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**ABSTRACTS BOOKLET**

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SUSTAINABLE DEVELOPMENT



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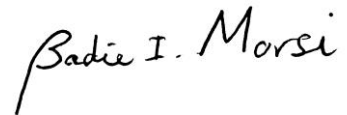
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On behalf of the Thirty-First Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation to Mrs. Heidi Peck for her dedication and professionalism; and Dr. Laurent Sehabiague and Mr. Omar Basha for their invaluable assistance in preparing this Abstracts Booklet.

Thank you,

A handwritten signature in black ink that reads "Badie I. Morsi". The signature is written in a cursive style with a large initial 'B'.

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

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**SESSION 1**  
**Clean Coal Demonstration and Commercial Projects: Future of Coal**

**The Evolving Role of Declining US Coal**

James Stevenson, IHS Energy, USA

Coal in the US has undergone a series of major transitions over the past decade, due to changes in the global coal markets, the domestic competitive landscape, and the regulatory environment. More changes are coming. Domestic coal consumption is in decline, but it is not a smooth decline, with coal being called upon to make up periodic demand surges – a role to which it is not well suited. How will these changes shape US coal going forward? How will US coal react to the international coal market as it evolves over the coming decades? We present the IHS Energy outlook for US coal through 2040.

**Outlook and Opportunities in the U.S. Coal Market**

John Bridges, J.P. Morgan Securities LLC, USA

We see US coal as a fuel of the past present and future. While a gradual decline in coal's contribution to the energy mix should be expected, having a mixed portfolio of energy sources is important as was seen last winter when gas shortages threatened the power grid. The US coal space is adjusting to the challenges of new emissions controls, low priced natural gas and poor rail service. We expect the next few years to be volatile as the shale gas industry finds markets for its products. However, we expect a smaller more efficient coal sector to emerge with a bigger export footprint. We analyze the impact of these market forces and discuss the best strategies and investment opportunities in the coal space.

**Making Room for Coal Generation Under the NSPS Rule**

Joel Theis, DOE/NETL, USA

Currently, a large amount of coal capacity is expected to retire due to EPA regulations, thereby creating a need for new baseload generation. Baseload capacity is inherently a high capital cost resource, and whether markets are regulated or restructured, investors will need an incentive to build any type of baseload capacity. The analysis presented demonstrates how new coal generation with carbon capture, and utilization or storage, could be viable under certain tax incentives. A case is made on how investment and production tax credits at levels similar to those enjoyed by renewable energy could succeed in making coal and CCS commercially viable. In addition, we argue that the industry would benefit by modifying current capacity markets to be more conducive to the construction of baseload capacity by implementing a process that enables the initiation of long-term multi-lateral contracts.

**The Importance of Baseload Power Renewal**

Peter C. Balash, DOE/NETL, USA

An examination of historical trends involving electricity generation and economic growth indicates that there is a profound need for new baseload power expansion. In addition, the age profile of the existing baseload power fleet, both coal and nuclear, raises concerns about the viability of relying on this fleet for substantial levels of generation. The analysis suggests that several hundred gigawatts of baseload capacity may be needed over the next twenty-five years. The timing of impending coal plant retirements, set against long-term projections of new gas-fired capacity, gives rise to reliability issues. These issues highlight risks of lessening fuel diversity when utilization of one source, natural gas, is expected to grow in multiple sectors simultaneously.

**Coal's Future in a Carbon-Constrained World: How Did We Get Here, and Where Do We Go Now?**

Eric Grol, DOE/NETL, USA

The recently proposed New Source Performance Standard (NSPS) and Existing Source Performance Standard (ESPS) will limit CO<sub>2</sub> emissions from new and existing electric generating units, respectively. These rulemakings are anticipated to have a significant impact on the future use of coal for domestic electric power generation. This presentation will discuss the technical and market implications of these rulemakings, with an emphasis on coal's future in this new energy paradigm.

In the near term, construction of new supercritical coal capacity has fallen dramatically, due to the NSPS requirement that all coal generation meet an emission

limit of 1,100 Lb CO<sub>2</sub>/MWh. This mandate requires the use of carbon capture and storage (CCS) on any new coal facility.

In the longer term (2020 to 2030), operating hours of existing coal units are expected to be cut significantly, due to a component of the proposed ESPS that encourages expanded dispatch of existing natural gas combined cycle ahead of coal. This reduction in coal operating hours is particularly problematic for utilities that decided to implement capital-intensive environmental retrofits for other recent regulatory initiatives, such as MATS and CSAPR: these units will have difficulty recovering their retrofit costs and meeting return on investment goals, if their annual operating hours are reduced due to the proposed ESPS.

This presentation will provide an in-depth explanation of the technical and economic rationale used to support these rulemakings, as well as the expected electricity, coal, and natural gas market implications. Finally, suggestions on how coal can remain an economic and dependable option for domestic fossil energy use will be offered.

**SESSION 2**  
**Coal Mining: Geological and Ground Control Issues**

**Geotechnical Studies Related to Crossing a Geologic Fault Using a Longwall Mining Method**

Yoginder P. Chugh, Harrold Gurley, Behrooz Abbasi, Southern Illinois University Carbondale; Joseph Hirschi, Illinois Clean Coal Institute, USA

The goal of this study was to assess if analytical tool/s and data can be developed to quantify incremental displacements around a geological fault as longwall face moves toward it and past it. Such data would be invaluable to plan mining layout and ground control and to ensure safety of mine workers while maintaining production. A coal company was faced with crossing a 3-m fault in the development entries and the face while mining a 375 m wide longwall face. Limited data was available on the geometry of the fault. There were concerns related to spatial displacements along the fault plane as the face approached and crossed it. These could result in additional loading on the development entries as well as in the face area that could affect ground control in the face area. A field monitoring and observational study and numerical modeling study was performed to develop data that would assist the company to plan for additional supports in the development entries and take appropriate safety measures while advancing toward the fault and crossing it. Field measurements consisted of roof-to-floor convergence, and rectangular rosettes in the immediate roof using already installed roof bolts. Numerical modeling consisted of constructing a 3-D structural model using the FLAC3D with the fault plane incorporated as an ubiquitous joint. Limited data on geometry of the fault with estimates of the cohesion and frictional parameters were used for modeling. Based on analyses and field observations data, the coal company was informed of impending movements along the fault plane and associated impacts on the development entries. Additional stiff supports were installed in head gate entries around the stage loader and equipment and 60-m outby of the longwall face (solid). As the longwall face approached the fault, predicted movements were manifested by severe loading on the installed supports. The authors assisted the company efforts in successfully crossing the fault without affecting face productivity.

**Using Shield Leg Pressure Data to Assess Longwall Ground Control Performance in the Face Area**

Yoginder P. Chugh, H. Gurley, Southern Illinois University Carbondale; Greg Smittle, Marco Corporation, USA

Periodic weighting, and formation of roof cavities are common events on a longwall face while mining. Australian mines extensively use shield leg pressure data to successfully provide early warning of such events. However, such studies in Illinois longwall mining operations have never been performed.

SIUC and Marco professionals in USA and Germany are working together with a coal company in Illinois to develop such a capability. Leg pressure data are being analyzed to correlate with weak floor strata characteristics, immediate roof lithology, and presence of geologic anomalies such as faults and dykes. Additional analyses may include effect of shield setting pressure, and face advance rate on ground control performance in the face area.

**SESSION 3**  
**Gasification: General – 1**

**An Overview of U.S. DOE's Advanced Gasification Technologies Program**

Jenny B. Tennant, DOE/NETL, USA

The U.S. Department of Energy's (DOE) Gasification Systems Program's goal is to reduce the cost of electricity with carbon capture, while increasing power plant availability and efficiency and maintaining the highest environmental standards. While it is expected that low natural gas prices in the United States may preclude integrated gasification combined cycle (IGCC) power plant deployment throughout the Nation in the near future, many advanced and developing countries across the world have coal, and will use coal, to make power. Lower-cost IGCC will allow power to be produced from this coal in an environmentally benign way – with carbon capture adding only a minimal economic burden.

A unique feature of gasification is its versatility with regard to the products that can be made, with the potential to both increase a coal conversion plant's profitability and reduce financial risk. To take advantage of this unique benefit, the main emphasis of technology development supported by the DOE Gasification Systems Program is on those technologies that advance progress on the low-cost IGCC with carbon capture goal, as well as on lower-cost gasification and syngas processing for chemical and liquid fuels production. Additional benefits to this approach are: (1) it is more in sync with industry needs, which is important to support U.S. economic stability, and since private cost share is a critical aspect of DOE research and development (R&D) support; and (2) industrial-scale demonstration of IGCC technologies is a lower-cost, less time-consuming, and lower-risk way to transition IGCC technologies into commercially ready packages.

The Gasification Systems Program is currently supporting several major projects, such as: (1) demonstrating, on a 50-MWe industrial gasifier slipstream, an efficient and cost-effective, high-temperature syngas cleaning technology integrated with carbon capture; (2) testing, at multiple tons-per-day scale, a high-temperature ceramic membrane air separation technology, with lower capital cost and energy requirements than conventional cryogenic processes, to produce high-purity oxygen; and (3) developing cost-effective technologies for high-hydrogen content syngas to be used for production of valuable products, such as chemicals, fertilizers, and transportation fuels, as well as high carbon capture IGCC applications. Additionally, the program has been supporting the improvements in reliability, availability, and maintainability (RAM) associated with gasification-based energy conversion systems. These, and several other ongoing R&D projects, support DOE's vision of near-zero emissions power generation by reducing the cost and improving the efficiency of capturing carbon dioxide from syngas derived from coal for production of power and other high-value products.

