace and influence of the syngas co-firing ratios to the combustion efficiency, temperature distribution and heat transfer in the furnace as well as NOx emission were measured and will be discussed in this presentation.

An Experimental Study on Slagging/Fouling Characteristics for Various Coals Using a 50kWth Pulverized Coal Combustion System

Jae Wook Lee, Kie-seop Kang, Taeyoung Chae, Ik Hwan Na, Won Yang, Energy System R&D, Korea Institute of Industrial Technology; Changkook Ryu, Sungkyunkwan University, SOUTH KOREA

In Korean coal power plants, rising coal prices have recently led to the rapid utilization of low lank coals such as sub-bituminous coal with low calorific values and low ash fusion temperatures. Using these coals beyond the design range has resulted in important issues including slagging and fouling, which cause negative effects in boiler performances and unstable operations. The purpose of this study is to observe slagging and fouling characteristics resulted from burning various ranks of pulverized coals. We have tested 3 different coals: FLAME (bituminous), KCH (sub-bituminous) and Moolarben (bituminous) coals in the pilot system of $50kW_{th}$ scale. A stainless steel tube with preheated air inside was installed in the downstream in order to simulate water wall. Collected ash on the probe and the slag inside the furnace near burner were analyzed by SEM (scanning electron microscopy) to verify the formation degree, surface features and color changes of the pasty ash particles. Induced coupled plasma and energy dispersive X-ray spectroscopy were also performed to figure out the chemical characteristics of collected samples. As a result, KCH was observed that more slag was developed inside the walls of the furnace and on the probe than the other two kinds of coals, as shown in the calculation results of slagging and fouling indices as well.

Development of a Low NO_x Combustor

Sung-Hoon Shim, Sang-Hyun Jeong, Korea Institute of Machinery and Materials; Sang-Sup Lee, Chungbuk National University, KOREA

Low nitrogen oxides (NOx) combustion is proposed to reduce NOx formation during combustion and to decrease the cost for the control of NOx emissions. The objective of this study is to find an optimized design of the low NOx combustor and operating conditions. Combustion tests were conducted varying the design of the combustor and operating conditions such as nozzle diameters, fuel and air injection velocities, excess air ratio, flow pattern, combustor configuration, etc. The combustion performance was evaluated with the temperatures measured inside the combustion chamber and the NOx and carbon monoxide (CO) concentrations in the exhaust gas stream. Based on the combustion test results, the design of an efficient low NOx combustor was suggested.

Numerical Analysis of Fouling Chracteristic on the Heavy Fuel Oil Heat Recovery Steam Generator

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The power industries have been use heat recovery steam generator (HRSG) to increase efficiency of system. Especially, using of fuel such as heavy fuel oil (HFO) and pulverized coal, cause the formation of ash particle and lead to deposition problem on the HRSG tube surface. The deposition of ash particle contributes to the disproportion of temperature on the tube surface, finally decrease overall HRSG efficiency. In this study, the characteristics of ash particle deposition and distribution under different condition in a HFO-HRSG were predicted using a low temperature fouling (LTF) model coupled with a gas-solid two phase flow model. The LTF model was developed based on the governing force like as inertial impaction, elastic rebound force, van der Waals force and gravity. The LTF model was implemented as user defined function (UDF) in the FLUENT v.14 and evaluated at the simplified HRSG geometry. Grater ash deposits occur in surfaces when the particles were smaller and slower due to the higher adhesion force. The adverse gravity effect led to deposits at the back side of the tube when the particle size was 7.5um grater. The LTF model also shows the size distribution of HFO ash particle is important factor and deposition is dominant when the particle size is under 1um.

New Method of Characterizing Intrinsic Coal Combustion Behavior with TG

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Coal combustion behavior is one of the foundations for the technical evaluation of coal combusting utilization, and it is an important reference base for the design of coal-fired boiler. Thermogravimetry (TG) is a general method to characterize coal combustion process dynamically, some important parameters or indexes (such as ignition temperature, burn-out characteristics, combustion kinetics, and so on) can be figured out according to the TG curve, this method is usually employed in academic research and standards. However, it is found in the practice that there are remarkable distinctions between the results from different TG under the same conditions for the same sample, even if with the same TG (e.g. the lignite temperature difference reaches up to 120℃). The bad repeatability of weight lose curve brings large uncertainty to the results of coal combustion behaviors, which will mislead the researcher when use TG to examine coal combustion. In this article, some impact factors such as sample quantity, heating rate, oxygen concentration, oxygen flow and sample cell material are investigated, and the dominated impact factors and the coal intrinsic combustion behaviors are clarified. At the same time, a reasonable measure method with TG is established. It not only makes the TG to be a simple, rapid and scientific mean to describe coal combustion behaviors, but also presents a reasonable result for industrial design.

POSTER SESSION 3
CLEAN COAL AND GAS TO FUELS

Catalytic Hydroprocessing of Model Compounds Simulating Coal Tar

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Low-temperature coal tar produced during coal pyrolysis can be refined to obtain clean fuel oil. This process is carried out with hydrotreating catalyst that is normally used in petroleum industry, such as NiMo/Al2O3 or CoMo/Al2O3. However, they showed poor reactivity because of the presence of high proportion nitrogen and oxygen in low-temperature coal tar. MCM-41 supported nickel phosphide (Ni2P/MCM-41), as a promising catalyst, was prepared by temperature-programmed reduction of the corresponding phosphate. The sample was characterized by the X-ray diffraction and nitrogen adsorption measurement. The reactivity of the catalyst for hydrodeoxygenation (HDO), hydrodearomatization (HDA), hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) was investigated in a fixed bed reactor. O-cresol, 1-methylnaphthalene, quinoline and dibenzothiophene (DBT) were chosen as the model compounds of low-temperature coal tar. O-cresol HDO, 1-methylnaphthalene HDA, quinoline HDN, dibenzothiophene HDS and simultaneous HDO, HDA, HDN, HDS were respectively tested at different temperatures with constant pressure (6.0 MPa), liquid hourly space velocity (3.0 h-1), hydrogen-to-oil volume ratio (600:1). The results indicated that Ni2P /MCM-41 had great performance on HDO, HDA, HDN, HDS of single model compound recations and temperature had significant influence on the conversion and product selectivity. O-cresol and DBT were almost completely transformed at the temperature of 375°C, while 1-methylnaphthalene and quinoline reached the highest conversion at 300°C. When HDO, HDA, HDN and HDS occurred simultaneously, quinoline showed higher conversion by competitive absorption on the hydrogenation sites of the catalyst, leading to the conversion decrease of o-cresol, 1-methylnaphthalene and DBT.

Cu/SO_2 Catalysts Prepared by Different Methods for Hydrogenation of Ethyl Acetate to Ethanol

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In order to get a desirable catalytic performance on ester hydrogenation reaction, silica supported copper catalysts obtained by various preparation techniques were studied focusing on preparation routes, evolution of the catalyst precursors, size of copper particles, and the catalytic behaviors in hydrogenation of Ethyl Acetate. Three preparation methods were investigated: 1) ammonia evaporation (AE) method; 2) urea hydrolysis deposition precipitation (DP) method; 3) A novel precipitation method (NM) without external precipitant. Characterization of the catalyst precursors indicates that highly dispersed copper phyllosilicates were formed in both dried and calcined samples at lower copper loading even in NM samples without NH_3 precipitant. The precipitation condition affects both the initial chemical forms and the strength of chemical bonding of copper phyllosilicate species with supported silica. Both AE and DP samples were much easier to reduce than the NM sample, giving rise to the higher conversion (> 90%) and higher selectivity toward ethanol (> 98%) in hydrogenation of Ethyl Acetate reaction.

Development of Catalyst for Manufacturing High Calorie SNG

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SNG manufactured from Coal will start to supply as city gas in Korea at 2015. The SNG generally have over 98% methane and the heat is about 9,300 kcal/m^3 . And, for domestic using, the heat of SNG shall increase to over 10,200 kcal/m^3 . Normally LPG is used to increase the heat of SNG. But LPG price is double the SNG price in the base of calorie. So the addition of LPG makes SNG expensive.

In 1980',s Professor Inui(Japanese) developed catalysts to produce high calorie SNG. These catalysts can make the SNG in the mixture of C1, C2, C3, C4 and so on. And the heat is about 11,000 kcal/m^3

In this study, in order to evaluate the possibility of developing new catalyst for high calorie SNG, the catalysts have been tested. from these result KOGAS is developing new catalysts applicable to present SNG plant.

Determination of Toluene-Insoluble Content in Coal Pyrolysis Tar and Pitch

Yinhua Long, Shuai Zhao, Xiaofen Guo, National Institute of Clean-and-Low-Carbon Energy, CHINA

Oil is one of products of coal pyrolysis, and can be upgraded to more valuable transportation fuels. Therefore, research to obtain knowledge of physiochemical properties and chemical composition of pyrolysis oil is essential for better selection of oil processing technology. Toluene insoluble (TI) is an important index for physiochemical properties evaluation of coal tar and pitch. The existing domestic and international standard methods for the determination of TI content in petroleum tar and pitch are GB/T2292-1997, ASTM D4072, ASTM D431 and JIS K2425. There are advantages and limitations for these test methods regarding sample requirements, sample size, operation procedures, test instruments and operation conditions. Long analytical time and complicated operation procedures are major barriers for batch analysis. Due to high heteroatom content in coal tar and pitch, the conventional standard test methods for petroleum products are not applicable, and new analytical methods need to be developed. In this study, a modified test method for the determination of TI content in coal tar was developed after comparison studies of different standard methods. Ultrasonic extraction and vortex mixing technique were investigated for speeding up sample dissolution, and centrifugation was employed for the separation TI from toluene solution. Extraction time, extraction temperature, centrifugation time and centrifugation speed were optimized to obtain good separation effect and shorter analytical time. TI contents in different types of coal tar samples were determined with the developed method. The obtained data were compared with those from standard test methods. And the scope of application, data accuracy and precision of the modified test method for TI content in coal tar and pitch were investigated.

Research Progress of Suspended Reactor Hydro-Cracking Technology

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With the increasing number of the inferior and heavy crude oil, and the increasing need to clean product, and increasing scale of direct coal liquefaction, coal/oil co-processing and coal tar upgrading, the technology to hydrogenate the inferior oil/coal is on focus. The suspended reactor technology is more and more researched for high adaptability to feeds, simple process, high conversion and high light oil yield. The author introduced several promising suspended reactor hydrogenation technology by the technology feature, process condition and progress. The suspended reactor hydro-cracking technology has remarkable advantage and will be developed rapidly in processing inferior oil/coal in China.

Separation of Toluene and Methylcyclohexane by Dimethyl Sulfoxide

Jie Feng, Jianshu Hao, Wenjun Fan, Meixiang Wu, Wenying Li, Cuiping Ye, Taiyuan University of Technology, CHINA

In order to obtain naphthene from coal direct liquefaction oil and then to prepare the raw material of jet fuel, it is necessary to separate aromatics and naphthenic hydrocarbons which can form azeotrope in the following processing. Toluene, methylcyclohexane were adopted as the model compounds of aromatic and naphthenic hydrocarbon to test the liquid-liquid extraction solvent which were screened from about 40 conventional solvents. It was found that dimethyl sulfoxide (DMSO) was an optimal extraction agent to make separation of toluene and methylcyclohexane system. Furthermore, the liquid-liquid equilibrium data for the ternary system among toluene, methylcyclohexane and DMSO, the solubility curves were measured and the distribution relations of toluene in the methylcyclohexane and DMSO system were obtained. Finally the separation performance of DMSO is evaluated in the coal direct liquefaction oil.

Catalytic Effects of Iron-based Catalysts on Product Distribution of Long-Flame Coal Hydropyrolysis

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Owing to the lack of sufficient hydrogen radicals to stabilize the free radical fragments, the tar secondary pyrolysis lead to low tar yield and high content of heavy components in tar. The iron-based catalysts can dissociate hydrogen to obtain hydrogen radicals, and then combine with the free radical fragments in coal pyrolysis so that to restrain tar pyrolysis again. The effects of iron-based catalysts referred to Fe_2O_3, Fe_2S_3, oil-soluble of Fe_2O_3, FeS and $FeSO_4$ on the coal products distributions were investigated.

This paper took Shendong Flame coal as the investigated object, and the experiment was conducted with the temperature of 550 ~ 700 ^{o}C and pressure of 0.1 MPa in a fixed-bed reactor, and the coal partical size was 1.18 ~ 2.00 mm. The results were as follows: 1) It could get the lowest char yield (70.2%) with the catalyst of Fe_2S_3, the highest tar yield (8.4%) with the catalyst of oil-soluble of Fe_2O_3 and the highest gas yield (15.3 %) with the catalyst of FeS compared with char yield (73.5%), tar yield (7.9%), gas yield (12.1%) without catalyst. 2) The strong decompositiom capability of the iron-based catalysts had adverse effects on the tar yields, but the n-hexane soluble contents were all incremental. Particularly, with the catalyst of Fe_2S_3, the tar yield decreased from 7.9% to 7.0%, but the n-hexane soluble contents of the tar increased from 70.6% to 81.0%. The yield of lightweight components increased about 0.1%. 3) Gel Permeation Chromatography (GPC) analysis for tar showed that there was a reduction in the weight of molecular of tar, which from a side confirmed that the iron-based catalysts had effects to make the heavy oil light.