This presentation will provide a comprehensive evaluation of the technologies being developed, along with a detailed review of advances in gasification-based technologies that will enable low-cost, low-carbon emission, and coal-based energy systems.

**Dry Solids Pump Coal Feed Technologies Program**

Alan Darby, Scott McVey, Aerojet Rocketdyne, USA

Since 2007, Aerojet 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 2013, AR was awarded a new DOE NETL contract for continued development of the high pressure DSP. The Pittsburgh Coal Conference presentation will review the new pump development program and summarize the test activities to date to achieve the ultimate goals of delivering 400 ton per day (tpd) while discharging coal into a 1200 psi feed tank. The presentation will include a summary of the operational theory, then review the program plan, schedule, and results of testing that will be performed through the August 2014. Additionally, a Techno-Economic Analysis will be reviewed to compare the economic benefits of the DSP to the current state of the art lock hopper feed systems. The end product of the program is a commercial DSP that can deliver 1000 tpd of feed stock for future commercial gasification plants.

**Intermediate-Scale Validation of ITM Oxygen Technology**

Andrew W. Wang, Mark D. Hutcheon, Charles M. Woods, Lori L. Anderson, Phillip A. Armstrong, VanEric E. Stein, Air Products and Chemicals, Inc., USA

In the late 1980s Air Products identified a class 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 collaboration with the U.S. Department of Energy, Air Products has made substantial progress in developing ITM

Oxygen technology to be a cost-effective method of production. ITM Oxygen has the potential to integrate well with advanced power generation processes, as well as traditional energy intensive industrial processes requiring oxygen.

A number of important technical and project milestones were achieved in the past year and which will be reviewed in this paper. Most notably, construction of the 100 TPD Intermediate-scale Test Unit (ISTU) and subsequent commissioning of the facility were completed. This included installation and testing of a natural gas-fired expander which has performed as expected and will deliver over 5 MW of gross power production when operated with the ITM membrane system. Ceramtec has produced an inventory of modules for the first phases of ISTU testing. Data from the ISTU will support the design for commercial-scale systems. Progress will also be reported towards the CerFab ITM wafer module manufacturing facility; in 2014 wafer and module fabrication commenced at that facility. Module improvements made by Ceramtec have resulted in greater module mechanical robustness, as evidenced by long-term laboratory tests of a multi-wafer module indicating stable flux and purity performance over 7000 hours on stream through a number of shutdowns and restarts. Future development steps toward a large-scale Demonstration facility will be reviewed, as well as a proposed commercialization strategy and timeline.

**Simulation Research on the Fixed-bed Gasification Process in a Two-stage Combined Gasifier**

Yifei Wang, Weilong Jin, Longchu Zhu, Guangsuo Yu, Fuchen Wang, Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, CHINA

The novel two-stage gasification process which is combined entrained-flow for first stage and fixed-bed for second stage was shown in the study. The benefit of the second stage was to recycle the sensible heat from first stage syngas and enhance the energy utilization. The fixed-bed gasification reaction of second stage was individually investigated by numerical simulation. The simulated results were validated well with the experimental data in terms of gas concentration, gas flow rate and carbon conversion. The distributions of velocity, temperature, gas concentration, solid mass fraction and carbon conversion during the gasification process were analyzed. The influences of coal amount and particle size in the second stage on gasification reactivity were also discussed in the study. Results showed that the gas temperature was reduced and the effective gas concentration increased when first stage syngas flowing through the second stage coal layer. With the proceeding of gasification reaction, the temperature difference and changes of gas concentration become weaker comparing with initial values. The increase of coal amount of second stage showed a more significant heat recovery, but the heating rate and ultimate carbon conversion would be reduced, resulting a little lower gas-solid reaction rate and effective gas concentration in the initial period. The increase of particle size resulted in the decreasing of effective gas concentration and gas-solid reaction rate, which was attributed to the change of specific surface area and the increase heat transfer resistance from the particle surface to inside.

**Syngas-Based Annex Concepts for Chemical Energy Storage within Pulverized Coal Power Plants**

Christian Wolfersdorf, Kristin Boblenz, Robert Pardemann, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

An increasing supply of power from fluctuating renewable energy sources especially in Germany requires improved capability for part load operation of conventional power plants in combination with electricity storage solutions to ensure the security of energy supply.

Differential operational concepts are introduced to link a conventional lignite-fired power plant with a coal-based gasification block of comparatively lower thermal capacity (annex) with subsequent synthesis, dividing the overall coal mass flow into one part for the power plant and a smaller part for syngas production. The annex block comprises coal gasification, water electrolysis, gas treatment and synthesis of a storable fuel or chemical product (SNG, methanol), that can be used externally or for peak load power generation. The annex plant acts as an electricity consumer in times of high renewable energy production (chemical storage of excess electricity), which reduces the overall net power output to the grid of the linked conventional power plant without lifetime-consuming start-up and shutdown processes. In times of low renewable energy production, the annex plant can also provide peak load in line with the actual demand. The concepts are evaluated with the aid of suitable process simulation tools and compared to the single conventional power plant and alternative approaches to utilize and store excess renewable electricity. The focus is put on efficiency, CO<sub>2</sub> emissions and potential to supporting the conventional power plant operation at minimal load.

In case of coal gasification with subsequent CO-based synthesis of SNG, efficiency of the annex plants with different electrolysis capacities varies between 47.3 – 54.9 % (LHV basis). In comparison to other chemical storage concepts, such as the often discussed technology of CO<sub>2</sub>-based power-to-gas with Sabatier process (49.8 – 52.0 %), the annex concepts show a competitive or higher efficiency potential. Moreover, power-to-gas systems require additional effort for the provision of CO<sub>2</sub> suitable for the

SNG synthesis, which is typically not considered in the energy balance of power-to-gas concepts.

Specific CO<sub>2</sub>-emissions of the combined annex and pulverized coal power plant with synthesis and external utilization of SNG are reduced by 13 – 17 % compared to the stand-alone conventional power plant. The minimal load, meaning the net power output to the grid, can be reduced from 40 % for existing lignite-fired power plants to 24 % for annex concepts.

In addition to the improved capability of part load operation, there is a potential reduction of specific investment costs with the annex concepts by taking advantage of the power plant auxiliary equipment and infrastructure, e.g. for the disposal of waste gases, waste water or carbonaceous residues in the power plant.

## SESSION 4

### Combustion: Oxy-Combustion and Chemical Looping - 1

#### Chemical Looping Combustion Reference Plant Designs and Sensitivity Studies

Robert Stevens, DOE/NETL; Richard Newby, Vasant Shah, Norma Kuehn, Dale Keairns, Booz Allen Hamilton, Inc. - NETL, USA

The U.S. Department of Energy (DOE) provides a worldwide leadership role in the development of advanced fossil fuel-based energy conversion technologies, with a focus on electric power generation with carbon capture and storage (CCS). As part of DOE's Office of Fossil Energy, the National Energy Technology Laboratory (NETL) implements research, development and demonstration (RD&D) programs that address the challenges of reducing greenhouse gas emissions. To meet this challenge, FE/NETL is interested in evaluating advanced power cycles that will maximize system efficiency and performance, while minimizing carbon dioxide (CO<sub>2</sub>) emissions and the costs of CCS.

An emerging, coal-fired power plant technology, chemical looping combustion (CLC), is part of NETL's R&D portfolio due to its potential to significantly reduce the cost of producing power with CO<sub>2</sub> capture. In CLC, oxygen carrier particles replace the oxygen source (air or air separation unit (ASU)-derived oxygen) used in the conventional PC plant or in the oxycombustion PC plant. Therefore, CLC technology is, in essence, an oxycombustion technology being developed with focus on its potential for higher efficiency and reduced cost.

This study assesses the cost and performance for reference CLC configurations and evaluates the sensitivity to key CLC parameters. For purposes of the study, an atmospheric pressure, circulating fluid bed CLC process design was selected. Additionally, two oxygen carriers: iron oxide, Fe<sub>2</sub>O<sub>3</sub>, and calcium sulfate, CaSO<sub>4</sub>, were chosen. The former consists of a highly reactive but expensive particle whereas the latter employs a lower reactivity yet cheaper oxygen carrier material. For each of the carrier types, a reference design of the plant system based on a supercritical steam cycle with a conventional CO<sub>2</sub> compression technology was completed to specify operating conditions as well as estimate plant performance and cost by means of process simulation. The resulting temperatures, pressure drops, solids circulation rates, and off-gas compositions are characteristic of each oxygen carrier's properties. For each system, a series of sensitivity analyses were also conducted to evaluate the impact of key operating parameters on the plant's performance and/or cost. The reference design for each carrier system will be presented and compared to the performance/cost of a conventional pulverized coal (PC) power plant using amine-based CO<sub>2</sub> capture. The significance of carrier properties and key operating parameters will be discussed in relation to predicted plant performance and/or cost. DOE intends to use these results to examine the potential for CLC to achieve DOE R&D goals, identify CLC R&D gaps/challenges, and assess potential societal benefits of successful development.

#### Process Design and Parametric Analysis of a Staged, Pressurized Oxy-Combustion Power Plant

Akshay Gopan, Benjamin M. Kumfer, Richard L. Axelbaum, Washington University in St Louis; Jeffrey Phillips, David Thimsen, Electric Power Research Institute, USA

Pressurized oxy-combustion as a carbon capture approach has shown promise to both reduce capital cost and improve power plant efficiency compared to atmospheric pressure processes. Pressurization increases the dew point of flue gas moisture and allows for an economic recovery of the latent heat of condensation. It also reduces equipment size and eliminates air ingress, resulting in higher CO<sub>2</sub> purity in the raw flue gas. The effect of pressurization has been studied over the past few years.

A fuel-staged, pressurized oxy-combustion process to further improve efficiency by eliminating flue gas recycle requirement will be introduced. A fuel staging approach, with proper burner design, allows for control of the temperature and heat transfer during combustion in pure oxygen, eliminating the need for flue gas recycle. The additional potential benefits due to fuel staging are: reduced process gas volume, increased average radiation heat transfer, reduced oxygen demands, increased CO<sub>2</sub> purity, and reduced auxiliary power demands. In the fuel-staged, pressurized oxy-combustion (SPOC) process, combustion is carried in multiple pressurized boilers in

series. A fraction of the total fuel and all the oxygen is injected into the first stage (boiler). The excess oxygen acts as diluent assisting in the control of the temperature of the combustion products and heat transfer rate. After heat extraction from the first stage into the steam cycle, the products of combustion (CO<sub>2</sub> and H<sub>2</sub>O) and the excess oxygen are transferred to the next stage. In stage 2, additional fuel is injected and more oxygen is consumed. The process continues in multiple stages till nearly all the oxygen is consumed.

Plant modeling results show that the SPOC process can increase the efficiency by more than 5 percentage points over the reported first generation oxy-combustion plants. The increased efficiency is due to both an increase in pressure allowing for the recovery of the latent heat in the flue gas moisture, and the staged process allowing for a reduction of the auxiliary load for recycling flue gas. This increase in efficiency and reduced equipment sizes lowers the capital and O&M costs compared to an atmospheric oxy-combustion process.

The performance and cost results of a 550 MWe SPOC power plant modeled in ASPEN Plus will be presented. The effect of process parameters such as operating pressure and fuel moisture on the net plant efficiency will also be demonstrated.

#### Experimental Determination of the Kinetics of Pressurized Oxy-Fuel Char Combustion

Ethan S. Hecht, Christopher R. Shaddix, Manfred Geier, Sandia National Laboratories, USA

Oxy-fuel combustion of coal has received much attention recently as a promising way to continue to generate electrical power from coal while implementing carbon capture and storage (CCS). Utilization of oxy-fuel combustion of coal with CCS could significantly reduce CO<sub>2</sub> emissions and thereby mitigate the climate change due to this greenhouse gas. The efficiency penalty associated with the implementation of oxy-fuel combustion with carbon capture as compared to air-fired combustion without capture (roughly 10 percentage points when using boilers operating at 1 atm) can be reduced by around 3 percentage points to only a 7% efficiency penalty through better heat integration, which can be enabled by combusting the fuel in a pressurized environment. Oxy-fuel combustion of coal under pressure also prevents air leakage into the system and may produce lower NO<sub>x</sub> emissions than oxy-combustion under atmospheric pressure. Kinetic models and rates of pressurized oxy-fuel coal combustion are valuable for system design and process optimization, facilitating rapid implementation of this promising technology.

In this work, we utilize an electrically heated, pressure-capable entrained flow reactor to generate experimental conditions to investigate oxy-combustion of pulverized coal in a pressurized environment. In controlled experiments we conduct in-situ optical measurements of particle temperatures and collect partially reacted chars for analysis of the extent of burnout, using a well-established ash tracer technique. For the optical temperature measurement, we developed a system that includes a horizontal optical probe to collect the thermal radiation from individual particles falling in the vertical reaction tube. The optical probe consists of a water-cooled sheath, collection optics coupled to a fiber-optic bundle that conducts the collected light to a two-color pyrometer. In order to minimize the influence of thermal radiation from the reactor tube wall, a water-cooled background surface is mounted in the wall opposite of the optical probe. In the work presented here we discuss the details of the system design, experimental methods, and present some initial results on the kinetics of pressurized oxy-fuel char combustion.

#### Impact of Oxygen Enrichment on Biomass Flame Stability, Emissions and Burnout

Dale Tree, Steven Owen, Daniel Ellis, Brigham Young University; Yuan Xue, Hwanho Kim, Kenneth Kaiser, Air Liquide, Delaware Research and Technology Center, USA

One of the most significant challenges facing power generation with coal combustion is the need to reduce CO<sub>2</sub> emissions. Co-firing of biomass with coal is a practical approach to CO<sub>2</sub> reduction whereby CO<sub>2</sub> neutral biomass can be used to displace a fraction of the CO<sub>2</sub> produced by coal while utilizing the existing coal infrastructure. Other advantages include potentially lower sulfur and mercury emissions and lower sulfur related corrosion. Aside from fuel delivery, preparation, and availability issues, potential problems with biomass combustion include: increased potassium and chloride (in some fuels) causing deposition and corrosion issues, increased NO<sub>x</sub> formation (in some fuels), poor flame stability and potentially poor burnout. Flame stability and burnout problems are related to particle size which is typically larger for biomass than coal. The objective of this work was to measure and characterize the impact of oxygen enrichment (small flows of localized oxygen injection) on biomass flame characteristics and emissions. Two fuels were investigated, hard wood and straw, which were ground to mean diameters of 500 μm and 300 μm respectively. Variables investigated included oxygen flow rate, oxygen insertion location, and secondary air swirl number. Measurements obtained included flame lift-off, exhaust NO concentration, and loss on ignition (LOI). The results showed that below a calculated swirl of 1.4, the flame began to lift from the burner exit. A trade-off curve between NO and LOI was found whereby decreasing NO can be obtained at the expense of

increasing LOI and vice versa. One can move along the trade-off curve by adding oxygen (increasing NO and decreasing LOI) or by changing the swirl (increasing swirl increases NO and decreases LOI). When oxygen was added to the center tube of the burner, the flame became more attached and was more stable. Adding a small amount of oxygen (~5%) was found to slightly improve the trade-off by decreasing both LOI and NO. Straw particles were more difficult to burn out than wood particles. Straw particles that remained unburned appeared to originate in the knees or connection points within the straw which are more dense and less volatile than the rest of the straw.

#### Experiments on Mercury Oxidation in an Oxy-Fuel Fluidized Bed Combustor

Hui Wang, Yufeng Duan, Qiang Zhou, Chun Zhu, Min She, Southeast University, CHINA

Most emphasis has been put on air-combustion, rather than oxy-combustion in the mercury speciation test and adsorption development. In this work, experiment research has been conducted in a fluidized bed to learn about the impact of combustion temperature, oxygen concentration, and excess oxygen coefficient on homogeneous mercury oxidation under O<sub>2</sub>/CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> combustion. The results suggested both Hg<sub>0</sub> concentration and proportion increased with the increase of temperature in the oxy-coal combustion. Mercury is also primarily in the elemental form at high temperatures under oxygen combustion. The effect of CO<sub>2</sub> weaken mercury oxidation is very huge. The percentage of Hg<sub>0</sub> and Hg<sub>2+</sub> will increase as the excess oxygen coefficient rises under oxy combustion.

### SESSION 5

#### Clean Coal and Gas to Fuels: Syngas to Fuels - 1

##### Pilot-Scale CTL Process Development in Korea

Heon Jung, Korea Institute of Energy Research, KOREA

We have been working on developing a pilot-scale indirect coal to liquids process since 2007. The construction of the pilot plant has finished in 2013 and several test runs were carried out. The plant has a 10-ton-per-day slurry-fed coal gasifier, an acid gas removal unit and a 15-barrel-per-day slurry bubble column Fischer-Tropsch reactor. We have our own iron-based FT catalyst and it was manufactured in a large quantity to be tested in a pilot reactor. The development history and experimental results will be introduced. We have also finished a pre-feasibility study of a demo-scale CTL plant based on our FT technology to be built in Mongolia. Some of its economic data will also be presented.

##### Gasification, Warm-Gas Cleanup, and Liquid Fuel Production with Illinois Coal and Biomass Blends

Joshua J. Stanislawski, Scott G. Tolbert, Tyler J. Curran, Michael J. Holmes, University of North Dakota, Energy & Environmental Research Center; Jason K. Smith, Connecticut Center for Advanced Technology, Inc., USA

The Energy & Environmental Research Center (EERC) is completing a project with the Illinois Clean Coal Institute, the Connecticut Center for Advanced Technology (CCAT), and the U.S. Department of Energy to demonstrate advanced coal and biomass-to-liquid technologies using Illinois No. 6 coal. The project builds on work that is currently under way with CCAT evaluating the performance of coal and biomass blends in EERC gasifiers. The Illinois No. 6 coal and biomass for this test program are gasified in the EERC's entrained-flow gasifier, as high-temperature systems are most suitable for gasification of the selected feedstock. The syngas produced is cleaned using warm-gas cleanup techniques, including hot-gas filtration and fixed-bed desulfurization. The syngas is synthesized into liquid fuel in the EERC's fixed-bed Fischer-Tropsch (FT) reactor. The overall goal of the testing is to determine the impact of warm synthesis gas on the performance and life of FT catalysts and compare the performance to sweetened syngas.