Recycling of Tail Gas in Fischer-Tropsch Bubble Column Slurry Reactors and its Impact on the Coal-to-Liquid Process

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Oil is not an everlasting source of energy and studies in the last 50 years have shown that the world production would peak as a result of rising world energy consumption and continuous depletion of oil reserves. As the price of crude oil keep increasing, the coal to liquid (CTL) process using the Fisher-Tropsch (F-T) technology which converts coal into liquid fuel becomes a strategic alternative especially for countries such as China, Pakistan and India with huge coal reserves. At the heart of The CTL process lies the F-T reactor in which the syngas is converted into liquid hydrocarbons. In order to maximize syngas conversion it is a common practice to recycle the F-T reactor tail gas. In this research effort, a simulator based on a comprehensive computer model for F-T Slurry Bubble Column Reactor (SBCR) developed in our laboratory was used to predict the impact of tail gas recycling on the performance of a conceptual commercial-scale SBCR for syngas conversion using Fischer-Tropsch (F-T) synthesis. The simulator was also linked to ASPEN Plus to perform a complete simulation analysis on the integrated CTL process.

POSTER SESSION 4
SUSTAINABILITY AND ENVIRONMENT

Study on the Optimal Coupling Paths between Nuclear Energy and Coal-Based Synfuels Processes

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Coal-based synfuels plants are facing serious pressure on CO_2 emissions reduction. Developing the coal-based synfuels system coupled with nuclear energy is an effective approach to reduce CO_2 emissions. This work analyzes CO_2 emissions features in the coal-based synfuels system, and further investigates three coupling paths between the coal-based synfuels system and nuclear energy. Subsequently, an inherent-safety and low-carbon coal-based synfuels system coupled with nuclear energy is proposed. In the coupled system, valley nuclear power is provided to conventional water electrolyser for hydrogen/oxygen production, and oxygen and hydrogen are supplied to the coal gasification and fuel synthesis processes, respectively. The simulation results show that the coupled system can reduce about 50% raw coal consumption and almost all CO_2 emissions compared to the conventional coal-based synfuels system, meanwhile it can improve the peak shaving capacity of nuclear power plants.

Approaches to Developing Methodology for Evaluation of Energy Efficiency of Coal Chemical Processes

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Coal chemical process, or an energy-chemical industry park, is characterized as a huge system, which is consisted of various devices, processes and utilities. Energy efficiency is of great significance for coal chemical industry with the aim to realize energy saving and emission reduction, because it can deeply assess coal chemical process in the aspects of energy utilization status, potential of improvements and profitability. The methodology means the processes and procedures to achieve the goal of assessing energy efficiency. So far, a number of methods andtools for energy analysis and efficiency evaluation have been set up, including heat balance analysis, exergy analysis, thermoeconomics, pinch technology as well as emergy analysis. However, during the application of these methods or tools, some issues were encountered, including a lack of basic data, difficulty in obtaining basic data, limited scope of analysis, immaturity of software development, poor connection with simulation software and the low match degree with coal chemical systems.

In this paper, approaches to establishing an integrated energy efficiency assessment methodology for coal chemical processes were proposed, which can be concluded as followings: (1) methods to evaluating energy efficiency of single device, unit operation and heat exchanger networks are to be screened or developed. Then the coal chemical systems are disassembled into "points" (devices, units and operations), "lines" (processes) and "planes" (coal chemical industry or a chemical industry park), at the same time, energy efficiency assessment are carried out in multi-aspects of "quantity", "quality" and "profitability" (technical economy) by previously screened or developed methods. (2) A database of physical and physic-chemical parameters of mass flows in coal chemical process is to be researched and established. (3) Devices, processes and systems are to be modeled with the aid of various process simulation softwares. (4) At last, an integrated energy efficiency software platform for coal chemical process is to be established. This software platform should be able to support all of the above-mentioned software. Moreover, it should include a program that can unify units of data which are inputted and outputted the models. It should also have an algorithm, which has the function that can convert energy efficiency analysis results of several devices or processes into a unified basis.

Besides, in order to effectively use the methodology for evaluation energy efficiency of coal chemical process, the following requirements still need to be well studied. These requirements include exploring measuring means of mass flow parameters and physical constants, accurately modeling for elementary component and the entire coal chemical process, developing energy efficiency software platform for coal chemical process.

POSTER SESSION 5
CARBON MANAGEMENT

The Study on the Carbon Fixation in Berea Sandstone with Different Concentrations of Brine ($NaCl/CaCl_2$) Solution

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Many investigations for underground disposal of CO_2 from large industrial sources also demonstrated as the most effective technology to reduce greenhouse gas emissions. Brine and CO_2 relative permeability data of CO_2 are required in order to understand the characteristics of CO_2 fluid flow and displacement which injected CO2 into aquifer and storage mechanism. Many studies show only few CO_2-brine relative permeability data at aquifer condition. As a part of Otway project in Australia, KIGAM(Korea Institute of Geoscience and Mineral resource) developed a high pressure 2-phase separator to quantitatively measure fluid saturation of CO_2-brine relative permeability and introduced a closed circulation system to consider CO_2 solubility and Ajou university investigates the carbonation using industrial waste and the reaction of Berea sandstone with CO_2 and brine concentration in deep saline formation. The experiments were performed with a CO_2 geological storage reactor which is composed of four units in order to experiment in different conditions such as temperature, pressure, time, brine concentration during the experimental period. The reactor allows for continuous injection of CO_2 and brine into rock cores and withstand up to 250 bars. The core is wrapped in a core holder in order to fix the core element during the experiment. A compressor and pressure booster injects CO_2 pressurized tank, sequentially CO_2 in the tank is injected to CO_2 geological storage reactor using a HPLC pump. The reactor is connected with autographic recording system and it record temperature and pressure during the experiment. Experiments are proceeded using a Berea sandstone and reactor temperature and pressure 50℃, 150bar at three different brine concentrations (5wt%, 15wt% and 25wt). Additionally, an accelerated carbonation using ash from KPU and Russia coal has been performed to sequestrate CO2 in the form of carbonate through the supercritical carbonation reactor.

Kinetic and Cyclic Performance of the CO_2 Chemisorption on Li_4SiO_4 Doped with Alkaline(K, Al)

Xiaoxiang Chen, Yongchun Zhao, Junying Zhang, Chuguang Zheng, Huazhong University of Science & Technology, CHINA

The efficient removal and sequestration of CO_2 from hot gas streams is required in consideration of the serious environmental issues in the near future. Various kinds of solid materials have been examined as CO_2 sorbents based on physical or chemical reactions these years. Among these materials, lithium-based ceramic exhibits good chemisorption capacity and thermal stability under high temperature. Li_4SiO_4, with a closed-pack structures, is such kind of ceramic sorbents based on the reaction between lithium and CO_2. Previous works have indicated that lithium diffusion process is the main limitation for CO_2 absorption. In this work, further investigation was made by doping alkaline elements (K and Al) into Li_4SiO_4 through coprecipitation method. Both kinds of the materials were characterized by X-ray diffraction (XRD), N_2 adsorption, scanning electron microscope (SEM) and nuclear magnetic resonance (NMR). A set of CO_2 absorption experiments was conducted using a thermogravimetric analyzer for doped and pure Li_4SiO_4. The CO_2 chemisorption capacity of the K/Li-Si and Al/Li-Si samples was tested and compared with that of pure Li_4SiO_4 with similar experiments. It was determined that each materials have similar kinetic behavior, and the presence of potassium on the K/Li-Si sample promoted the kinetic reaction of the CO_2 capture while the presence of $LiAlO_2$ on the Al/Li-Si sample did not reduce the CO_2 capture. Moreover, cycle absorption-desorption performance tests were carried out in a packed-bed tube furnace under a temperature swing regeneration. The cyclic performance tests indicated that both materials exhibited a slower trend of reduction in chemisorption capacity after twenty cycles when compared with that of pure Li_4SiO_4. Furthermore, thermal stability observed on the Al/Li-Si sample can be attributed to the presence of aluminum.

Influence of SO_2 on CO_2 Adsorption on Activated Carbon

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Activated carbons (ACs) were found to be promising materials for CO2 capture from flue gas. Flue gases usually contain many compounds other than CO2, such as N2, SO2, H2O, NOX. SO2 may have a strong influence on CO2 adsorption, because it is easy to be adsorbed on AC, but has not been well studied. This work reports our recent study on adsorption of SO2 and CO2, individually or simultaneously, on two ACs made from coconut shell and anthracite to understand the influence of SO2 on CO2 adsorption. The experiments are carried out in a fixed-bed system with online mass spectroscopy at temperatures of 0 to 20 oC and pressures of 0.10 to 2.00 MPa. It is found that the ACs adsorbs SO2 more strongly than CO2, and the adsorption mechanism can all be presented by the D-R equation, $\ln V=\ln V0-(RT\ln(P0\mathrm{T}/P)/\beta)2/E02$. At the experimental conditions used, the adsorption capacity of CO2, in ml/g, is twice of that of SO2, which allows estimation of one compound's adsorption capacity based on data of the other compound.

Process Simulation and System Design of the PCC Unit for Coal Fired Power Station

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CO_2 removal from flue gases in coal-fired power plants is a key technology for the reduction of greenhouse gas emission. Recently, this technology has become of great interest due to the steady increase in the consumption of fossil fuel in world wide. Amine-based absorption process is the most well-known CO_2 capture technology, which has been commercialized in chemical industries. Regarding to post combustion CO_2 capture (PCC) for power plant, this technology is considered to be energy and capital intensive, requiring developments in absorption solvents innovation and system design optimization.

In this work, in order to improve the performance of the PCC unit using amine solvent, process simulation has been conducted on engineering software. ASPEN Plus model of a 1 million ton per year (1Mt/y) CO_2 capture unit for 660MW coal fired power station has been created by using rate-based calculation method. This model takes into account the impact of equilibrium reactions on the mass transfer, thermodynamic nonidealities, and the characters of the packing material.

Heat/material balance data can be obtained from this model for process evaluation, parametric studies on lean solvent loading, stripper pressure, L/G ratio, comparative studies are carried out to find the optimal performance of this system. Further optimization is discussed by introducing energy saving design into the simulation. This model will be modified according to the exiting PCC demonstration experiments, in order to work on more complex solvent formulations. System integration of large scale PCC unit to coal fired power plant can be developed with the results obtained.

Carbon Dioxide Carbonation of Municipal Solid Waste Incinerator Fly Ash and the Impact on Metal Mobility

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Incineration technologies are widely used to treat municipal solid waste (MSW), municipal solid waste incineration will generate a lot of solid resides and atmospheric emissions. Due to the alkalinity and the presence of leachable heavy metals, MSWI fly ash is classified as hazardous waste in China. Another, as the increase of CO_2 in atmosphere in recent years, it causes climate change and global warming. CO_2

carbonation of municipal solid waste incinerator (MSWI) fly ash could reduce greenhouse gas emissions and toxicity of the MSWI fly ash.

In this paper, CO_2 carbonation of the MSWI fly ash was studied with pure CO_2. The influence of reaction time and reaction temperature was evaluated to determine their impact on the carbonation. The fly ash sample used in this study was collected from the MSWI facility in Shanghai. Minerals changes in fly ash were investigated by means of the X-ray diffraction and the amount of CO_2 absorbed by carbonation treatment were analyzed by the thermogravimetric-differential scanning calorimeter. The leaching of heavy metals in fly ash were investigated after the CO_2 carbonation treatment. After the carbonation, $Ca(OH)_2$ in the fly ash disappeared and $CaCO_3$ formed. Treatment of carbonation reduced the pH from 11.3 to 7.5. Under the four temperature conditions (30℃, 50℃,70℃ and 90℃) test, the better CO_2 absorption occurred about at 90℃. Under the four time conditions (0.5h, 1h, 1.5h and 2h) test, the better CO_2 absorption occurred about at 2h. It suggests that increasing the reaction time and the reaction temperature can slightly increase the amount of CO_2 that absorbed by the carbonation process. The leaching toxicity of heavy metals Pb and Cr were effectively reduced after the carbonation treatment from 8426.1 μg/L to 0.38 μg/L, 284.23μg/L to 54.84μg/L, respectively. The leaching concentrations of Co, Ni Cu and As were also decreased after the carbonation treatment. Co: from 21.37 μg/L to 7.25 μg/L; Ni: 322.06 μg/L to 93.70 μg/L; Cu: 54.15 μg/L to 8.94 μg/L; As: 87.74 μg/L to 55.86 μg/L. However, the leaching toxicity of Cd in Shanghai fly ash was increased after the carbonation treatment from 0.04 μg/L to 2.81 μg/L, the reason was unknown. The experiment demonstrates that MSWI fly ash could be carbonated under a low temperature. It is of useful to decrease the leaching of heavy metals in MSWI fly ash by the CO_2 carbonation.

Simultaneous Sequestration and Extraction of Geothermal Energy using CO_2 from an IGCC Plant as a Heat Transfer Fluid for Power Generation from EGS

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Utilization of CO_2 from fossil fuel power plants is an important aspect to be considered as an alternative to sequestration in mitigating the global climate change. Geothermal energy has a potential of 100 GWe to supply base load electricity. Utilizing the heat energy from the geothermal sites for the production of electricity presents a great opportunity for the simultaneous extraction of geothermal energy and sequestration of CO_2 emitted from the fossil fuel power plants. In conventional enhanced geothermal systems (EGS), water is used as circulating fluid for mining the geothermal heat energy. In arid regions where there is an acute shortage for water, CO_2 can be used as a heat transfer fluid for the extraction of geothermal energy for power generation from organic Rankine Cycle (ORC). CO_2 captured by pre-combustion method is more suitable for heat compared to that captured by post combustion method as it is discharged at high pressure suitable for sequestration. Therefore, after considering air-blown combustion, oxy-combustion and integrated gasification combined cycle (IGCC), pairing IGCC with EGS was found to produce a symbiotic combination for the simultaneous extraction of geothermal heat energy and sequestration of CO_2. This paper models the utilization of CO_2 as a heat transfer fluid for the extraction of geothermal energy and utilizing the heat for the production of electricity from the ORC. The simulations were conducted in ASPEN Plus version 7.3. The first part focused on well simulation with CO_2 as a heat transfer fluid for extraction of geothermal heat energy to predict the temperature profile and pressure profile along the le length of the injection well and the production well. The second part focused on the modeling of organic Rankine cycle for the generation of electricity by utilizing the pressure and geothermal heat energy of CO_2.