Because of the need for cryogenic cooling, the capital and operating costs for traditional cold-gas cleanup are significant. The energy penalty of cooling and reheating both syngas and solvent can also be significant. This limits gas sweetening for synthetic fuel production to very large installations that can benefit from economies of scale. Small-scale coal-to-liquid (CTL) plants may operate profitably by generating higher-value chemicals, but given the comparatively low value of transportation fuel, FT synthesis normally operates economically at a large scale.

The large energy penalty created by cold-gas cleanup can be mitigated by hot- or warm-gas techniques. H<sub>2</sub>S and other key contaminants can be removed using these technologies. Warm-gas cleanup is a promising alternative to gas sweetening at the small scale because it requires less maintenance, does not have the significant energy penalty associated with cooling and reheating gas and liquid streams, and has lower utility costs. However, warm-gas cleanup cannot capture all gas contaminants. Some gas cooling is required to condense water and gasifier tars. Warm-gas technologies

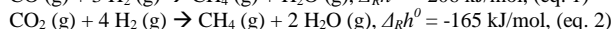
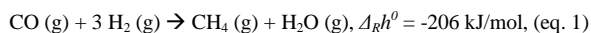
currently cannot effectively remove CO<sub>2</sub>. Gas sweetening with physical or chemical solvents remains the only commercially available way to remove CO<sub>2</sub> from syngas.

The proposed technology will take advantage of commercially available warm-gas cleanup sorbents and will determine the overall increase in thermal efficiency when using warm-gas cleanup versus conventional solvent technology. High levels of moisture and CO<sub>2</sub> will reduce the overall production efficiency of the catalyst. Iron-based catalysts may be very susceptible to this reduction because of high water-gas shift activity in the presence of moisture. The expected reduction in FT liquids production will also be determined. This paper reviews the results of the testing and compares liquid fuel production efficiency with warm-gas cleanup techniques to traditional methods.

#### Production of SNG in a Slurry Bubble Column Reactor

Manuel Götz, Rainer Reimert, Siegfried Bajohr, Karlsruhe Institute of Technology (KIT), GERMANY

Methanation is a heterogeneously catalyzed reaction of CO and/or CO<sub>2</sub> with H<sub>2</sub> (eq. 1 and 2) which can be used to produce Synthetic Natural Gas (SNG) based on gases consisting mainly of CO, H<sub>2</sub> and CO<sub>2</sub>, like, e.g., raw gases from coal or biomass gasification.



The use of SNG has some advantages as compared to the solid fuels coal or biomass. First, SNG can easily be transported via pipelines. In many countries the natural gas infrastructure is well developed. Second, its combustion is highly efficient and causes low emissions of harmful gases like SO<sub>2</sub>. Finally, SNG is a versatile fuel which can be used to produce heat and power but it can also be applied as a highly efficient and low polluting fuel for cars in internal combustion engines.

During the 1970s and 1980s, many reactor concepts for realising the methanation reaction to produce SNG were investigated and developed. Some of these concepts are based on a series of adiabatic fixed-bed reactors including a gas recycle loop to moderate the temperature in the reactors. The main difference between these concepts is the number of reactors in series. However, these concepts have a high investment, a high thermal load on the catalyst, and possible mass transfer limitations due to the necessarily large catalyst particle size as drawbacks.

Other concepts are based on fluidized-bed reactors. These reactors allow for an effective removal of the reaction heat. Alas, the mechanical load on the catalyst causes attrition and ultimately entrainment of the catalyst.

A new methanation process aims to combine some of the advantages of fixed- and fluidized-bed reactors such as an effective removal of the reaction heat and simultaneously a low thermal and mechanical load on the catalyst. Furthermore, the catalyst can be replaced during the process. The idea is to use a slurry bubble column reactor by filling the reactor volume with an inert heat transfer liquid and to suspend the catalyst in this liquid. The reacting gases as well as the produced methane would flow as bubbles through the liquid. As a result of the high heat capacity of the liquid phase, a three phase reactor system is able to intermediately store the heat of the methanation reaction with only a small rise in temperature. Possible disadvantages include mass transfer limitations in the liquid phase as well as decomposition and evaporation of the heat transfer liquid. Current research activities focus on identifying suitable heat transfer liquids and optimizing the liquid-side mass transfer. Additionally, the catalyst lifetime in a three phase system has to be compared with the lifetime in a two phase system.

The heat transfer liquid is used directly inside the reactor and therefore it needs to have high thermal and chemical stability. So far, dibenzyltoluene is used as heat transfer liquid because of its high thermal stability.

In the presentation, results of the current research will be reported. This includes measured data for a three phase reactor (data for bubble size, gas holdup and CO- and CO<sub>2</sub>-conversion in the slurry reactor) as well as calculations comparing the potentials of the different reactor types (fixed-, fluidized-bed, and three phase methanation).

### SESSION 6

#### Coal Science: General - 1

##### Column Flotation of Hard-to-Float Subbituminous Coal Using the Blend of Trimethyl Pentanediol Derivatives as Surface Active Materials and Pico-Nano Bubbles as Secondary Collector

Felicia Peng, Yu Xiong, Jinxian Chen, West Virginia University, USA

Subbituminous coal, a lower rank of coal, is difficult-to-float by using a single frother such as MIBC and a single collector such as kerosene or fuel oil in a flotation column, equipped with conventional bubble generation devices for milli and micro size bubbles. The froth flotation of the fine coal separation process is based on the

differences of wettability between coal and mineral particles. The existing of higher quantity of oxygenated functional groups on coal particle surface can reduce its hydrophobicity compared to the higher rank of coal such as bituminous coal. The lack of hydrophobicity sites on the coal particle surface makes the coal surface hard to resurface by the oily collector alone, resulted in harder to float. Previous work shows that the surfactants can be used to activate the oxygenated surface, by selecting the group of such as fatty acids, trimethyl pentanediol derivatives, hydroxylated ether amine, etc. In the present study, the blend of trimethyl pentanediol derivatives as frother and surface active material and kerosene as collector are used in column flotation of subbituminous coal. The frother made of trimethyl pentanediol derivatives provide the better spreading of oily collector on the coal particle surface, froth stability, and selectivity.

The flotation column has 2-in diam and 152 cm height, equipped with a static-mixer and a venture cavitation tube for pico-nano bubble generation, and a double funnel tailings separator for generating cyclone effect for recirculating and discharge of tailings are used. At initial stage a design of experiment of column flotation testing is conducted to determine the approximate optimized operation conditions. The results show that 85-90% of combustible material recovery and 11-13% of clean coal ash content can be obtained by further using single parameter flotation testing. The effect of pico-nanobubbles is to act as secondary collector to increase the bubble and coal particle attachment and reduce the debouchment, in additional to the oily collector as primary collector, to increase the recovery of lower rank fine coal flotation. Furthermore, clean coal with the combustible material recovery of greater than 80% and ash content of 9%, by desliming minus 45  $\mu\text{m}$  size fraction particles of feed coal before column flotation are also achieved.

### **Improving the Rail Car Unloading of Solid Fuels**

George D. Dumbaugh, Kinergy Corporation, USA

The fast unloading of solid fuels transported in bottom dump Rail Cars made of Aluminum or Steel can be challenging when corporate finances are limited. This presentation will explain the achievement of a fast Rail Car Unloader at a relatively low cost.

An upgraded design of a trackside Rail Car Discharger is now in productive use and being appraised. This kind of Unloader pneumatically extends a rubber bumpered, longitudinal member that engages and vibrates the car. Previously, it was only designed to unload cars constructed of Steel at a moderate rate.

When oil became more costly, the rail cars began to be made of Aluminum. This reduced their freight cost. The use of Aluminum cars prompted the upgrading and redesign of this kind of Discharger. It was an engineering challenge because all the stresses transferred to the car by the vibration had to be markedly reduced.

Also, the unloading time of a 100 Aluminum car Unitrain that has a 100 ton load in each car was wanted to be done in 4 hours. This equates the unloading capability of a Rotary Car Dumper.

The first redesigned and modernized Discharger has been in productive service for more than 2 years. It confirms it can equal the unloading time of a Rotary Car Dumper at less than a fifth of the cost!

If it is wanted, and upon request, an observed fast unloading of Aluminum cars filled with 100 tons of Coke in southwest Ohio could probably be arranged.

### **Coal Ash as a Potential Scrubber for Quarry Fine Wastes**

Roy Nir Lieberman, Yitzhak Mastai, Bar-Ilan University; Yaakov Anker, Samaria and the Jordan Rift Regional R&D Center; Haim Cohen, Ariel University, ISRAEL;

Xavier Querol, Oriol Font, Institute of Environmental Assessment and Waster

Research ((IDEA) Consejo Superior de Investigaciones Cientificas (CSIC), SPAIN

Israel imports ~13Mtons of Bituminous coal annually. These coals are burnt in 4 coal fired power plants and produce ~1.3Mtons of coal fly ash and ~180kton of bottom ash (in 2013) as a residue. Strict environmental regulations in Israel allow imports of clean coals, thus, the imported coal undergo beneficiation to reduce the mineral content including sulfur. Therefore, the fly ashes produced in Israel are very basic upon immersion in water (liquid to solid ratio of 10, South African Fly Ash, SAFA, pH>12.5, Colombian Fly Ash, COFA, pH>10.5). These high pH levels are the result of dissolution of lime from the ash in the water.

Recently, it has been found that class F fly ashes show excellent scrubbing and fixation properties for acidic wastes, mainly from the phosphate and oil regeneration industries, which contain also variety of toxic trace elements. In this study we have investigated scrubbing of very fine wastes from quarries in Israel and the Palestinian Authority. These wastes are very fine particles that at present could not be used in the concrete industry.

The results have shown that class F fly ashes have the ability to act as an efficient encapsulation reagent for the quarry sludges. During the fixation process an aggregate is being formed, which can be used in the concrete production industry as a partial substitute for sand or aggregates in the concrete mixture. Leaching experiments, via the European Directive (EN12457-2) method, have proved that both the aggregate product and the concrete produced are in accord with the compliance test for leaching and the leached water is within the D.L. standards in Israel and also under the hazardous limits

of the European Directive. Furthermore, concrete produced (in which the scrubbed product partially substitute cement and aggregate) is stronger than the regular concrete produced.

### **Study on Kinetics of Char Gasification with CO<sub>2</sub> and Steam by the Method of Shared Active Sites**

Wei Huo, Zhijie Zhou, Yifei Wang, Zhenghua Dai, Yan Gong, Guangsu Yu, Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, CHINA

Two coals and a petroleum coke were gasified with a mixture of steam and CO<sub>2</sub> using a TGA. The partial pressures of steam and CO<sub>2</sub> varied from 0.025 to 0.075MPa. CO<sub>2</sub>/steam chemisorptions of chars were also carried out using the TGA to measure chemisorption quantities. In order to estimate the interactions by char-steam-CO<sub>2</sub> reaction, two conventional models were used to fit the experimental data. However, the models can't describe the interactions by char-steam-CO<sub>2</sub> reaction exactly. In this study, a new model based on the Langmuir-Hinshelwood model was proposed. The proposed model assumes that char-CO<sub>2</sub> and char-steam reactions share active sites partially. The results show that the proposed model can evaluate the interactions by char-steam-CO<sub>2</sub> reaction accurately. Moreover, two new parameters in the proposed model do not vary with gasification conditions. They are found to depend on the carbon active sites of the char by the results from chemisorption tests.

### **SESSION 7**

#### **Clean Coal Demonstration and Commercial Projects: Optimizing Clean Coal Technologies**

#### **Public Communication and Collaboration for Carbon Capture, Utilization, and Storage Technology: Acceptance, Education, and Outreach**

Douglas C. Brauer, David Larrick, Richland Community College, USA

The international awareness of global warming concerns creates unique issues of societal acceptance of technologies that promote environmental sustainability. This creates unique opportunities for partnerships between higher education, business/industry, and communities to positively sculpt public perception of a project's environmental impact and gain the public trust in its conduct. The need for collaborative partnerships is heightened with the potential confusion between multiple technologies perceived in societal circles as having potentially negative sustainability impacts (e.g., hydraulic fracturing and carbon capture and storage).

Richland Community College is currently engaged in the USA Department of Energy project "Illinois-Industry Carbon Capture and Storage" (IL-ICCS), which is to demonstrate the viability and effectiveness of commercial-scale carbon capture, utilization, and storage (CCUS). This project began in June 2010 to capture and store more than 2.5 million metric tons of carbon dioxide (CO<sub>2</sub>) over three years from the company's ethanol facility in Decatur, Illinois. The IL-ICCS project is to demonstrate commercial-scale CCUS by capturing CO<sub>2</sub> emissions from the Archer Daniels Midland Company, Decatur, Illinois, USA, ethanol facility and storing them deep underground. In concert with this, the ongoing community education and outreach activities conducted by the College have successfully engaged the public to a widespread understanding that CCUS technologies safely reflect the best interests of the community.

In embarking on this project, a psychodynamic strategic perspective was taken to guide the College in its approach to communication, education, and outreach for the project. This involved understanding the local and regional stakeholder personalities to mold the way we would do things, what we would do, and where we would be heading. The scientific and technical nature of this project necessarily provided a need to understand and leverage local and regional demographics, culture, and the existing college/community trust relationship in establishing an aggressive outreach and education activity. A team, or group, effectiveness theoretical construct was applied to facilitate the development and implementation of "communication" and "outreach" tactical strategies to increase the likelihood of CCUS acceptance by community partners.

To facilitate CCUS education and outreach as part of Richland's role in this partnership, Richland established and constructed the iconic National Sequestration Education Center (NSEC) on Richland's campus in the Richland Agribusiness Applied Technology Park. The NSEC is a local, regional, national, and international focal point for CCUS community outreach and education by providing an innovative experiential learning and knowledge transfer environment. The NSEC provides unique educational value to researchers and visitors from around the world by experiencing the sequestration technologies demonstrated on the Richland campus and in the surrounding region communities.

The uniqueness of this project to include a community college has resulted in: 1) the establishment of a global educational center (i.e., the NSEC) with close proximity to two CCUS projects; 2) the creation of the world's first CCUS community college



Associate of Science and Associate of Applied Science degrees; and 3) the delivery of CCUS educational outreach activities to over 3,400,000 people since 2011. The community responsibility demonstrated in this project has resulted in over 900 domestic jobs, including 250 local jobs and the creation of over 10 permanent jobs. The local economic impact is estimated to be over \$30,000,000 USD. However, more importantly this project has transitioned research to commercial demonstration advancing national and global practices and policy regarding CCUS and it has become a global centerpiece for CCUS research, economic, and educational value.

### **DryFining™ Begins its 5th Year of Commercial Operation**

Charles Bullinger, Great River Energy, USA

Great River Energy, in conjunction with the Department of Energy (NETL) and others developed a technology which dries and refines/cleans feed coal in a fluidized bed utilizing residual heat at Coal Creek Station; a two by 600 MW lignite coal-fired electric generating station in central North Dakota. Initial prototype verification testing was conducted via Round 1 of DOE's Clean Coal Power Initiative. Eight 125 ton per hour commercial fluidized beds, four per boiler, began operation in December of 2009 and has been processing 1000 TPH coal ever since.

In December of 2013, DryFining began its 5th year of commercial operation. This paper will provide some background, testing results, emission performance and operational experience as this system was implemented on the coal flow to these two boilers. Significant efficiency improvement and emission reductions can be realized with the adaptation of this technology to those burning low rank coals or those who have switched to wetter or washed, low sulfur coals. A summary of what has been learned will also be given.

### **Case Study of an Improved Online Coal Analysis System**

Albert Klein, IPCI Indutech Process Controls Inc.; Anthony Garaventa, NRG, Conemaugh Power Plant; Mike Santucci, ECG Engineering Consulting Group, USA

To improve the coal handling facility at a power-station, an online analysis of the coal along with a stockpile management program is needed to generate optimal blends. After installing the first XRF online coal analyzer in 1998 at DTE Monroe power-plant, Indutech® continuously improved the patented technology. This resulted in the OXEA® Online X-ray Elemental Analyzer. The newest generation is now installed at Conemaugh Generation Station which is operated by NRG Energy. This XRF-analyzer in combination with the PMD Microwave moisture meter is able to determine Ash, Sulphur, BTU and Moisture content as well as ash viscosity and fusion temperatures. The improvements of OXEA allow the power-plant to control and meet environmental tolerances to a higher precision than had been previously possible. The installation of the analyser along a bypass belt allows for periodic calibration based on the results of secondary samples, which are taken by an automated sampling system and analysed in the laboratory. This semi-automatic system allows batch verification of the analyzer and recalibration, if necessary.

The assortment of coal qualities and costs makes enhanced fuel management apparent if the economic opportunities are to be realized. The integration of state of the art, computer capabilities, real-time fuel analysis, fuel flow modeling, understanding of coal combustion characteristics and operational experience has prompted ECG to develop a fuel management tool; AccuTrack. With this tool adaptation to the Conemaugh Station, fuel quality and quantity are tracked through receiving, storage, reclaim, blending (if required) and loading to the boiler to optimize time-dependent dispatch economics, demand capability and reliability. AccuTrack also provides detailed operator information regarding controllable real-time and projected fuel/combustion parameters.

### **Improving the Energy Efficiency of a Mid-Size Power Plant by Reduction in Auxiliary Power and Improved Heat Transfer**

Jeffrey Green, Justin Harrell, James Mathias, Southern Illinois University, USA

An older, mid-sized coal fired power plant was studied to improve overall plant efficiency. The power plant consists of a Circulating Fluidized Bed (CFB) boiler to produce up to 120 MW and a pulverized coal boiler with a scrubber that produces up to 180 MW. Both boilers are connected to separate steam turbines and feed water heaters and lake water provides cooling to both cycles through the condenser. The study examined the potential use of variable frequency drives (VFDs) on various motors as well as areas of increased heat transfer.

In older power plants, fluid flow rates are often inefficiently controlled using dampers or valves while their motors stay at full speed. By removing the controlling devices and instead controlling with a VFD, a significant amount of electricity can be saved. Previously this power plant very successfully installed VFDs on the motors of the blowers providing combustion air and powering the scrubber. Motors that were studied this time were Primary Air, Secondary Air, and Induced Draft blowers for the CFB, two boiler feed water pumps, and condensate pumps. A thorough analysis was done of hourly data that included motor amperage, flow rates and pressures, and potential energy savings at each hour was determined accounting for pump, motor, and VFD inefficiencies. Preliminary results show annual savings of all six motors to total 38.5

GWh, and a 2.05% increase in overall plant efficiency. Total project costs are near \$2.5 million resulting in a simple payback period of less than two years assuming 0.04 \$/kWh.