Regeneration of CO_2 from CO_2-Rich Mea Solution by Using the Novel Concentration Swing Desorption Technology

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It is accepted that an increase of mass concentration of CO_2-rich solvent may result in the reduction of CO_2 regeneration energy consumption. However mass concentration of CO_2-lean solvent may not be increased without limitation due to the negative effects of concentration increase such as the accelerated corrosion to absorber, solvent viscosity increase and CO_2 absorption driving force losing. This may be paradox and an insuperable barrier for the conventional CO_2 capture process due to the constant mass concentration of solvents between absorption and desorption stages. Therefore, a novel regeneration concept named "concentration swing desorption (CSD)" was put forward in the study to regenerate CO_2 from CO_2-rich solvent. In this concept CO_2-rich MEA solution formed in the CO_2 absorption stage was not introduced into the desorber directly, but firstly separated into two phases called the diluted phase and concentrated phase by using the membrane water absorption technology. The diluted phase mainly consists of free water and the concentrated phase covers almost all the absorbent solute and absorbed CO_2. Then only the concentrated phase was regenerated and the generated lean-CO_2 MEA solution was successively mixed with the diluted phase to dilute back to the initial absorption concentration status, which was introduced into the absorber to remove CO_2 again. So benefits to develop CSD technology might include good CO_2 capture performance and an opportunity on reducing the regeneration energy consumption greatly. The simulation results by using Aspen Plus® software showed that as the concentration of the concentrated rich MEA solution increases, the reboiler heat duty reduces considerably. And after rich MEA solution was concentrated from 30 wt% to 60 wt%, the weight specific reboiler heat duty can be reduced from 3.94 GJ/t CO_2 to 2.43 GJ/tCO_2 by about 38.33%. In addition, determining how to concentrate CO_2-rich MEA solution is the keystone for CSD technology. In this study the membrane water absorption technology was adopted to separate water from CO_2-rich MEA solution, and the effects of some key parameters including water absorbent temperature, flow rate, mass concentration and rich MEA solution temperature, flow rate, temperature on water removal performance were investigated. Results showed that aqueous calcium chloride solution ($CaCl_2$) can be used to remove water from rich MEA solution. And when the temperature and flow rate of rich MEA solution were fixed at 70 ℃ and 5 ml/min and the saturated aqueous $CaCl_2$ solution with 60 ml/min was selected as the water absorbent, the concentration of rich MEA solution can be concentrated from 30 wt% to 40.7 wt% by using a single-stage membrane process. But when dual-stage membrane water absorption process was adopted, the concentration of rich MEA solution can be concentrated to 52.5 wt%, which implies that membrane water absorption technology is viable for concentrating rich MEA solution.

Greenhouse Gas Emission of Coal to Liquids Technologies and Reduction Potential Analysis

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Coal-replace-oil seems a feasible technical route for the oil security of China, which is promoting rapid development of coal to liquids (CTL) technologies in the latest years. The main technologies of CTLs, including direct CTL, indirect CTL, coal-methanol-to-gasoline (CMTG), and coal-tar-to-gasoline (CTTG), are now under industrial demonstration, and their commercialization prospect is promising. These CTL technologies are becoming important alternatives for traditional petroleum refining to meet the increasing demand of liquid fuels of China, but meanwhile they may lead to a large amount of greenhouse gas (GHG) emission if they are put into practice industrially. This study estimates the GHG emissions of these four technical routes based on the life cycle assessment (LCA) methodology, and compares their potential impacts on climate. The contribution of each process for GHG emission is identified and then reduction scenarios are put forward and reduction potentials are analyzed accordingly. Carbon dioxide capture and storage (CCS) is employed as an important technology for GHG reduction in this article. The GHG reduction potentials of direct CTL, indirect CTL, and CMTG technologies combined with CCS are excavated and their competitivenesses are compared with oil refining technology.

Assessing the Feasibility of using Ionic Liquids as Physical Solvents for Selective Capture of CO_2 from Fuel Gas Streams

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Three Ionic Liquids (ILs), namely hmim[Tf2N], TEGO IL K5 and TEGO IL P51P were used as physical solvents in the Aspen simulator, employing the Peng-Robinson Equation of State (P-R EOS) with Boston-Mathias (BM) alpha function and standard mixing rules, to develop a conceptual process for CO_2 capture from a shifted warm fuel gas streams produced from Pittsburgh # 8 coal for a 400 MWe power plant. The solubilities of CO_2, H_2, N_2 and H_2S in the IL's were determined at pressures up to 30 bar and temperatures from 300 to 500 K, and were used to obtain the binary interaction parameters (δ_{ij} and l_{ij}) between the shifted gas constituents and the ILs. Both δ_{ij} and l_{ij} were correlated as functions of temperature. Moreover, the density, viscosity, vapor pressure, critical properties and surface tension of the solvents were determined within the same pressure and temperature ranges.

The conceptual process developed consisted mainly of 4 adiabatic absorbers; 3 flash drums arranged in series for solvent regeneration using the pressure-swing option; and 2 pressure-intercooling systems for separating and pumping CO_2 to the sequestration sites. The compositions of all process streams, CO_2 capture efficiency, and net power were calculated using Aspen Plus for the IL solvents. The CO_2 capture capacity and energy of the process employing each of the IL's were subsequently compared to other carbon capture solvents.

Modified Carbon Adsorbents with High Thermal and Oxidative Resistance

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Coating of carbon materials by a layer of heat-resistant compound, such as silicon carbide, is widely used to improve the mechanical properties and for the obtaining heat- and oxidation stable materials. The continuity of the silicon carbide coating and the absence of defects are requirements of high thermal-oxidative stability of materials.

The purpose of this paper is to investigate the possibility of carbon adsorbents obtaining (CA) with combining properties of the sorption activity and increased resistance to thermal oxidation.

Activated carbons derived from coal: AG-3 (AG), CAD-iodine (CD), raw cellulose fibers (CF) and carbon cellulose fiber-based sorbent (ACM) were investigated as raw materials. As a silicon-containing additive was used polycarbosilane (P) {-(CH3)SiH-CH2-}m{-Si (CH3)2-CH2-}n, - polymer containing 50 wt.% of Si and forming SiC and / or SiOC (oxycarbide) when heated. The silicon-carbon materials obtaining consists of the treating the CA or carbon precursor by the solution P in chloroform, evaporation of the solvent and carbonization by heating to a 900 °C in argon flow. In the case of carbon precursor stage of activation was carried out in CO2 flow at 900 °C to different degrees of ablation.

The IR spectra of Si-containing carbon sorbents (SCS) characterized by spectral band at 1245 cm^{-1} (Si-C bond) and a broad band in the range 1100-700 cm^{-1} (Si-O in oxycarbide or/and Si-C in silicon carbide). In specters of some samples, low-intensity bands with maximum around 1100, 800 and 480 cm^{-1} are represented, indicating the presence of small amounts of SiO2. After heating in air, unburned residue, containing atoms C, O and Si, which confirms the presence in the sample of silicon oxycarbide, remains. In the case of fibrous sorbents silicon oxycarbide has a fibrous form corresponding to the initial microstructure of the fibers. Content of silica on the material surface varies from 0,2 to 17 wt. %, oxygen – from 6 to 36 wt.%.

The influence of the P amount in the SCS structure on the sorption activity on the rate of thermal and oxidative decomposition and on the residue quantity after heating in air at 500 oC were investigated. It was found that the sorption activity (surface area, sorption of benzene, iodine) of the studied samples depends on the amount of added P and oxidation time. The amount of added P varies from 1 to 50 wt. %, oxidation time – 3 and 5 hours. Porous and sorption characteristics decreased with increasing amounts of added P, but even with large amounts of P, these characteristics are at a high level and consistent with the requirements of many industrial sorbents.

An increasing of sorbent surface area after 5 hours of oxidation at 500 ^{o}C was found. It can be explained by disclosure of internal pores of the sorbents at a burn up of some carbon layers on the surfaces of the materials. Introducing of Si-containing layers on the sorbent surface can save carbon matrix in the oxidation processes. It results in saving sorbents residues after 3 and 5 hours and decreasing of oxidation rate compared with non-modified sorbents.

The reason of retarding the interaction of carbon with oxygen is blocking reacting carbon centers by silica atoms. The emission of CO2 at thermal and oxidative decomposition of sorbents was studied. The shift of high-temperature maximums of CO2 emission intensity increased about 30 o with increasing of the amount of adding P to 15 wt. %. Due to these properties, modified SCS can be used over a long period of time in oxygen-containing gaseous mediums at high temperature compared with non-modified sorbents.

So, the surface of synthesized SCS is covered by non- continuous layer of silicon oxycarbide. The modified sorbents are characterized by high thermal and oxidative resistance compared to the non-modified sorbents and by high specific surface area and sorption capacity. These sorbents can be useful for cleaning hot gas and vapor oxygen and CO2-containing mixtures, as a catalyst support in high-temperature catalytic processes in the presence of oxygen- containing compounds, in the heating elements.

POSTER SESSION 6
COAL SCIENCE

Surface Characterization of Ultrafine Fly Ash Interaction with Mercury

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Fly ash is a primary by-product of the coal combustion process whose emission is limited by particulate control devices, such as electrostatic precipitators or fabric filters. Despite capture efficiencies of up to 99.95%, coal-fired power plants in the United States still emit on average 300 tons of fly ash per day. The release of fly ash into the environment is a public and environmental health concern for two reasons. First, the particle size of released fly ash is generally smaller than 2.5 μm (PM2.5) and current research suggest that inhalation of small particles can have an adverse health effect. The second concern is because of the presence of toxic trace metals/metalloids, such as mercury (Hg), selenium (Se), and arsenic (As), which may exist as either a component of fly ash, or partition onto fly ash as the flue gas cools. Therefore, it is important to understand the characteristics of fly ash and, specifically, the interaction between trace metals and fly ash components. In this work, various experimental methods were carried out to investigate fly ash interaction with Hg. Bituminous coal fly ash particles below 0.1 μm were partitioned using membrane filtration, and both filtered and non-filtered fly ash samples were exposed to methane combustion flue gas, supplemented with SO_2, NO_x and HCl, that contained Hg in a packed-bed reactor to model Hg sorption. Characterization studies including scanning electron microscopy (SEM) and X-ray diffraction (XRD) were carried out on the fly ash samples to determine changes in their morphologies and mineralogy before and after reaction. Sorption reaction products were characterized using synchrotron-based x-ray fluorescence mapping (XRF) to determine which elements Hg is associated with on the fly ash particulate matter. Mercury hot spots were further analyzed with micro x-ray absorption near edge structure spectroscopy (μ-XANES) to determine the form of Hg contained in these regions. Results indicate that significantly more Hg is associated with the filtered fly ash sample when compared to the non-filtered sample. XRF analysis shows that the Hg is partitioned into two major regions in the samples: Fe associated and non-Fe associated. Mercury content in the sample is correlated with Fe, S (reduced), Cl, Br, and Cu, and to a lesser degree with Se and As. There is no discernable association between Hg and the alkali metals, the alkaline earth metals, and the lighter transition metals and the Hg hot spots detected are not associated with the Fe-oxides contained in the fly ash. μ-XANES analysis of the Hg hot spots indicates that these regions are dominated by HgS (cinnabar) crystals. These results indicate that ultrafine fly ash particles could be the primary sorbent of Hg from a gaseous phase.

The Radiation Characteristics of Radicals in CH_4 Co-Flowing Jet Diffusion Flame

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The OH* and CH* chemiluminescence in two-dimension, which were used to characterize the flame radiation, has been measured in CH_4/O2 co-flowing jet diffusion flame by using hyperspectral and ultraviolet cameras. The results show that OH* and CH* chemiluminescence can reflect the structure of diffusion flame. The changes of gas velocity can affect the flame structure and peak intensity of radicals, as the gas velocity increases, the radial diffusion of flame is restricted. The distributions of OH* and CH* are different with equivalence ratios in laminar and turbulent flows. As the equivalent ratio increases in laminar flows, OH* distribution range gradually becomes large, while CH* mainly exists within the flame front. But in turbulence, the effect of equivalent ratios on radicals' distribution range is reduced, the OH *and CH * peak intensity also changes with equivalent ratios.

The Chemical Structural Characteristics of Coals Rich in Semi-Fusinite

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Three coals (YJL, WEST, and PSOC-858), rich in semi-fusinite, from China, USA, and South African were studied to find their chemical structural characteristics by using FTIR (Fourier transform infrared spectroscopy), ^{13}C-NMR (Solid-state ^{13}C NMR spectroscopy), and Py-GC/MS (Pyrolysis-gas chromatography-mass spectrometry), respectively. Meanwhile, the basic information of these coals was analyzed by proximate, ultimate and petrographic analyses. The results showed that the samples used were characterized by high aromatic carbon intenstities. The aromaticities of coals used are from 0.72-0.79. YJL has relatively high aliphatic group when comparing to WEST and PSOC-858. From the spectra of FTIR, YJL has the stronger the intensity of peak at 1453 cm^{-1}.The result of Py-GC/MS show that all the pyrolysates are almost composed of alkylbenzenes, alkylphenols, alkylnaphthalenes, alkylphenanthrenes, and homologous series of n-alkanes and n-alk-1-enes.YJL has higher relatively intensity of alkanes/alkenes in pyrolysates.

"Vehicle" Role of Solvent in Direct Coal Liquefaction Process

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It is well accepted that solvent plays an important role in the direct coal liquefaction (DCL) process for improving coal conversion. This role is realized mainly through two aspects: 1. dissolving, swelling and dispersing coal particles, products and intermediates; 2. providing and transferring hydrogen to free radicals, which are intermediates generated via covalent bond cleavage. The solvent is, therefore, often referred to hydrogen vehicle due to its hydrogen donor and transfer function. The hydrogen vehicle solvent provides hydrogen by converting itself to dehydrogenated product which then be hydrogenated by gaseous hydrogen. The hydrogen providing and transferring behaviors of the vehicle solvent were reported in this presentation. The technique of electron spin-resonance spectroscopy (ESR) was applied. The solvents used include a process-produced recycle solvent, tetralin and naphthalene. It was confirmed that the concentration of the free radicals decrease with the increase of the concentration of tetralin in solvent under inert atmosphere. The free radicals, generated from coal pyrolysis, can be stabilized by two ways under inert atmosphere: 1. hydrogenation by obtaining hydrogen from the hydrogen donor solvent; 2. self-stabilization through condensation reaction. It was found that stabilization reactions by hydrogen donor solvent are favorable at higher temperature. It was also found that the Fe-base catalyst can improve the coal conversion under H_2 atmosphere but it also can cause the dehydrogenation reaction of hydrogen donor solvent under inert atmosphere, which may leads to the decrease of coal conversion. Comparing with the Fe-based catalyst, the Mo-based catalyst is more efficient in promoting the hydrogen transfer reaction of the solvent, especially when sulfur is added.

Pyrolysis of Liulin Coal Simulated by GPU-Based ReaxFF MD with Cheminformatics Analysis

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Mechanisms investigation of coal pyrolysis will aid efficient and clean coal conversion and utilization. However, the heterogeneous nature of coal and the complexity of the process have made it very difficult to determine the mechanisms of coal pyrolysis even with state-of-the-art experimental approaches. Reactive force field (ReaxFF), a useful and promising bond order potential, allows for reactive molecular dynamics (ReaxFF MD) simulations for modeling large and complex molecular systems involving chemical reactions. In this investigation, GMD-Reax, the first graphics processing unit (GPU) enabled ReaxFF MD program with significantly improved performance surpassing CPU implementations on desktop workstations, was employed to explore the initial chemical mechanisms and products distribution in pyrolysis of a complex subbituminous Liulin coal molecular model with 28, 351 atoms. The model was constructed based on a combination of experiments and classical coal models. The chemical and physical parameters of the coal model are broadly consistent with experimental data including industrial analysis, elemental analysis and ^{13}C NMR data of Liulin coal. The ReaxFF MD simulations of pyrolysis of the Liulin coal model at temperatures from 1000 to 2000 K using NVT ensembles were performed to investigate the effects of temperature on the products profile and the initial chemical reactions. The detailed chemical reactions of the pyrolysis simulation has been generated by using a C++ program that was newly created for examining the complexity of the chemical reaction network in ReaxFF MD simulation. It was found that more than 2500 reactions may occur at 2000 K within a 250 ps simulation period with a trajectory output interval of 12.5 ps. The coal thermolysis process is primarily initialized by bond dissociation of alkyl-aryl ether bridges. The amount of six-membered ring structures was observed to decrease with time and temperature due to their conversion into five-membered rings or 7 - 9 membered rings or even larger-membered ring structures that will further open and decompose into small fragments. The products profile (gas, tar and char) evolution tendency with time and temperature observed in the simulations are in agreement with the tendency in experimental observations in literature. The work presented here demonstrates a new methodology for investigating coal pyrolysis mechanism by combing GPU-enabled high performance computing with cheminformatics analysis in ReaxFF MD.

Study of Helianthus Annuus Stem Fast Pyrolysis by Using Py/GC/MS

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Analytical pyrolysis-gas chromatography/mass spectrometry (Py/GC/MS) was used in achieving fast pyrolysis of biomass or other polymer substrate, the best advantage of this methord is on-line and qualitative analysis of the pyrolysis products. In this study, we reported a practical method for analytical absolute content of helianthus annuus stem pyrolysis products at different pyrolysis temperature (300℃、400℃、500℃、600℃、700℃). Internal standard substance is the key of quantitative analysis in PY/GC/MS. They must be stable at pyrolysis temperature, and have very good linear relationship between content and MS singal and also have a very low detection limit Our experimental results show that the 1, 3, 5-Tri-tert-butylbenzene (TTBB) is a suitable ISTD in quantitative analysis in PY/GC/MS. Pyrolysis gas products of CO_2 and organic compounds (phenols, ketones, anhydrides, esters, aldehydes, alcohols, acids, aromatic, heterocyclic, etc.) are classified and calculated the absolute quality. When the pyrolysis temperature at 500℃, the total absolute quality of the organic compound is 69%, and the absolute quality of the CO_2 is 6%.

The Performance Research of DCFC with Shenfu Semi-Coke as Fuel

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Due to fuel extensive adaptability, the direct carbon fuel cell (DCFC) can employ carbonaceous solids such as coal, semi-coke, petroleum coke, biomass, and organic polymer waste as fuel. In this paper the performance of DCFC with Shenfu semi-coke as fuel and Yttria-stabilized zirconia (YSZ) as electrolyte is investigated using electrochemical measurements at the temperature range from 700-850^{o}C. With the increase of operating temperature, the maximum power density increases, and the ohmic resistancee decreases. The effect of atmosphere in anode cavity of DCFC at 850^{o}C is conducted by gas chromatography (GC) analysis. The results show that the anode reactions consist of the reverse Boudouard reaction and the electrochemical reaction of CO.

A Preliminary Study on Coal Graphitization in High Temperature

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The graphite powders are widely used in different areas such as paint and battery because of its corrosion resistance, thermal stability, acid resistance, and high heat conduction. In this paper, the graphitizations of Taixi anthracite and Shenfu bituminous were reported. At 1500℃ in nitrogen gas (<1500℃), and then at 2500℃ in argon gas with metal or nonmetal compounds as catalysts in a medium frequency induction furnace. It was found that graphited Taixi anthracite has better-developed crystalline structure, but graphited Shenfu bituminous coal has relatively poor crystalline structure after high temperature graphitization.

Variations in Characteristics of Extract with Coal Rank of Four High-Organic-Sulfur Coals in China

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The relationship between extraction yields and organic sulfur contents, on a dry and ash-free basis of high-organic-sulfur coals of different ranks from four coalfields in China, which include Chenxi (0.77% *R*o,r), Guiding (1.29% *R*o,r), Hedong (1.55% *R*o,r) and Heshan (1.93% *R*o,r), have been studied by using proximate analysis, sulfur forms, Soxhlet extraction, gas chromatography-mass spectrometry(GC-MS). The relationship of the extraction yields and coal rank follow the trend of low sulfur coals. The high content of organic sulfur often enhance the extraction yield. The results from GC-MS showed that there were evidence of algae and bacteria input in the samples. Proportions of sulfur-containing organic structures were different in different coal. The dibenzothiophene fraction of organic sulfur increases with coal rank. There are four types of organic sulfur compounds were identified from samples, including dibenzothiophene, benzonaphthothiophen, phenanthrothiophene and benzobisbenzothiophene. The organic sulfur compounds is similar. The four types are all identified in Guiding and Heshan coals. But phenathrothiophene has not been detected in Chenxi coal and benzobisbenzothiophene has not been detected in Hedong coal.

Coupling of Volatile Radical Fragments in TGA Crucible During Pyrolysis of Coal

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Thermal gravimetric analysis (TGA) is frequently used to study coal pyrolysis due to its ability to measure de-volatilization (mass loss) history. It is generally recognized that the de-volatilization process is very complex but can be categorized into two steps, thermal cleavage of covalent bonds that generates volatile radical fragments (VRFs) and coupling of VRFs to form stable products. The coupling reaction is usually assumed to be very fast and completes quickly before VRFs are able to leave the sample crucible of TGA. This, however, is questionable because tars obtained from pyrolysis of coals were found to have large amounts of radicals, about 10^{17} spins/g or higher. This implies that coupling rate of some of the VRFs, possibly the lager ones, is quite slow. It further suggests that the mass loss registered in TGA includes not only the gaseous and liquid products formed in pyrolysis, as commonly recognized, but also solid products (char) that may form later, outside of the crucible, by coupling of the large VRFs. The slow coupling rate of the large VRFs has not been well studied and is even doubted by many. This work studies coupling activity VRFs indirectly by altering residence time of pyrolysis volatiles either in the coal sample or in the upper void space of TGA crucible.

The experiments are carried out using the same amount of coal sample in TGA crucibles of different shape and size. The DTG data are compared qualitatively with that of $CaCO_3$ decomposition (its reverse reaction CO_2+CaO=$CaCO_3$ simulates reaction of volatiles to form non-volatile product). It is found that the DTG peak of $CaCO_3$ decomposition shifts to a higher temperature with an increase in CO_2 residence time in $CaCO_3$ bed or in the upper void space of the crucibles, due to increased reaction of CO_2 and CaO. The DTG peak of coal pyrolysis, however, changes little with the crucible shape and size, suggesting limited coupling of VRFs in TGA crucible for solid products. Detailed results and discussion will be presented in the conference along with pyrolysis results of other model compounds.

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Compare with CO Regeneration and Thermal Regeneration of V_2O_5/AC Catalyst-Sorbent for SO_2 Removal

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SO_2 removal from flue gas is a significant work in energy and environmental protection. Dry desulphurization technology based on activated carbon-supported materials does not produce subsequent waste and can produce elemental sulfur or H_2SO_4, which received more and more attention recently. However, it is necessary to devise a facility to treat SO_2 desorbed in the regeneration unit. Therefore, direct reduction SO_2 to elemental sulfur by regeneration gas of CO would be a good choice. In this paper, CO is used as regeneration gas and/or as a reducing agent to reduce SO_2 to elemental sulfur on V_2O_5/AC catalyst-sorbent. CO regeneration with traditionally thermal regeneration were compared, the results show that CO regeneration is more effective than thermal regeneration, and the best regeneration condition on sulfated V_2O_5/AC catalyst-sorbent is at 350°C for 90 min in 0.15%CO/N_2. CO regeneration promotes SO_2 desorption and decreases the consumption of activated carbon, which result in the recovery of the activity and stability of V_2O_5/AC catalyst-sorbent in the process of SO_2 removal.

Rapid Oxidation of Lignite to Produce Benzene Carboxylic Acids at High Temperatures

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The researches toward the production of chemicals from coals for a substitution of the petroleum have drawn the world attention recently. As a typical case, production of benzene carboxylic acids (BPCAs) which are the sources highly demanded (e.g. TPA and PMA) in the polymer industry or in the pharmaceuticals industry (e.g. trimesic acid) by the oxidation of coal is a potential way to replace the petroleum-route. And the usual method to oxidize the coal with satisfying BPCAs yield employs conditions that temperature 220 °C-270 °C, reaction time 0.5 h-3 h and alkali/coal mass ratio 2/1-6/1 in the water. The high-input alkali in the method is a big limiting factor to the industrialization of the process. In the present study, we carried out the lignite oxidation reaction at temperature from 280 °C to 320 °C never employed. Interestingly, it was found that when the temperature increased, the needed alkali amount to get a satisfying (20 wt%) BPCAs yield decreased, and when it reached 300 °C, the needed alkali/coal mass ratio decreased to 0.8/1; moreover, the needed reaction time was shortened to only 1 min. The largely decreased alkali amount and reaction time in the oxidation of coal to obtain BPCAs was of great significance for the industrialization of the process.

Acknowledgement: The project is financially supported by the Natural Science Foundation of China (21076138) and the National Basic Research Program of China (2011CB201303)

Catalytic Oxidation of Lignite to Produce Chemicals in High-Temperature Water

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The researches toward the production of chemicals from coals for a substitution of the petroleum have drawn the world attention recently. As a typical case, production of benzene carboxylic acids (BPCAs), which are the sources highly demanded (e.g. TPA and PMA) in the polymer industry or in the pharmaceuticals industry (e.g. trimesic acid) by the oxidation of coal, is a potential way to replace the petroleum-route. However, the attainment of BPCAs from coal oxidation consumed a large amount of alkali and the application of catalytic approach for coal oxidation was failed although many catalytic systems were tried.

In the present work, a catalytic system for lignite oxidation to produce BPCAs was proposed. In this system, sodium metavanadate dissolved in water can form several kinds of vanadium-oxygen species, which possesses a high oxidative potential to catalyze selectively the lignite oxidation reaction. The results showed that at temperatures of 120 °C-180 °C and an oxygen pressure of 3 MPa, Xiaolongtan lignite was converted to BPCAs and small-molecular fatty acids mainly including formic acid, acetic acid and oxalic acid. At a temperature of 140°C and for an oxidation time of 3 h, the conversion of coal is 68.3% and the yield of BPCAs is 12.9%, and the yield of small-molecular fatty acids is 38.0% including 14.5% of formic acid, 13.3% of acetic acid, 7.2% of oxalic acid, 3.0% of succinic acid. The conversion of coal increases with oxidation time and temperature, while the yields of BPCAs and small-molecular fatty acids can reach a maximum value with increases of oxidation time and temperature. The catalytic oxidation of lignite to produce BPCAs and small-molecular fatty acids was achieved successfully for the first time.

Acknowledgement. The project is financially supported by the Natural Science Foundation of China (21076138) and the National Basic Research Program of China (2011CB201303).

Utilization of Photocatalytic Reactions to Conversion of Different Rank Coals and CO_2 into Methanol

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In this paper, we report several typical coals in China (such as the Shenfu coal, the Huating coal, the Jincheng coal, etc.) as photocatalyst and reactant in the photocatalytic reduction system of CO2. All of raw coals were crushed to D90<25μm and then the coal powders were suspended steady in a kind of mixture aqueous solutions in a gas–liquid-solid heterogeneous photocatalytic reactor, respectively. We investigated the effect of irradiation time, the coal powder consumption, etc. on the target product (methanol) yield of CO2 photocatalytic reduction. It was found that the different rank coals expressed the significant difference in photocatalytic reactivity with CO2 and the low-rank coal is better than the high-rank coal. The highest methanol yield is 461.32μmol/L when Shenfu coal (a kind of low-rank coal from shaanxi province, China) was added and the coal consumption is 1.0 g/L, irradiation time is 34 hours, CO2 flow is 200mL/min. Furthermore, longer irradiation time was needed to obtain high methanol yield and the methanol yield has clearly increase when the irradiation time was extended than 20 hours.