Energy is also wasted when hot gasses leave the system. Flue gas from the CFB is regularly near 320°F allowing for a large amount of potential heat recovery. One realistic scenario suggested heat recovery resulting in a 120°F degree reduction of flue gas temperature amounting to a 2.54% increase in cycle efficiency. A system in which flue gas enters a separate coated heat exchanger and partially condenses prior to leaving the stack has been determined to be suitable for this application. Coal drying proved to be the most viable use of recovered waste heat from exhaust, it would upgrade incoming coal from 11,000 Btu/hr to 11,740 Btu/hr resulting in savings of \$2.28 million annually for a payback period of just 2.1 years.

## **SESSION 8**

### **Coal Mining: Monitoring and Managing Gas in Mines**

#### **Coal Mine Methane Developments in the United States**

Jayne Somers, United States Environmental Protection Agency, USA

Methane is a potent greenhouse gas, accounting for 15 percent of all global greenhouse gas emissions in 2005. Since methane has a much shorter atmospheric lifetime than carbon dioxide (CO<sub>2</sub>), reducing methane emissions can achieve considerable climate benefits over the next 25 years. Coal seams often contain significant quantities of methane (CH<sub>4</sub>) and CH<sub>4</sub> released to the atmosphere from gassy mines during coal extraction is a major source of greenhouse gas emissions. Methane emissions from coal mining activities constitute approximately 8% of total global human-related methane emissions.

Coal mines around the world have recognized that methane is a clean energy resource that can be captured and used productively. Coal mine methane (CMM) is currently utilized for power generation, natural gas pipeline injection, vehicle fuel, industrial process feed stocks, on-site mine boilers, mine heating, and home heating distribution systems. Upgrading mine degasification systems can often improve gas quality and create favorable project economics.

The United States has been a leader in coal mine methane (CMM) recovery and use since the 1990's. There are now 15 projects at active underground mines in the U.S., as well as 26 abandoned mine methane projects. Recovery and use projects at active underground U.S. mines reduced methane emissions by approximately 49 Billion cubic feet in 2010. In an exciting new development, a ventilation air methane (VAM) mitigation project at the CONSOL McElroy mine in West Virginia was installed by Verdeo Sindicatum. Operational since September 2012, this commercial-scale VAM project will reduce methane emissions by an estimated 920 mmcf/yr. Another innovative CMM project at the Oxbox Elk Creek mine will generate 3MW of electricity for the Aspen Ski Company when it is complete this year. These projects are a win-win for the coal companies, project developers and the environment. They provide an added revenue stream for the coal mine and can improve both safety and mine productivity.

As part of the U.S. Greenhouse Gas Reporting Program, actual data on methane emissions from underground coal mines has been submitted by gassy underground coal mines since 2011. The data collected will help inform stakeholders, particularly the underground coal mining industry, of CMM emission sources on public and private lands. The detailed data will also shed light on the specific sources of methane from active underground coal mines and highlight project opportunities for the U.S. coal industry.

In April 2014, the California Air Resources Board (CARB) Board approved amendments to the state's greenhouse gas cap-and-trade program. The Board also voted to adopt a new protocol that would generate compliance-grade carbon offsets for mine methane. The Mine Methane Capture offset protocol provides a new opportunity for achieving compliance-grade greenhouse gas emissions reductions from sectors which are not under the cap. These amendments will be effective July 1, 2014. Also in April, the Bureau of Land Management (BLM) released an Advance Notice of Public Rulemaking (ANPR) to examine steps to reduce methane from mining operations on public lands. As part of President Obama's recently released Strategy to Cut Methane Emissions, a component of the Climate Action Plan, the BLM announced that it is seeking public comment on a possible rulemaking that could reduce the waste of methane from mining operations on public lands.

The presentation will cover U.S. coal mine methane emissions, U.S. CMM utilization and destruction projects, Federal policies and State incentives for CMM capture and utilization, the CARB mine methane capture protocol, and other new developments.

#### **The Technical and Economic Feasibility of Flaring to Reduce Greenhouse Gas Emissions from the Global Coal Mining Industry**

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

As a greenhouse gas, methane is second only to carbon dioxide in contributing to global climate change. Coal mines are one of the five major sources of anthropogenic methane emissions contributing 6 percent of total man-made emissions (Global Methane Initiative 2011). Estimated worldwide coal mine methane (CMM) emissions totaled 589 million metric tons of carbon dioxide equivalent (MMT<sub>CO2E</sub>), or about 41.2 billion cubic meters (BCM) and emissions are expected to grow to 671 MMT<sub>CO2E</sub> (46.9 BCM) by 2030 according to the U.S. Environmental Protection Agency (USEPA 2012).

CMM capture and use has become a significant policy priority in many countries, including the United States, especially as mining is trending to deeper and gassier coal seams. The increasing use of methane drainage provides a quality gas stream for utilization, reducing greenhouse gas emissions and improving mine safety whilst unlocking the energy value of the CMM. In some cases, however, markets for the gas are not readily available, gas wells are physically stranded, project economics are not favorable, or mining companies simply do not maintain the capacity for CMM utilization. Even where CMM is utilized, projects rarely use all gas available. In these instances, drainage systems vent methane to the atmosphere without energy recovery. In the United States, for example, 7 billion cubic feet (198 million m<sup>3</sup>) was vented to the atmosphere from gas drainage systems in 2012 according to the Inventory of U.S. Greenhouse Gas Emissions & Sinks 1990-2012 produced by the USEPA. This is the equivalent of 2.8 million tonnes of CO<sub>2</sub> emissions.

Flaring, or thermal destruction, of stranded or excess gas has become an increasingly popular solution because it is a cost-effective method of reducing greenhouse gas emissions where energy recovery is not technically or economically feasible. Although slow to be adopted by the global mining industry due to safety concerns and limited economic and regulatory drivers, CMM flaring is growing in acceptance worldwide and many projects have been implemented in recent years. The GMI International Coal Mine Methane Project Database identifies 40 mine methane capture projects that are using, or have used, flares, either in conjunction with energy recovery technologies, or as a stand-alone mitigation technology. Today 20 of those are in operation in 7 countries including: Australia (6), China (3), Mexico (3), Russia (2), South Africa (1), Ukraine (3), and the U.S. (2).

In addition to these projects, there could be a substantial increase in the number of US projects if the California Air Resources Board adopts a mine methane capture protocol in April 2014 for its Cap-and-Trade system. The economic incentives from participation in the Cap-and-Trade system will spur development of many flaring projects at gassy underground coal and non-coal mines in the U.S. during the next three years.

This paper will: (i) review the available technology options for flaring CMM, principally comparing and contrasting enclosed (ground) flares with open (candlestick) flares; (ii) identify the appropriate use of flaring as a stand-alone or integrated GHG mitigation option under various operating and market conditions; (iii) discuss proper design and sizing of flaring projects; (iv) present project economics under various revenue scenarios; (v) provide two case studies; (vi) identify U.S. prospects for flaring based on the U.S. CMM Inventory and the U.S. Greenhouse Gas Reporting Program; and (vii) provide a list of projects worldwide.

## SESSION 9 Gasification: Gas Cleaning

### Advanced Acid Gas Separation Technology for the Production of Syngas via Low Rank Coals

Fabrice Amy, Shubhra J. Bhadra, Jeffrey R. Hufton, Jeffrey W. Kloosterman, Ellen M. O'Connell, Air Products and Chemicals, USA

The Sour PSA technology is being developed to replace the solvent-based Acid Gas Removal systems currently employed to separate sulfur containing species, along with CO<sub>2</sub> and other impurities, from gasifier syngas streams. This approach utilizes pressure swing adsorption (PSA) concepts to generate a sweet H<sub>2</sub> or syngas product stream along with an enriched CO<sub>2</sub>/H<sub>2</sub>S stream. The latter stream can be transformed into an elemental sulfur or sulfuric acid stream and a sulfur free CO<sub>2</sub> stream applicable to CO<sub>2</sub>-capture or non-CO<sub>2</sub>-capture opportunities. Previous development efforts have been focused on demonstrating the concept of H<sub>2</sub>S/CO<sub>2</sub> separation, evaluating the sensitivity of the adsorbent to sour gas trace components, and estimating the economic advantages of the process. The potential for implementing Sour PSA in the production of chemicals from coal is the focus of a recently awarded DOE funding. Project goals include developing process configurations to produce 2:1 H<sub>2</sub>:CO syngas by sour PSA and comparing to a base case conventional technology. An additional project goal is to use syngas produced at the National Carbon Capture Center to assess the stability of PSA process performance and the impact of trace impurities on the adsorbent when operated over longer periods than previously tested. These past and current efforts will be highlighted in the presentation.

### Sulfur Release Behavior during Pyrolysis of a Bituminous Coal Fractions: The Relationship with Sulfur Forms, Char Particle Size Distribution and Morphology, and Char Conversion

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

Investigation of sulfur release from coal during high temperature gasification is crucial to designing control measures for fouling and corrosion related issues, and developing hot-gas-cleaning research strategies. The aim of this study is to investigate the release of sulfur as a function of initial coal particle sizes (PS6: 75-106 μm, and PS3: 212-420 μm), density of coal fractions (SG1: <1.3 g/cc, SG2: 1.3-1.6 g/cc, and SG3 (mineral rich fraction): 1.6-2.6 g/cc), and temperature (1573 K, 1673 K, 1793 K) under reducing atmosphere (mixture of N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>) in a laminar flow furnace with an overall objective of arriving at a detailed sulfur release mechanism at high heating rates. The results show that the release of sulfur is strongly influenced by the initial coal particle size (PS6>PS3), char fragmentation, temperature (1793 K>1673K>1573K), and sulfur forms. The strong correlation between char particle size distribution and sulfur release indicates that the mass transfer limitations play an important role in the release of sulfur. Besides mass transfer limitations, the sulfur forms also seem to play an important role with sulfur from pyrite being released at a greater proportion. The other parameter that could affect the sulfur release is minerals in high density fraction. However, at this point it is not clear to what extent minerals play a role in the release of sulfur. More experiments will be conducted to arrive at a detailed sulfur release mechanism during pyrolysis.

### Toward a Technology to Mitigate Syngas Cooler Plugging and Fouling

Mike Bockelie, Kevin Davis, Rand Pummill, Martin Denison, Tim Shurtz, Jost Wendt, Reaction Engineering International; Kevin Whitty, Mustafa Can Celebi, Andrew Fry, Cristina Jaramillo, Zhonghua Zhan, University of Utah, USA

To become cost competitive with conventional power plants, gasification plants need to improve plant economics, efficiency, and increase plant availability. The current syngas coolers used in Integrated Gasification Combined Cycle (IGCC) plants offer high efficiency, but their reliability is generally lower than other process equipment used in the gasification island. The syngas cooler is a fire tube heat exchanger located between the gasifier and syngas combustion turbine. Downtime events associated with the syngas cooler are often due to ash deposits. Deposits can develop on surfaces upstream of the syngas cooler, break loose, and then lodge in the syngas cooler tubes causing plugging or increased erosion in the tube. Likewise, deposits can form on the fireside surface of the syngas cooler tubes that leads to fouling of the syngas cooler. Both ash deposit mechanisms result in reduced equipment life and increased maintenance costs. Through funding from the DOE, Reaction Engineering International (REI) has investigated deposit formation in the syngas cooler and techniques to mitigate the plugging and fouling of the syngas cooler. In this paper we will provide an overview of small scale experiments being performed at the University of Utah and modeling being performed by REI that highlight our progress on this challenging task.

### Pilot-Scale Capture of Mercury, Arsenic, and Selenium from Warm Syngas at Elevated Pressures by Palladium Sorbents

Karen J. Uffalussy, Evan J. Granite, Henry W. Pennline, DOE/NETL; Tony Wu, Subhash Datta, Robert C. Lambrecht, John M. Wheelton, National Carbon Capture Center, Southern Company, USA; Hugh G. C. Hamilton, Stephen Poulston, Liz Rowsell, Wilson Chu, Andrew W. J. Smith, Johnson Matthey Technology Centre, UNITED KINGDOM

Warm gas cleanup of fuel gas from integrated gasification combined cycle power plants is important in order to preserve both their higher thermal efficiencies and to eliminate dirty water circulation and treatment systems. Six pilot-scale tests of palladium on alumina sorbents for the removal of trace contaminants from several types of coal-derived syngas at elevated temperatures and pressures were conducted at the Southern Company National Carbon Capture Center. Between 96 – 100% removal of mercury, arsenic, and selenium from all syngas types, sour and sweet, was observed at 500 °F and elevated pressures of 150 – 200 psig. The results indicate that the Pd sorbents exhibit large capacities for the capture of Hg, Se, and As under varying conditions and over extended test periods. Current preliminary work also shows that the sorbent is not only regenerable, but that the sorbent is just as effective at capturing these contaminants after regeneration. Future work and tests will focus on use of lower loadings of Pd, higher syngas flow rates, and further regeneration cycles in the removal of the trace contaminants, as well as the possible removal of other contaminants.

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### **Removal of Carbon Disulfide by CUO During Reactive Milling with Anthracite Carbon as Milling Aid**

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The paper was about morphology, phase composition and crystal structure of the materials during the process of CuO being reduced to Cu<sub>2</sub>O/Cu nanoparticles, increasing the absorption of CS<sub>2</sub>. Anthracite coal which had been demineralized was added as milling aid to prevent welding of the materials during milling. The particle size of the materials from 1 h of milling was at the range of 150-300 nm and the crystallite size was below 30 nm. The Cu<sub>9</sub>S<sub>5</sub> and C-S bonds were detected after absorbing CS<sub>2</sub> at 150 °C. The Cu<sub>2</sub>O/Cu nanoparticles were easier in The Cu<sub>2</sub>O/Cu nanoparticles and carbon additive might have a synergistic effect on desulfurization, absorbing sulfur easier than that of CuO.

The CuO can be reduced to Cu<sub>2</sub>O and Cu with Mg as reducing agent during milling and the as-milled materials were proposed as desulfurizer in this work. Because of some combination of shear and impact in milling, the particles are generally deformed or broken up. Thus, the as-milled materials can generate a large number of defects and energy, which may favor the desulfurization. Here, the structure and morphology of the as-milled materials were investigated. This approach provides a novel solution for removing CS<sub>2</sub> in mild conditions.

### **SESSION 10 Combustion: Oxy-Combustion and Chemical Looping - 2**

#### **Techno-Economic Analysis of Coal-Direct Chemical Looping for Power Production**

Tritti Siengchum, Luis G. Velazquez-Vargas, Douglas Devault, Tom Flynn, Babcock & Wilcox Power Generation Group, Inc.; Andrew Tong, Samuel Bayham, L.-S. Fan, The Ohio State University, USA

The Coal-Direct Chemical Looping (CDCL) process is an advanced oxy-combustion technology that has the potential to enable substantial savings in the cost and energy penalty associated with carbon dioxide capture from coal-fired power plants. The CDCL process consists of a unique moving bed reactor, namely the reducer, where pulverized or crushed coal is fully converted using iron-based oxygen carrier particles. The oxygen carrier is reduced from Fe<sub>2</sub>O<sub>3</sub> to a mixture of FeO and Fe while the flue gas is a stream of CO<sub>2</sub> that can be sequestered. The reduced FeO and Fe oxygen carrier mixture is then re-oxidized to Fe<sub>2</sub>O<sub>3</sub> using air in a combustor reactor, liberating heat to produce steam for power generation. The iron-based CDCL process has shown the potential for lower capital and operating costs as compared to first generation carbon capture technologies such as amine-based solvent system. Further, CDCL does not require an air-separation unit (ASU). Eliminating the ASU results in a significant reduction in capital and operating costs.

Through collaborative efforts, Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) and The Ohio State University (OSU) have developed a preliminary design and operating philosophy for a 550 MWe commercial scale CDCL power plant. Based on the results of the techno-economic evaluation, B&W PGG projects that the CDCL process will achieve 96.5% CO<sub>2</sub> capture with only 26.8% increase in the cost of electricity when compared to a supercritical pulverized coal-fired power plant. These performance estimates exceed the U.S. Department of Energy's goal of 90% capture at less than 35% increase in the cost of electricity. The advancement in the design of the CDCL process, the latest experimental data, and the result from the techno-economic study a commercial CDCL plant will also be presented and discussed in this paper.

#### **Kinetics of Redox CLC Reactions for Selected Carriers Based on Fe Pigments from Pigments Industry**

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

Presented paper covers results of research work on novel fuel combustion method that is called Chemical Looping Combustion (CLC). The CLC is believed to be the promising, since the concentrated CO<sub>2</sub> stream is produced after water condensation without any energy penalty for CO<sub>2</sub> separation. The objective of this work was to study kinetics of both reduction and oxidation reactions for selected oxygen carriers.

Essentially, the oxygen carrier is crucial for development of CLC technology. Since the synthetic oxygen carriers are expensive (Cu, Co, Ni based), the researchers attempt to find the cheaper alternatives for those oxygen carrier. One of the solution is to use the raw materials as ores or concentrates from metallurgical industry, other is to use municipal wastes or low cost products from chemical industry.

In the present work, Fe-based oxygen carrier was selected for redox kinetics analysis. Oxygen carrier was prepared by mechanical mixing of Fe<sub>2</sub>O<sub>3</sub>-based and TiO<sub>2</sub>-based pigments. Test have been performed at isothermal conditions (800 to 950 °C) in multiply redox cycles using TG (thermo-gravimetry). Reduction and oxidation reactions of oxygen carrier were carried out by using 3% H<sub>2</sub>/Ar and synthetic air, respectively. The sample showed promising results as sufficient reactivity with the fuel and also stable, repeatable performance. Kinetic parameters such as an activation energy, the pre-exponential factor and the reaction model were determined for redox reactions by using model fitting method.