Mercury, Trace Elements Release Characteristics during Integrated Process of Coal Pyrolysis with Methane Steam Reforming of Low-Rank Coals

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The release and distribution of trace elements in low-rank coal upgrading processes is closely relevant to its transformation in fuel gases and subsequent release into the environment. This paper presents a study on fates of mercury, arsenic, selenium and some other trace elements during mild-thermal upgrading and integrating process of coal pyrolysis with steam reforming of methane (CP-SRM) of Chinese lignite (HLH and XLGL) and subbituminous coal (SM). Experiments were conducted on a bench-scale fixed bed under atmospheric pressure. The effects of pyrolysis temperature (450-750 °C, in 50 °C increments), pyrolysis atmosphere (H_2, N_2, CP-SRM), tar yield and industrial catalyst (Ni/Al_2O_3, involved in CP-SRM process) were studied. The gas-phase mercury was analyzed by an atomic fluorescence mercury analyzer according to the Ontario Hydro Method (OHM). The contents of trace elements in chars were analyzed by Inductively Coupled Plasmas-Mass Spectrometry (ICP-MS). It was observed that the release ratio of mercury and some volatile trace elements increase monotonically with temperature over 1 hour. The maximum release ratios of most volatile elements were obtained under CP-SRM atmosphere with the highest tar yield. Elemental Hg (Hg^0(g)) is the dominant species at most of the temperatures and holding times examined whereas high temperatures and long times enhance mercury oxidation. It was also observed that with the temperature increasing from 450 to 750 °C, the percentage of oxidized Hg(Hg^{2+}(g)) increased during pyrolysis and CP-SRM process. Comparative studies on trace elements emission under different conditions indicated that the release and distribution of trace elements may correlate with the atmosphere and tar yield in different process. However, no obvious correlation between release ratio of trace elements and industrial catalyst in CP-SRM progress was observed.

Fundamentals and Pilot Test for Jetting Pre-oxidation Fluidized Bed Gasification Adapting to Caking Coal

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Experimental studies on jetting pre-oxidation fluidized bed gasification (JOFBG) adapting to caking coal were performed in both a laboratory fluidized bed reactor and a 140 kg/h pilot plant. In the JOFBG coal is entrained and jetted into the zone just above the bottom dense bed of the fluidized bed gasification reactor via an oxygen-containing gas so that the coal is first pre-oxidized in the jetting gas and its formed char then drops into the bottom dense bed to undergo the fluidized bed gasification. This preoxidation is suggested effective to destroy the caking propensity of the coal so that the JOFBG is adaptive to caking coal, which should be difficult in the conventional fluidized bed gasifier. First, the destruction of coal caking propensity was investigated in a laboratory fluidized bed that adopted N_2 as the fluidizing gas and jetted the coal in 0.5-1 mm into the bed through a vertical O_2-containing gas stream from the bed center. The necessary conditions of the preoxidation for destroying the caking propensity of a kind of coal with a caking index of 20 were clarified to be at temperatures above 950 ℃and with ER above 0.1 for the the air jet. The variations in temperature and produced gas composition in the reactor were also measured to justify the result of caking propensity destruction. On the basis of the labpratory test, a 140 kg/h pilot plant according to JOFBG was built, and the coal with a caking index of 20 was successfully gasified using air and O_2-enriched air as the gasification agent. The heating vale of the resulting product gas varied in 2.9-5.0 MJ/Nm^3 and it decreased with raising the oxygen percentage applied to the gas jetting. Raising the oxygen percentage for the jet caused more of the produced gas formed in the bottom dense bed of char gasification to burn off in the jetting zone. The optimal proportion of the oxygen for the gas jet or coal pre-oxidation was found to be about 37% against the total oxygen required by the gasification. Enriching the O_2 content in the gasification agent to about 30 vol.% greatly enhanced the gasification rate of coal in the JOFBG.

Behavior of Mercury Oxide over Activated Carbon in Simulated Coal Combustion Flue Gas by Temperature Programmed Decomposition Desorption-Mass

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Stabilities and/or decomposition characteristics of mercury compounds themselves and over solids are very important for the design of solid sorbent for mercury vapor removal from coal derived flue gas and fuel gas. However data available presently on the mercury compounds' stability and decomposition behaviors are inadequate.

In our previously research, we reported that mercury could react with oxygen absorbed in activated carbon (AC) to generate HgO, and HgO further could react with HCl to form $HgCl_2$ which could be adsorbed on AC surface. When there is SO_2 present in the simulated flue gas, HgO would be reduced by SO_2 and it decreased the mercury removal capability of AC; or after HCl decomposed to Cl_2 on AC surface, Cl_2 could react with SO_2 to form SO_2Cl_2, so that there is not enough HCl to react with Hg and as a result, the Hg removal capability of AC decreased.

The purpose of this research is to investigate the mercury desorption pathway of the HgO/AC which was pretreated with gases composed of HCl-H_2O or SO_2-H_2O or HCl-SO_2-H_2O by temperature programmed decomposition desorption (TPDD) method.

1) When the HgO/AC was treated with HCI-H2O, the peak of mercury was observed in the TPDD treatment of AC after mercury removal in the presence of HCl.
2) The treated HCl was absorbed in samples and changed to Cl_2 on AC surface. Two desorption peaks of Cl_2 were obtained during the TPDD treatment of HgO/AC and the peak at higher temperature was also observed when treated with AC without HgO with the same process.
3) The TPDD peak of mercury (M/Z=202) was presented near 240°C when the HgO/AC was pretreated with SO_2-H_2O. The temperature range of this peak was consistent with that of AC which was pretreated with 500ppmSO_2-H_2O.
4) When the AC with HgO was pretreated with 100ppmHCl-500ppmSO_2-3%H_2O, the desorption peak of HgO was observed at the intermediate place of that pretreated with HCl and SO_2 respectively. From the TPDD spectra of HCl, Cl_2 and SOx , it is probable that through the pretreatment of composed gases, compounds consists of Cl, SOx and Hg were generated on the AC surface and during TPDD the compounds were firstly decomposed to mercury vapor and then Cl_2 and SO_3(or H_2SO_4) at the higher temperatures.

Mechanical Activation Method for Preparation of Carbon Sorbents

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In this work we applied mechanochemical treatment for modification of coals reactivity, their thermochemical transformations and hence the formation of porous and sorption characteristics of carbon materials prepared on their basis. For the preparation of sorbents with high surface area mechanochemical treatment of coal alkali-mixtures was used.

In the experiments naturally oxidized humic coals from Kuzbass deposits with particle size 0.2-0.5 mm at different stages of metamorphism and of different brands were used: brown (B), jet (J), low-caking (LC) and lean (L) coals.

Table. Characteristics of the pore structure of carbon materials prepared by mechanical activation of coals mixed with alkali with subsequent carbonization.

Coal brand	**Specific surface area, S_{BET} m^2/g**	**Total pore volume V_Σ cm^3/g**	**Micro pore volume V_{mi} cm^3/g**	**Meso pore volume V_{me} cm^3/g**	**Relative content of micro pores V_{mi}/V_Σ, %**	**Relative content of meso pores V_{me}/V_Σ, %**	**Average pore diameter nm**
B	**1038**	**0.73**	**0.42**	**0.31**	**57**	**43**	**2.1**
J	**1365**	**1.09**	**0.56**	**0.53**	**52**	**48**	**2.4**
LC	**968**	**0.87**	**0.41**	**0.46**	**47**	**53**	**2.7**
L	**989**	**0.64**	**0.44**	**0.2**	**69**	**31**	**1.9**

The highest values of specific surface area (S_{BET} = 1365 m^2/g) and pore volume (V_Σ = 1.09 cm^3/g) are observed for the carbon material produced from the coal J by its mechanochemical treatment in mixture with KOH. Its high surface area is due to the contribution of both micropores and mesopores.

As a result of preliminary mechanical activation of coal-alkali mixtures, processes of thermal destruction of coals of all brands are intensified. This is caused by high dispersion of the particles, better homogeneity of the mixture and formation of active sites of different nature on the newly formed surfaces. Therefore, preliminary mechanical activation of coals by their grinding with alkali can be recommended for the preparation of sorbents with developed pore structure.

Coal Pore Structure

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The pore structures of 20 samples of natural coals were studied by methods of low temperature nitrogen adsorption and mercury porosimetry

The studies by the method of low temperature nitrogen adsorption were performed in an instrument ASAP-2400 (Micromeritics Instrument Corporation, Norcross, GA, USA) after samples pretreatment at 150ºC and residual pressure below 0.001 mm Hg, measuring isotherms of N_2 adsorption at the temperature of liquid nitrogen 77 K in the range of relative pressures from 0.005 to 0.991. The data were processed by the standard procedure using the Barret-Joyner-Halenda method with the calculation of specific surface area (A_{BET}, m^2/g), volume of pores in the range 1,7-300 nm ($V_{pores\ (1.7\text{-}300\ nm)}$, cm^3/g) and differential pore size distribution.

Based on the results obtained by the method of low temperature nitrogen adsorption, all samples were found to have low values of specific surface area, which is characteristic for samples with low pore volume or samples with closed pores inaccessible for nitrogen molecules. The results of the measurement of differential pore size distribution of coal samples show that in the measured range of pore sizes from 1.7 to 300 nm the predominant pore diameter ($D_{eff.}$ –effective pore diameter) is 3.8-4.2 nm.

The studies by the method of mercury porosimetry were conducted in an instrument AutoPoreIV 9500 with the calculation of the total pore volume (V_Σ, cm^3/g) and the volume of pores in the range of 1.7-300 nm.

The comparison of the volume of pores in the range of 1.7-300 nm determined by the two methods shows that the volumes of mesopores found by mercury porosimetry is 2-10 times higher than those determined by the method of low temperature nitrogen adsorption. The number of pores with these diameters in samples found by mercury porosimetry is 10-30 times greater than the number determined by N_2 adsorption method. This difference in the results of the pore structure measurements obtained by two different methods is evidence that closed pores are present in all studied coal samples.

Full number of physico-chemical properties of these 20 samples will be presented and discussed.

Modeling of Lignin Pyrolysis Based on Bond Dissociation and Fragments Coupling

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It is generally accepted that pyrolysis of hydrocarbons, though very complex, follows two fundamental steps, thermal cleavage of chemical bonds to yield radical fragments and coupling of the radical fragments to form stable or final products. Although huge amounts of experimental studies can be found in the literature on pyrolysis of coal, biomass and organic wastes limited information is available on simulation of the pyrolysis. Furthermore the available simulation studies often concentrated on the coupling steps, rely heavily on experimental data, and therefore were somewhat empirical. This presentation reports our recent attempt on pyrolysis simulation based on only the two fundamental steps, bond cleavage and coupling of the fragments, using lignin as the model compound.

Based on the 13 types of chemical bonds in lignin and its pyrolysis products, we can estimate 4 fragments generable via bond cleavage. Based on the bond dissociate energies of the bonds and Boltzmann distribution we can estimate the extent of the bond cleavage for each bond at a temperature in a finite time interval. The coupling of the fragments is assumed to be random and can be described by the Monte Carlo algorithm, which yields the amounts of new bonds in the same time interval. The distribution of chemical bonds in the pyrolysis is acquired by repeating these steps. A relation between the simulation time and the actual pyrolysis time is established by comparing the experiment results in the literature and the simulation data on different time scales.

The simulation is then carried out using various second level assumptions, including selection of bond dissociation energies, weighting factors for coupling of fragments. Compared with NMR data of lignin pyrolysis experiment, it is found that the model reasonable simulates the trends in change of bonds at various temperature and time span. The simulation study suggests that the assumptions made to the bond cleavage step are more important than that made to coupling step for suitability of the model.

Research on Crushing Mechanism and Separation Characteristic of ZGM Coal Mill

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The holes of ZGM95 coal mill incoal-fired power plantshave been firstly drilledin Chinato collect the coal samples fromvarious points in the separator under the different operation condition. The material property is analyzed by the float-sinktestandthe sample size distribution.The circulating rate and material flux of the separator and cone zoneare calculatedby the mass balance modelsof circulating load. Moreover, the influence rules of the mill coal feed, air quantity, hydraulic loading force and coal property on the circulating rate and internal material distribution are discussed by the quantity and quality balance. The circulating rate and input materialfluxof the separator and cone zoneall increase with the mill air quantity.

ANFIS-Based Level Control System for Flotation Column

Cheng Sheng, China University of Mining and Technology; Jingya Wen, Inner Mongolia University of Science and Technology, CHINA

The pulp level in a flotation column fluctuates frequently as a result of the changes to the nature of the pulp and the varying flow rate, thereby affecting the amount and grade of the concentrate. An automatic control system can be used to control some parameters that affect the flotation process, and even to control the recovery and the grade of the concentrate, Therefore, the stability of product quality can be guaranteed at the same time. According to the application of the flotation characteristics of the flotation column, exploring the application of adaptive fuzzy neural network control in flotation column level control system, and testing the performance of the design by Matlab/Simulink simulation to optimize parameters of the flotation column level control system. The simulations show that level control in the flotation column becomes smoother and more rapid with the ANFIS controller. Compared to fuzzy control methods, the overshoot in valve position, the adjustment time and the robustness of the controller are all improved.

Arsenic Occurrence and Enrichment in Single Pyrite Segregated by Float-Sink in Coal Sample from Guizhou, China

Chong Tian, Junying Zhang, YongChun Zhao, Chuguang Zheng, University of Science and Technology, CHINA; Rajender Gupta, University of Alberta, CANADA

For quantitative understanding the occurrence of As in coal samples, an advanced technique, which is low-temperature ash plus gravity separation via float-sink process, is adopted in the research work. Not only the inorganic constituent termed mineral matter can be isolated completely without any alteration from the coal, but also heavy minerals such as pyrite can be segregated from quartz and clay minerals which are abundant and commonly identified in coal. The technique is capable of defining quantitatively the mineral matters and their associations with trace elements in coals. The separated fractions from coal including low temperature ash (LTA), light minerals (LM), and heavy minerals (HM) are detailed characterized by X-ray diffraction (XRD), field emission scanning electron microscope equipped with energy-dispersive X-ray analysis (FE-SEM/EDS), and the high resolution inductively coupled-plasma mass spectrometry (ICP-MS) for determining the mineral compositions and also the distributions of trace elements. This paper presents the experiment results on As occurrence in a typical high arsenic (approachingto 265μg/g) coal from Guizhou, southwest China, where endemic arsenism is suspected as a consequence of the coal combustion. Meanwhile, the first quantitative analysis on the enrichment of As in single pyrite particles, segregated via float-sink process with the low temperature ash produced from coal, measured though FE-SEM/EDS particle by particle is also obtained.
The results show that As occurrence in the coal present as both organic and inorganic combination mode, the relative percentage of the organiccombination mode of As account for 28.40%, the rest is in inorganic combination mode. As is enriched in the segregated heavy minerals (approaching to 650μg/g) majorly composed of pyrite, which indicates that the As has a positive correlation with pyrite. Further, the EDS analysis indicates that each distinct single pyrite particle contain a certain amount of As with an average of 3.5% (wt%), while the maximum concentration reaching to 6.3% (wt%). The results confirm that the inorganic combination mode of As, more specifically defined as pyrite combination mode, is the predominant mode in the coal.

Reaction of Carbon Disulfide and Magnesium during Milling with Carbonized Anthracite as Milling Aid

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CS$_2$ reacted with magnesium by means of reactive milling in the present investigation. SEM observation shows that the particle size of magnesium is reduced efficiently with the help of coal as milling media by its sharp and hard edges. XRD analysis indicates that CS$_2$ can react with Mg on the surface of small particles to yield MgS and crystallitic carbon of graphite structure during ball milling over 0.5 h. With the increase of reaction, MgS layer hinders the reaction of CS$_2$ with the Mg in the particle core. The anthracite coal peels away the MgS formed and during milling, exposes the virgin metal surfaces to CS$_2$, and decreases the particle size and diminishes the limitations imposed by slow diffusion on the rate of the overall metal-sulfide transformation. In addition, FT-IR analysis shows that CS$_2$ can chemically absorb on the surface of carbonized coal with abundant surface dangling bonds induced by milling.

Development of Alumina & Silica-Based High Valuable Products from Fly Ash

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Vast quantities of fly ash which are produced from coal-fired power plants have caused serious environmental pollution for air, soil and underground water. The accumulated fly ash over the years requires massive landfill. On the other hand, fly ash is high valuable resource such as alumina and silica. The high-alumina fly ash(HAFA), collected from the west of Inner-Mongolia typically contains 49.5% alumina, 40% silica, 1.5% titania, 1.6% hematite and 3.2% lime. A novel method has been developed to efficiently recover alumina and silica from HAFA. The method achieved an alumina recovery rate as high as 91.26%, comprised mainly (a) pre-desilication process, (b) calcining desilicated FA with a proper additive, (c) the sintered clinker dissolving process, (d) sodium aluminate desilication process, (e) carbon dioxide decomposition, and (f) calcining alumina hydroxide process. The detailed information for these processes will be disclosed in this paper.

A Study on Sintering Process of Alumina Extraction from Fly Ash

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Fly ash is an industrial by-product generated during the combustion of coal in power plant. In Inner-Mongolia, the content of Al2O3 in fly ash can reach as high as 50wt%. This high alumina fly ash (HAFA) is believed as a substitute resource to bauxite, which is becoming a shortage of alumina industry in China. This paper presents recent results of Al extraction sintering process from fly ash.
The alumina extraction from fly ash is based on the application of hydrometallurgical processes. A pre-desilication process was carried out to improve the Al/Si ratio. The de-silicated FA is sintered with CaO and Na2CO3. An orthogonal experiment was designed to optimize the extraction efficiency. Detailed analysis and characterization was carried out by using thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). The results indicated that an alumina extraction efficiency of 91% could be achieved by this method and the mechanism of alumina extraction was studied in this paper.

Inorganic Particle Formation in Blended Coal Combustion

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Blended coal combustion is a routine practice in most Chinese coal-fired power plants. Limited work has suggested that interactions between constituent coals can have important effects on particle emissions from blended coal combustion. However, the underlying mechanisms are less known. The present work aims to explore the mechanisms of inorganic particle formation in blended coal combustion. A sub-bituminous coal with a high content of sodium and a bituminous coal with high contents of aluminosilicates are well mixed to produce blended coal samples with different composition. The blended coal samples are combusted on a well-controlled drop tube furnace. The generated particles are size-segregated and collected through a cyclone and a 13-stage low pressure impactor. The samples are subjected to comprehensive analyses by computer-controlled scanning electron microscopy (CCSEM), scanning electron microscopy plus energy-dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD), and so on. Special emphasis is put on the effects of interactions between sodium and aluminosilicates in constituent coals.

The Mechanism of Gravity Shedding of Ash Deposits in Coal Fired Boiler

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The accumulation of ash deposits on furnace walls and heat exchanger tubes cause the slagging and fouling problem found in pulverized coal fired boilers. Ash deposits reduce a boiler's overall heat transfer coefficient due to its low thermal conductivity. These deposits need to be removed to restore the overall heat transfer coefficient to previous levels. There are two main processes for the shedding of ash deposits. The first involves the use of mechanical and/or thermal shock devices, such as soot-blowing, whereby pressurized steam is used to cause a mechanical and thermal shock. This process is referred to as 'artificial shedding'. The second achieves shedding without the use of any operational and/or mechanical actions. Examples include erosion and gravity shedding. The purpose of this study is to examine experimentally the gravity shedding mechanisms of ash deposits. A horizontal furnace, which simulated the temperature profile found in boilers, was used in this experiment. The pulverized coal, which was supplied between 3 and 4 kg/h, was fired in this furnace. The pulverized coal was used typical bituminous coal. The gravity shedding of ash deposits was observed by placing a water-cooling tube into the furnace during combustion. The cross-sectional surface of the water-cooling tube was then examined using scanning electronic microscopy. The ash deposits before shedding were found to have a thickness of between 2 and 3 millimeters. The bottom area of the ash deposits consisted of ash particles, while the top area of the ash deposits partly consisted of sintered ash particles. After shedding, the remaining ash layer was found to have a thickness of between 300 and 500 micrometers on the tube surface.

Investigation on the Correlation between Coal Property and Combustion Character of Low Rank Coal

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Coal is the biggest resource of primary energy in china, about 80% of coal is consumed in coal-fired power plant and industry boiler, most of raw material is low rank coal (LRC). LRC is a younger solid fossil fuel compared to bituminite and anthracite, it has complicated chemical structure and composition and higher chemical reactivity. The combustion character is the most important guideline for the technical evaluation of coal combustion utilization, and it is dominated by the properties of LRC. To understand the influence of coal properties is essential for the design and develop of combustion application. In this research, the properties of several LRCs, including chemical composition, oxygen adsorption and so on, are measured, and the combustion character is examined by a new method developed by our lab with a thermogravimetry (TG) analyzer. The correlation between coal properties and coal combustion behavior is then established. It will not only help understand the influence of coal properties on combustion behavior, but also develop a quick prediction model of combustion reactivity for LRC.

Arsenic Physical and/or Chemical Adsorption by CaO during Cooling Process of Simulated Air and Oxy-fuel Combustion Flue Gas

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Arsenic is a ubiquitous element in fly ash of coal combustion and the toxicity of arsenic compounds depends not only on the quantity, but also on its chemical form as well. Arsenic is predominantly present as vapors at the operating temperature of coal combustion and the physical and/or chemical adsorption are strongly affected by calcium compounds during flue gas cooling process. In the present study, the effects of CaO on the arsenic speciation migration under simulated flue gas of air and oxy-fuel combustion are investigated at temperature ranged from 300 to 900 ^{o}C. The oxidation of arsenic was enhanced at high temperature. Compared with interaction between arsenic vapors and CaO under simulated flue gas of air combustion, the arsenic oxidation was suppressed under simulated flue gas oxy-fuel combustion. The interaction between CaO and CO_2 and/or SO_2 competed with arsenic oxidation by forming $CaCO_3$ and $CaSO_4$. Furthermore, physical adsorption by CaO was considerable at low temperature while $CaCO_3$ and $CaSO_4$ were capable of arsenic adsorption at high temperature.

Petrology and Mineralogy of the Super-High-Organic-Sulfur Coals of Late Permian from Chenxi Coalfield, Southern China

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The super-high-organic-sulfur (SHOS) coals of Late Permian from the Chenxi Coalfield, in Hunan Province, south China, deposited in a carbonate tidal flat environment. The chemistry, petrography and the forming environment of the Chenxi coals have been investigated. The organic sulfur content of the Chenxi coals could be as high as 9.53%, on a dry basis, which account for more than 80% of the total sulfur. Microscopic observation revealed that the Chenxi coals are composed of vitrinite 60.1-78.1%, inertinite 21.9-39.9%., and the mineral 6.2%-30.3%. The high detrovitrinite and low telovitrinite contents, indicating low preservation of plant structure, resulted from alkaline conditions permitting bacterial activity and decay of plant material. The excess inertodetrinite revealed that the Chenxi coal seam had experienced intermittent oxidation process during the overall reducing and alkaline environment. The present of gelinite, swelled fusinite and macrinite suggested a turbulent environment, *e.g*. the fluctuations water level of paelomire. The SHOS coals from Chenxi formed in an alkaline aquatic environment influenced by both bacteria activity and the episodic oxidation process.

Roles of Anthracite Coal in Preparation of Magnesium-Based Hydrogen Storage Materials

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The functions of anthracite coal in the preparation of MgH_2 for hydrogen storage from magnesium by means of reactive milling under hydrogen atmosphere were investigated. The anthracite coal plays three roles in the milling process. The first role is dispersive agent to prevent Mg particles from cold welding during milling, where the powders show moderate and very slight aggregation after 3 h of milling when the coal additives are 20 wt.% and 30 wt.%, respectively, but seriously weld into bulk and adhere to the surface of milling balls and the inner walls of milling vials when they are less than 10 wt.%. The second one is milling media to reduce the size of Mg particles efficiently by its sharp and hard edges. TEM observation shows the particle size of MgH_2 is around 20-60 nm in the presence of 30 wt.% of anthracite coal after 3 h of milling and, meanwhile, the crystal grain size is approximately 29.7 nm from XRD analysis. The third role is lubricant to prevent the particle shape from becoming irregular. TEM observation shows MgH_2 particles are oblique hexagonal prism. In addition, morphology observation indicates that the coal can separate Mg particles to prevent them from melting together, and FT-IR analysis shows that hydrogen can chemically absorb on the surface of coal with abundant surface dangling bonds induced by milling. The hydrogen capacity of coal is over 1.39 wt.% on hydrogenated carbon basis determined by volumetric method.

Thermal Cracking of Representative Model Compounds of Low Temperature Coal Tar

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The thermal cracking behaviors of representative compounds of low temperature coal tar were systematically investigated using single stage fixed-bed reactor under hydrogenating and non-hydrogenating conditions. The effects of toluene as both solvent and cracking initiator on the thermal cracking behaviors of compounds were elucidated. The products were identified by means of gas chromatography (GC) and gas chromatography mass spectrometry (GC-MS). Results indicate that, the primary reactions occur as gas-phase; the conversion ratio increases with the temperature increasing. The partially thermal cracking of solvent offers the active radical species to accelerate the formation of low molecular substances; herein, gaseous matters are dominating over 90% of total products, and the reaction prefers to generate smaller molecular hydrocarbon, such as C1 and C2.

Catalytic Upgrading of Coal Pyrolysis Tar over Char-Based Catalysts

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Catalytic upgrading of coal pyrolysis tar was investigated in a dual-stage reactor over char without and with impregnated metal species (denoted as metal-char). The metal precursors are metallic chlorides including $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$, and the char was made by pyrolyzing the tested coal in N_2 at 800 ℃ for 3 h. The pyrolysis integrated with a downstream secondary upgrading caused the lower total tar yield and the higher non-condensable gas yield but the fraction of light tar (boiling point < 360 ℃) obviously increased to allow slightly higher total yield of light tar, which would greatly facilitate the downstream processing for the tar. When the secondary upgrading at 600 ℃ over a layer of char having a mass of 20% of the tested coal, the resulting gas yield and light tar fraction in the tar increased respectively by 31.2% and 25% in comparison with the coal pyrolysis only at 600 ℃. Over the metal-char catalysts, which were 5% of the tested coal in mass, good upgrading effect was obtained at 500 ℃. The catalytic tar-upgrading activity decreased in an order of Co-char > Ni-char > Cu-char > Zn-char, and over Ni-char the realized light tar yield and its content in the tar increased by 14.1% and 30.8%, respectively. The upgrading effect also lowered the contents of element N and S in the resulting tar by 44.8% and 48.2%, respectively. NH_3-TPD clarified that the acidity of the char-based catalysts increased when a metal was impregnated, and the order in acidity was the same as for the upgrading activity shown above. Consequently, the secondary catalytic cracking involved in coal pyrolysis mainly converted heavy tar components (pitch) into light tar and pyrolysis gas, and the acidity of the catalyst played an important role in determining the upgrading effect.

Modeling and Simulation of Coal Devolatilization Behavior of Single Particles with Different Heating Rates

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Coal devolatilization is believed to be the first important chemical conversion step in most of coal utilization processes, as the heating history and release of volatile matters in coal particles have a significant impact on the overall reactor performance. A comprehensive heating and devolatilization mechanism model with special consideration of the *particle-scale physics* (such as the heat transport inside particle) was established to better understand the basic rules in coal devolatilization under different conditions, especially under some extreme conditions (such as high temperatures greater than 1800 K and milliseconds of reaction time). The chemical percolation devolatilization (CPD) model was improved based on the experimental data of coal pyrolysis, which was further applied to describe the physical and chemical transformations of various kinds of coal to explore the dominant role of coal rank in coal devolatilization process. The predictions of the improved CPD model agreed well with the experimental data under different conditions.

The effects of surrounding gas temperature, gas composition and particle size on particle heating history and coal devolatilization behavior were simulated based on this mechanism model. The results revealed that the heat transport resistance inside particle is of great importance for large particle heating in pure hydrogen atmosphere, which would impede the thermal energy transportation from surrounding gas to the particle. The heating rate and devolatilization time were then related to temperature of surrounding gas, thermal conductivity of heating gas, and diameter of particles. It was summarized that the coal devolatilization time has excellent linearity with the particle heating rate using the double logarithm coordinate, independent of the operating conditions and coal ranks.

According to the proposed single-particle heat transfer model, it was recommended that the particle residence time in high temperature zone should be larger than the corresponding coal devolatilization time under the same conditions in the practical application. Since the proposed model works well in understanding the heating history and devolatilization behavior of a single particle with different heating rates, this model can provide more scientific foundation to help design the industrial reactor, eventually to guarantee the overall coal conversion performance.

A Study on Tar and its Hexane Soluble Fraction Produced in Pyrolysis of 23 Chinese Coals

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Pyrolysis is regarded as a simple method to directly obtain oil from coal. The condensed volatile product of coal pyrolysis, however, is tar, a complex mixture containing not only oil, but also compounds difficult to be refined such as asphaltene, pre-asphaltene and even solids. With a huge amount of coal pyrolysis studies in the literature it is still not clear about the oil content of tar and its variation with coal rank. Furthermore, most researches studied mainly the total tar yield in broad temperature ranges with little attention to yields of tar and oil with an incremental change in pyrolysis temperature.

This presentation reports pyrolysis results of 23 Chinese coals with attention on yields of tar and oil in 5 temperature ranges, 110-300, 300-400, 400-500, 500-600, and 600-800 ^{o} C. The experiments are carried out in a fixed-bed vertical quartz reactor from ambient temperature to 800 ^{o}C at a heating rate of 10 ^{o}C/min under an N_2 flow of 100 ml/min. The tars collected sequentially in the temperature ranges are extracted by hexane to determine the yields of hexane soluble fractions (HS, representing oil), which are then characterized by HPLC. The yields and HS composition are correlated with coal rank (C%). It is found that the peak temperature of tar formation increases with an increase in C% of coal. The HS yields are generally about 1.5 wt% of coal and their formations, which reach the maximum at the C% of 81, have a small change with increase of coal rank. The HS consist of mainly 1 and 2-ring aromatic compound groups with the highest yields at pyrolysis temperatures of 400-500 ^{o}C. The aliphatic contents of HS are low but observed at all pyrolysis temperature ranges. Detailed results and discussion will be presented in the conference.

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Separation and Identification of Low Temperature Coal Tar Compounds Using Silica-Gel Column Chromatography

Xiongchao Lin, Ying Yang, Deping Xu, Yonggang Wang, Yi-Ming Hu, Hai-Yong Zhang, China University of Mining &Technology, CHINA

The n-Hexane soluble fraction of coal tar derived from low temperature pyrolysis of a brown coal was separated using a silica-gel column chromatography (SGCC). A series of fractions were successfully eluted by nine different mobile phases in sequence with polarity from weak to strong. All fractions were identified and analyzed by Gas Chromatograph Mass Spectrometry (GC-MS). Results indicate that chromatography combined with SGCC was an effect approach on the separation and analysis of low temperature coal tar. More than seventeen fractions were separately obtained through SGCC process including aliphatic chains, olefinic groups, naphthalene homologues, biphenyl homologues, 3-ring system, 4-ring system, oxygen-containing compounds, phenols, nitrogen-containing compounds and residue fractions, etc. And moreover, the order of each fraction from the SGCC extractions was aliphatic chains > olefinic groups > 2-, 3-, 4-ring aromatic systems > O-containing compounds > phenols > N-containing compounds.

Effect of Tetrahydrofuran Extraction On XLGL Lignite Pyrolysis in N_2 Atmosphere

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It is considered that coal consists of mobile and fixed phase which will exhibit different performance during thermal conversion. In this work, Xilinguole lignite (XLGL) was extracted with tetrahydrofuran (THF), and the effect of the extraction on coal pyrolysis was investigated at 450^{o}C~700^{o}C under N_2 atmosphere. The results indicate that the variation of extract yield along with time is in accordance with Logistic equation. The pyrolysis results of XLGL and its extraction residue (XLGLR) show that the tar yield of XLGLR is lower than that of XLGL due to removal of extract, but the temperature with maximum oil yield of XLGLR is about 50^{o}C lower than that of XLGL. When the weight loss of extract (XLGLE) pyrolysis in different temperature was added to XLGLR tar yield, the total yield is higher than tar yield of XLGL at 400^{o}C ~600^{o}C. XLGLR pyrolysis shows lower water yield and higher gas yield than XLGL, but similar char yield. These results indicate that the extraction pretreatment is beneficial to adjust the product distribution to form more tar and gas. Schafer method was used to determine the total acidity and acid distribution of XLGL, XLGLR and their chars obtained at 600^{o}C. The results show that the –OH variation of XLGLR during pyrolysis is larger than that of XLGL although –OH is the main oxygen contained group. GC analysis of pyrolysis gas shows that the gas from XLGLR pyrolysis has slightly higher contents of H_2 and low carbon hydrocarbon than that from XLGL. ^{1}H and ^{13}C NMR of tar indicate that the tar from XLGLR has higher aromaticity than that from XLGL. GC analysis of tar shows that the phenols in XLGLR tar are significantly higher than those in XLGL tar at the same pyrolysis temperature, especially at higher temperature.

Composition and Utilization of the Co-Products from Lurgi gasifier

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During the coal gasification of coal utilizing Lurgi's FBDB Gasification Technology for the Production of Raw Gas, by products with the majority of various hydrocarbons in liquid streams are produced. A detailed analytical study of the by-products on its composition and chemical structure was carried out for the further processing and utilization. In this study, the comprehensive analysis results show the possibility of the effective utilization of the by-products.

In this work, to analysis the chemical composition of the by-products, GC/MS and comprehensive GC/MS were used to analyze the volatile fractions of the byproducts. An efficient method is developed for the simultaneous determination of aromatics, aliphatics and phenols present in the by-products. The analysis results shows the light fraction is characterized by a high aromatic content of Benzene , Toluene and Ethylbenzene & Xylene (BTEX), whereas various heavier fractions contains non trivial mixtures of compounds with no large concentration but a limited number of chemical classes, where the focus of the study was on classes of compounds instead of individual compounds. Moreover, since the structured chromatograms produced by comprehensive GC allow clear visualization of chemical classes, the similarities and differences between samples were also studied.

For the non-volatile of the by-products, the use of Gel permeation chromatography and Thin-layer chromatography as a separation tool were studied to fractionate the by-products into different groups of compounds, these are aliphatics, aromatics and acids. The FT-ICR MS was used to determinate the elemental composition, $C_cH_hN_nO_oS_s$ and identify the compound classes.

The results from our study shows that the by-products is an important feedstock for aromatic chemicals, especially chemicals and carbon-based materials. Therefore, as a feed stock for aromatic chemical, specialty chemicals is the promising way for high-value utilization of the by-products from Lurgi gasifier.

Effect of the Group Composition of Low Rank Coal on Combustion Reactivity

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Combustion for electric power generation is the most important commercial utilization of coal, and will remain in the next several decades. However, the behavior of coal combustion is complicated because coal is not a homogeneous chemical compound, instead is a composition of a wide variety of hydrocarbon compounds and heteroatom-containing compounds with lots of chemical structures largely unknown, esp. for low rank coal. Small molecules that are widely known as parts of the coal structure have strong influence on the combustion reactivity of coal. Nevertheless, the fundamental understanding of the influences and the correlation between the small molecules and the coal combustion behaviors is insufficient to support the development of coal combustion technologies. In this paper, the low rank coal is subject to extract with several solvents, so that the extracts and residues with different composition are obtained. The extracts are analyzed by GC/MS, and the combustion behavior of residual are tested by thermogravimetric (TG) analyzer. The effect of the extracted group composition on the ignition index, combustion reactivity and burnout index of the coal are disclosed accordingly.

POSTER SESSION 7
COAL MINING

Strata Response Principle and Stress Distribution Characters of Pre-Driven Recovery Room

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Pre-driven recovery room provide opportunity to improve the moving speed of mining equipment. But complex stress distribution around recovery room that interfere in the transfer mechanics of the normal loading. Coal pillar stress, Convergence, shield load and roof sag were monitored around the recovery room of 4302 working face in Sihe coal mine of the Jincheng coal district in China. It evaluates load transfer mechanics along the working face.

The Reasonable Analytical Value of Canopy Aspect Ratio of the Two-Leg Shield Powered Support

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Basing on the distribution regulation of load of canopy, this paper makes the force resolution of hydraulic leg's load on the canopy and according to the mechanics model of elastic rock beam, the paper analyses the roof stratum's defection changes resulted from the powered support in terms of coal mining face with and without immediate roof, so to reduce the position of load of overlying strata above mining face on the powered support and get the canopy aspect ratio, that is the ratio between the length of the forward canopy projection (the distance of canopy tip contact to top dead centre of leg) and the length of the rear canopy projection (the distance of rear contact point of canopy to top dead centre of leg), analytical solution of canopy of two-leg shield powered support. The results show that analytical solution is in basically consistent with the empirical data, so as to give a theoretical explanation of acting mechanism and distribution of powered support's outer load on the canopy.

Study on Spreading Route of Micro-Seismic Initial Arrival Wave in Rock Strata

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In order to rationally explain the spreading route of the micro-seismic initial arrival waves in the strata and improve the monitoring and measuring accuracy of the micro-seismic monitoring and measuring system, from the abnormal phenomena of the site micro-seismic spreading, with the basis theory of seismic wave, a model was established individually with the spreading way and route of the seismic initial arrival wave in the single rock stratum and interface of the passed rock strata. The analysis on the spreading route of the micro-seismic initial arrival wave when the seismic sources and the seismic collector in a same rock stratum or not in a same stratum as the initial arrival wave passing the interface of the rock strata. Based on the circumstances, the seismic collector layout principle of the micro-seismic monitoring and measuring system was optimized. With the site correction, the horizontal directional position error of the micro-seismic monitoring and measuring system could be reduced from 37.5m before optimized to 5.7m and vertical directional position error could be reduced from 33.4m to 3.0m. Thus the abnormal phenomena of the micro-seismic spreading was solved in certain degree.

Gas Monitoring as a Prevention System of Mine Workings in Polish Coal Mines

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Due to the depth of mining in Polish coal mines some co-existing hazards, such as methane, rock burst or spontaneous fires ones, occur. Systems preventing from natural hazards must ensure the safety of conducted mining work.

This paper presents mining regulations concerning using automatic methanometry, which must be observed in Poland. The main principles of building in gas sensors as well as air thermodynamic parameters in mining areas and development headings are presented. The principles are presented on the basis of monitoring examples and controlling methane and fire hazards in driven headings and longwalls ventilated by means of U and Y ventilation systems. Special emphasis is given to extra prevention measures in roadways and in a methane drainage system, which are not required by regulations, but which are taken in mines. Such prevention systems considerably improve safety in Polish coal mines.

POSTER SESSION 8
SHALE AND COAL BED GAS

Adsorption Isotherm Measurements of Gas Shales Using Rubotherm Microbalance for Subsurface Temperature and Pressure Conditions

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The global average temperature has increased consistently over the last century, partly due to the observed increase in the atmospheric carbon dioxide concentration. One possible approach to stabilize and reduce CO_2 emissions is to capture at point sources, inject and store CO_2 into gas shale, where significant amounts of methane are present and can be exploited and recovered. Due to a higher adsorption affinity for CO_2 on carbonaceous materials, in comparison with methane, the adsorbed methane inside the gas shale may be displaced by the injected CO_2, thereby potentially enhancing methane recovery efficiency. However, the adsorption properties of CO_2 and methane on gas shale are not fully understood, and need to be investigated in detail experimentally and theoretically.

In our recent work, the excess adsorption isotherms of CO_2 on gas shale samples have been measured under subsurface temperature and pressure conditions, using a Rubotherm magnetic suspension balance.

A sample from the Eagle Ford reservoir in Texas, United States is used in this study. The temperature was set at 125 °C, which is the subsurface temperature for the shale sample, and measured the adsorption isotherm under varying pressure conditions. The sample was studied in both core chip and powdered forms. Our preliminary results show that under 140 bar, the shale sample in chip form gaives a gas capacity of around 0.02 gram of CO_2 per gram sorbent, while the same sample crushed into powder has a higher gas capacity of 0.06 gram of CO_2 per gram sorbent. A possible explanation for the higher gas capacity of the powdered sample is that it is easier for gas molecules to get adsorbed on the powder, since the macropore mass transfer resistance has been reduced by crushing the core chip. Therefore, the adsorbent sites become more accessible. In order to further investigate the adsorption properties of gas shale, adsorption isotherm measurements are underway for carbon-based and clay-based model materials to determine the relative roles that each of these natural systems play on the overall shale adsorption mechanism and capacity estimates.

Evolution Characteristics and Mechanism of Macromolecular-Nanopore Structure in Tectonically Deformed Coals

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The macromolecular structural evolution could induce changes in the nanopore structure of Tectonically Deformed Coals (TDC), which is the most important reservoir space for Coalbed Methane. The X-ray diffraction, fourier transform infrared spectroscopy, laser raman spectra and low-temperature nitrogen adsorption methods are applied to investigate the evolution characteristics and echanism of macromolecular-nanopore structure in TDCs, using coal samples from Huaibei-Huainan coalfield. The total aromatic ring and secondary structural defects that were generated in brittle deformational coal are fewer than those in ductile deformational coal. The results show that tectonic deformation with different deformational mechanisms (the ductile and the brittle deformation) breaks off the side chains (eg. aliphatic functional groups and alkene branched chains) of coal and produces the secondary structure defects, consequently reduces the structural stability of TDC, especially in ductile deformation, which means that the ductile deformation promotes the polycondensation in macromolecular structure of TDC.The conventional classification of primary structure of coal is not suitable for TDC due to tectonic deformational influence. The Table.1 is a combined classification from Hodot BB (1966), IUPAC (1982), Ju Yiwen (2005), Yidong Cai (2013), which is suitable for study on the nanopore structure of TDC. When d > 5nm, Surface Area and Volume have a good linear relation in brittle deformational coal, so mesopore and micropore are the main pore types in brittle deformational coal. But when d < 5nm, the volume decreases with the surface area increasing, so in ductile deformational coal the main pore types are sub-micropore and super micropore. Coal is composed by pores with different sizes and shapes andaromatic rings which are distributed around the pore walls. Pore is composed by variety of aliphatic functional groups, branched n-alkane chains that have broken off and the secondary structural defects in the macromolecular structure itself. The changes of macromolecular structure can affect the nanopore structure; include increasing the ultra-micropores and sub-micropores with the similar size of secondary structure defects, and promoting an interconversion among ultra-micropores, sub-micropores and micropores. The pore (2–5 nm) is the primary control on gas adsorption capacity (Cai Y et al., 2013). More occurrence space for CBM exists in ductile deformational coal than in brittle deformational coal or primary structure coal. It could explain the outburst and explosion of gas occurs in TDC, especially in ductile deformational coal. Therefore, tectonic deformation changes the macromolecular structure and produce secondary structure defects of TDCs, which are the main reasons for the coupled relationship between macromolecular structure and nanopore structure. Furthermore, the structural evolutions result in the differences of physical properties in TDC.

Application of Support Vector Machine on Organic-Rich Shale Lithofacies Identification: Shading Light on Predicting Marcellus Shale Productive Zones

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The shale reservoirs generally possess quiet distinct characteristics from conventional sandstone and carbonate reservoirs, especially the extremely low matrix permeability and organic matter richness. No economical gas flow could be achieved without hydraulic fracturing. The fracability, largely influenced by mineral composition, has been considered as one of the most important parameters for shale-gas reservoir evaluation. The total organic carbon (TOC) can clearly indicate the gas content due to the ‘self-source and self-reservoir’ feature of shale reservoirs. Through building 3-D model, shale lithofacies, primarily defined by mineral composition and organic matter richness, has shown advantages in recognizing productive zones of shale-gas reservoirs, designing horizontal wells and stimulation strategy, and aiding in understanding organic-rich shale depositional process.

A detailed 3-D shale lithofacies model depends on the integration of core data, wireline logs and 3-D seismic volumes, and bridging core-defined lithofacies with conventional logs is the critical step to provide reliable constraint data for geostatistical modeling. However, the relationship between lithofacies and wireline logs is complex and nonlinear, which could be solved by intelligent methods, such as artificial neural network (ANN) and support vector machine (SVM). The formulation of SVM utilizes the statistical learning theory and structural risk minimization principle which has been shown to be superior to the traditional empirical risk minimization principle employed by ANN. In practice, the SVM is easier and costs less time to training. With regard to the Marcellus Shale lithofacies identification, the SVM method gives higher cross-validation right ratio than ANN methods.

The pre-processing of training dataset, including normalization and the feature space selection of input variables, is extremely significant for any classification methods. Instead of using principle component analysis and stepwise discriminant analysis, we focused on the design of input variables through petrophysical analysis along with normalization of each logs. Eight parameters have been developed to enhance the ability of conventional logs in predicting shale lithofacies.

In this paper, we proposed the approach to identify shale lithofacies by SVM method and took Marcellus Shale in the Appalachian basin as an example to demonstrate its ability. A universal flow chart was also developed to guide the organic-rich shale lithofacies study in other basins.

Characterization of Organic Species in Liushuhe Oil Shale using GC/MS and DART/MS

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Identifaction of organic species in oil shale is benefit to the enrichment of organic geochemistry information and efficient utilization of oil shale resource. In the present study, the Liushuhe oil shale (LSHOS) from Heilongjiang province was extracted sequentially with carbon disulfide (CS_2), benzene, methanol, acetone and tetrahydrofuran (THF) under ultrasound condition, affording extracts E_1 to E_5, respectively. All of the extracts were analyzed with Gas Chromatograph-Mass Spectrometry (GC/MS), Direct Analysis in real time-Mass Spectrometry (DART-MS) and Fourier Transform Infrared Spectroscopy (FTIR). The results showed that the predominant components in E_2 were alkylated arenas, which accounted for more than relative content of 60 %. Moreover, the alkanes in E_2 have a carbon number range from C_{11} to C_{21}. Different from those in E_2, alkanes, alkylated arenas and oxygen-containing compounds have similar relative content (about 28 %) in E_1, and the alkanes in E_1 have a larger carbon number range from C_{13} to C_{31} with a predominance of odd carbon-number homologues. The main oxygen-containing compounds are alkyl alcohols and alkyl ketones both in E_1 and E_2. None compounds were detected in E_4 and less than 25 compounds were detected in E_3 and E_5, which are possibly ascribed to the polar compounds and high molecular weight (MW) compounds cannot vaporize in GC/MS. According to the results of DART-MS analyses, the MW of most compounds in E_2 and E_4 are less than 300, implying that these low MW compounds in E_4 might have high polarity. Nevertheless, many peaks with high mass-to-charge ratio (m/z > 500) were detected in the mass spectra of E_3 and E_5. Additionally, LSHOS and its extraction residue were characterized using proximate, ultimate and thermogravimetric analyses etc.

Numerical Simulation on Formation, Dissipation, and Retention of Coalbed Methane Containing Biogenic Gas in Luling Gas Field, China

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Coalbed methane (CBM) mixed by thermogenic and biogenic gases has been subsequently discovered and reported in the coal-bearing basins of the word. It is important to quantitatively investigate the relative amount of biogenic gas in CBM reservoir and the process of accumulation. To understand these, the Luling CBM exploitation site is taken as the study area. Based on the studied of geological evolution history and modified of CBM hydrocarbon model, accumulation characteristic of biogenic gas and accumulation effect of biogenic and thermogenic gases are emphatically discussed by using numerical simulation technology. Biogenic gas contributed to the methane content of coal seam presently is also quantitatively studied. Results show that biogenic gas has obviously contribution on cumulative gas production and gas content in the coalbed. An obvious periodicity exists in the process of CBM accumulation. The evolutionary process of CBM can be divided into three stages. They are primary biogenic gas, thermogenical gas, and secondary biogenic gas accumulation evolution stage. CBM containing biogenic gas migrate mainly in the way of diffusion, percolation, and cap outburst dissipation. However they migrate in different way at different evolution stage. In addition, primary biogenic gas has relatively small contribution on the gas content of coal seam presently, whereas secondary biogenic gas has much. Moreover, the content of primary biogenic gas occurred in the coal bed at Luling gas field is from 0.40 to 0.97 m^3/t, whereas the content of secondary biogenic gas is from 7.92 to 7.95 m^3/t.

Comparative Study of Enrichment Characteristics and Mining Technology of China’s Coalbed Methane and Shale Gas

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Coalbed methane and shale gas are important unconventional resources. At present, the coalbed methane in China has been produced commercially; however, the shale gas production is still at experimental stage. The source rocks of coalbed methane and shale gas will occur together in some energy basin, and they may be adjacent or in near or far layers. Although coalbed methane and shale gas are different in several aspects, such as their sources and occurrence layers, there are some similar situation, including the enrichment characteristics, the migrating procedure and the developing technology. The coalbed methane mainly enriches in the coalbeds with adsorption state, while shale gas enriches in the organic-rich mudstone or shale with adsorption and free state. Both coalbed methane and shale gas store in reservoirs with low porosity and permeability, and all their mining technology includes evaluating, testing, drilling and reservoir stimulation. If coalbed methane and shale gas occur in the same basin, then they could be exploited by the same well, therefore their exploiting efficiency will be improved, and the unconventional natural gas industry will be developed rapidly.

Optimization Method of Reasonable Formation Pressure Level in the Development Process of Coalbed Methane Wells

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According to the production process of coalbed methane wells, four stages are divided: drainage and depressurization stage, production rising stage, production stabilizing stage and production descending stage. The coalbed methane desorption-seepage continuous flow equation is established, and the optimization method of reasonable formation pressure in coalbed methane wells is also determined based on the desorption and seepage theory. That is, combine the theoretical method with the actual production information, the paper analyses the influences of the formation pressure drop speed on the time and value of peak production as well as cumulative production, optimizes the reasonable pressure drop speed of coalbed methane wells in the process of draining and producing in Jincheng area, China. Formation pressure drop speed can influence the peak production value and the time of it, the influence is calculated with practical data in this paper. The control function of the draining and producing system to the formation pressure, stable production period and the yield is also analyzed. Combine theoretical calculation with actual production information, the reasonable producing system is put forward: increase water-output rate appropriately in the drainage and depressurization stage; reduce water-output rate in the production rising stage; keep the displacement stable in the production stabilizing stage, and control the water production properly in the production descending stage. The research results have guided the field production effectively.

Productivity Prediction Model Establishment and Numerical Simulation of Coalbed Methane Wells

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Coalbed methane is stored in coal seam at an adsorption state, desorption-diffusion-seepage are the three different physical processes when developed. The effect of matrix porosity-cleat-artificial fracture in coal reservoir on coalbed methane production process is analyzed in detail. The fracturing fractures are regarded as the extension of wellbores, because the percolating resistance of coalbed methane in fracturing fracture is very small. Reasonable physical model of coalbed methane flow is designed based on this. According to Fick's law, Langmuir adsorption equation and Darcy's law, the continuity equation of coalbed methane output was established by law of mass conservation. The numerical simulation software of coalbed methane vertical wells fracturing producing is compiled on the basis. The influence of different factors on the capacity, the formation and extension of pressure drop funnel is analyzed using the software. The influence of permeability, initial formation pressure, Langmuir adsorption capacity on production and formation pressure distribution is relatively significant. Coal seam thickness has an obvious impact on the output, whereas it has little relation with the formation and extension of pressure drop funnel. The software has functions of historical matching and prediction. By matching the coalbed methane well production based on field practical data, the future production can be predicted accurately, thus providing the basis for the implementation of coalbed methane well production measures.

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The Major Geological Characteristics of Organic-bearing Shales: In Coal-Bearing Rock Strata from Huainan Mine, China

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Huainan mining area is located at the junction of the North China plate and South China plate area, which is affected by collision and collage between North plate and South plate, and suffers from Qinling - Dabie - Sulu orogenesis’s impact in the early Mesozoic, forming a complex and unique fold fault system. Huainan coal mine developed several sets of coal strata, we colleceted 19 shale samples from coal seam's roof and floor in Xieqiao mine, Zhangji mine, Xinzhuangzi mine, Panji mine in Huainan. By collecting relevant geological information for the study area and summarizing experience in successful gas shales, this manuscript make full use of organic geochemical testing, and high pressure mercury and other experimental testing methods to research shale’s main geological characteristics of Huainan coal-bearing strata. Classic gas shales investigation methods, X-ray diffraction and High pressure mercury, were coupled with standardized organic geochemical analysis procedures, such as total organic carbon determination.Furthermore, adsorption isotherm tests was conducted and analyzed.

Some conclusions are drawn:(1) Shale in Huainan coal-bearing strata has moderate organic carbon content, TOC average content of 1.98%，varying between 0.13%~8.58%. The organic matter type is mainly Ⅲ and a little Ⅱ$_b$. Thermal evolution of organic matter are relatively low, ranging from 0.61% to 1.48% R_o, the average is 0.93%R_o; (2) Mineral composition of shale mainly consists of clay minerals and quartz. Clay mineral content rangs from 27.6%~74.5% and average is 52.24%, while content of quartz rangs from 13%~55.8% and the averageis 35.08%. Carbonate, K-feldspar and plagioclase feldspar have very little content.Kaolinite content is highest among clay minerals,illite / smectite mixed layer minerals comes second.The concentrations of kaolinite average content is 67.05%, the average content of illite / smectite mixed layer minerals is 31.26%; (3) Effective porosity of shale is mainly ranging from 2% to 8%, and permeability is mainly distributed in (0.01 ~ 0.05) × 10^{-3}μm^2 range. Dark shale in the study area have its pore throat radius mainly distributed between 0 ~ 0.1um. Moreover, we conclude that the organic matter is the most important factor affecting the adsorption when we analysis the data of the different adsorption experiments. Meanwhile, adsorption properties of organic-bearing gas shale is closely related to reservoir pore system. From the isotherm curve we may infer that when the pressure is smaller（such as 4.6Mpa）, an open pore play a key role; However with the pressure increases the semi-open pore dominant and adsorbed gas gradually increase.These results will infavor of further evaluation of the hydrocarbon potential of the coal-bearing strata shale in China and provide a theoretical basis for coalbed methane and shale gas multiplayer producing in the future.