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### **SESSION 11 Clean Coal and Gas to Fuels: Syngas to Fuels - 2**

#### **High Hydrogen, Low Methane Syngas from Low-Rank Coals for Coal-to-Liquids Production**

Andrew Lucero, Kevin McCabe, Amit Goyal, August Meng, Jonathon Carroll, Santosh Gangwal, Southern Research Institute, USA

Syngas cleanup is a major challenge in any coal or biomass gasification application. Syngas from coal gasification is also typically low in hydrogen relative to distillate fuels which typically have H:C ratios of 2:1. As part of a DOE NETL sponsored project, Southern Research is developing a modified advanced gasification platform for the conversion of low rank coals to syngas for CTL and IGCC applications. The proposed process is enabled by the development of novel steam reforming catalysts to allow for high temperature conversion of tars, light hydrocarbons and ammonia in the presence of syngas contaminants such as high concentrations of H<sub>2</sub>S (1000 ppm). The goals of the process are to improve syngas yield, improve H<sub>2</sub>:CO ratio, reduce water gas shift requirements, and reduce downstream gas cleanup requirements. The experiments are focused on lab-scale synthesis, testing, and characterization of high-temperature steam reforming catalysts under severe deactivating conditions of a simulated low-rank coal synthesis gas. Experimental data will be focused on supporting a techno-economic analysis of the reforming process using a gasification technology, Transport Reactor Integrated Gasifier (TRIG). A coal to fuel with carbon capture model will be developed to determine the economic feasibility of the integrated process, including the catalytic steam reforming, in a commercial embodiment. This work will focus on initial results of the modeling and economic analysis.

#### **ZnO/ZSM-5 Nanocatalysts for Methane Upgrading**

Yungchieh Lai, Götz Vesper, University of Pittsburgh and DOE/NETL, USA

The low cost of natural gas and the vast amount of accessible shale gas reserves in the US has made production of aromatics, such as benzene, via catalytic dehydroaromatization (DHA) of methane an economically attractive pathway. The overall reaction is given by 6 CH<sub>4</sub> → 9 H<sub>2</sub> + C<sub>6</sub>H<sub>6</sub> and proceeds over zeolite-based catalysts at ~700-800°C with good selectivities (>60%) but low conversion. The catalysts for this reaction are bi-functional metal/zeolite systems in which the metal site activates methane, followed by oligomerization of the methyl to benzene on the Bronsted Acid Sites (BAS) of the zeolite. The good selectivity for the desired product benzene is attributed to the zeolite pore size which is similar to the benzene diameter (~ 6 angstrom). Among the metals investigated, the most intensively studied one is Mo/HZSM-5 due to its comparatively high reactivity. However, similar to other microporous zeolite materials, poor transport of primary reaction products result in rapid deactivation of the catalyst via coking. While this coke formation is reversible via oxidative regeneration of the catalyst, it results in an inactive oxidized form of the metal which then has to undergo a lengthy activation period to (re)form the active (oxy-carbide) phase. These issues motivate the search for more coking resistant and/or more easily regenerable catalysts for this reaction.

ZnO/ZSM-5 is a promising candidate since it is active in the oxide form and hence does not require further activation after oxidative regeneration of a spent catalyst. We therefore targeted the synthesis of a nanostructured ZnO@ZSM-5 catalyst with the following desired properties: (1) small ZSM-5 particle size and hierarchical pore structure to facilitate removal of the reaction products and hence reduce secondary coke formation; and (2) encapsulated and well dispersed ZnO nanoparticles in ZSM-5 to increase the selectivity toward benzene and avoid formation of hydrocarbon products on the external surface.

Here, we report the first successful synthesis of a nanostructured ZnO@ZSM-5 core-shell catalyst system which encapsulates size controlled (with  $d$  variable from ~4-10 nm) ZnO nanoparticles in a highly crystalline ZSM-5 shell. We will discuss the synthesis path, which is based on a systematic and well-controlled bottom-up approach, and present a detailed characterization of this composite. We will further demonstrate the formation mechanism of this composite and its changing mesoporosity by tuning ZnO properties. This will allow a rational design of ZnO nanoparticle encapsulation in ZSM-5 for DHA, and may find a wider application on other methane upgrading reactions. Reactive studies are currently on-going and first results suggest that the catalyst is indeed active immediately after oxidative regeneration, i.e. it allows to entirely remove the lengthy re-activation period required for Mo/ZSM5.

#### **Methane Reforming Strategies for the CO<sub>2</sub> Emission Reduction of Lignite to Liquid-Fuel Production System**

Yang Fan, Wenying Li, Taiyuan University of Technology, CHINA

CO<sub>2</sub> emission reduction and reuse is a hot topic around the world and especially in the coal chemical industry. Although coal is relatively abundant, liquid fuels derived from coal will have to face the barriers put by strict CO<sub>2</sub> emission limitations. Methane reforming with CO<sub>2</sub> would be a good choice to recycle CO<sub>2</sub>, while steam methane reforming can reduce the CO<sub>2</sub> generation from the source for many water-gas-shift-adopting processes. CH<sub>4</sub> can be easily and fully obtained from both coal pyrolysis unit and Fisher-Tropsch synthesis unit. By adopting the reforming process, syngas with relatively high H<sub>2</sub>/CO ratio could be added into the liquid-fuel production system. Thus, more carbon would be fixed into the products while relatively less is emitted. In this paper, these two reforming strategies with two CH<sub>4</sub> sources are investigated in two different liquid-fuel production systems, namely one with typical dry powder entrained-flow gasifier and the other with coal-water slurry entrained-flow gasifier. And then well-performed strategies are applied into the entire lignite to liquid-fuel system. Results showed that the CH<sub>4</sub> from coal pyrolysis and Fisher-Tropsch synthesis was insufficient in all strategies that were assumed to provide enough H<sub>2</sub> for adjusting the H<sub>2</sub>/CO ratio. Therefore, the water-gas-shift reaction is necessary for the lignite to liquid-fuel production system. By comparison, the process adopting the typical dry powder entrained-flow gasifier and the steam reforming of methane strategy is the best choice in the view of carbon to oil conversion ratio. The carbon tax plays a role of shrinking the gap between additional investment and CO<sub>2</sub> emission penalty.

#### **Economic Analysis of Gas to Liquid and Coal to Liquid Processes**

Sara Mohajerani, Samane Ghandehariun, Amit Kumar, University of Alberta,  
CANADA

Gas-to-liquid (GTL) and coal-to-liquid (CTL) processes convert natural gas and coal into synthetic crude that can produce several useful hydrocarbon fractions including liquid fuels, such as diesel and gasoline, and chemicals such as waxes. These products are more valuable than their natural resources (i.e., coal and gas). It must be mentioned that liquefaction processes are becoming attractive for the fuel market due to an uncertainty in global oil prices in the past few years. In addition, low prices of natural gas and coal in North America stimulate interest in GTL and CTL technologies and develop large market opportunities for GTL and CTL products. Moreover, large-scale plants provide commercial economies of scale; however, some small-scale plants are considering GTL as a method to monetize other natural gas resources such as shale gas and stranded natural gas. Several technologies are available to produce liquid products. The Fischer-Tropsch process is a leading method for producing liquid fuel from gas and coal. The objective of this work is to provide a techno-economic analysis to identify opportunities for cost savings and study the economics behind CTL and GTL processes. Invested capital expense is massive in the chemical industry and it is critical for decision-makers to have an economic understanding of these processes. In this study, first, a base-case flowsheet is created to determine the key processing steps of the plant. Afterwards, an economic analysis for GTL and CTL liquid fuels products is performed, and profitability, based on variation in feedstock cost, plant capacity, and product price, is investigated. Finally, the results are documented in terms of economic impacts and plant capacity needed in order to break even financially and to estimate the return on investment for the base-case study.

#### **Measurement of Surface Tension of Coal Slags**

Andre Horstenkamp, Michael Mueller, Forschungszentrum Jülich GmbH, GERMANY

In many high temperature conversion processes, like steel- and glassmaking processes or coal or biomass gasification, slags or slag like materials play an important role. In an entrained flow gasifier the slag layer on the wall acts on the one hand as a thermal barrier to protect the refractory lining but on the other hand it can cause fouling or other problems. Because of the inhomogeneous character of the used fuels several CFD models were introduced to get a better understanding of the slag behavior in a gasifier. To get reliable results out of these models the input data in form of physical slag properties like viscosity, density or surface tension are very important.

Therefore, the surface tension of different coal slags was measured and compared with the measurement of related synthetic slag systems. The surface tension was measured with the sessile drop method. For the measurement the slag was pressed to a sample and afterwards heated up in a furnace with an argon atmosphere. After the sample was molten, pictures were taken until the temperature reached 1500 °C. The surface tension of the samples was calculated after finishing the measurement by the drop shape on the photos. The related synthetic slags were firstly heat treated and afterwards the surface tension was measured. This procedure should show that the surface tension of synthetic slag systems is comparable to the surface tension of real coal slags with nominally the same composition.

#### **Investigation of Coal Particle Fragmentation Behavior in a Drop-Tube Reactor**

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Energy Process Engineering and Chemical Engineering, GERMANY

Thermochemical processes like pyrolysis, gasification and combustion play an important role either in energetic or non-energetic use of coal. All these processes take place at high temperatures. During the heating-up of the coal particles fragmentation processes may occur due to thermal stresses inside the coal particle and a pressure build-up caused by the devolatilisation of volatile matter.

The fragmentation could have a large impact on the coal particle size. As a result the reaction rate of the heterogeneous gasification or combustion reactions could increase significantly.

For experiments a pressureless drop-tube reactor with a maximum temperature of 1550°C (continuous operation) or 1600°C (temporary operation) was used. The reactor consists of an Al<sub>2</sub>O<sub>3</sub>-tube and has a heated length of 900 mm with an inner diameter of 40 mm. The reactor was flushed with nitrogen to prevent the entrance of reactive gases like oxygen. The particle behavior was directly observed with a high-speed camera (max. 1000 pictures/sec). Using this device in combination with a long-distance microscope it was possible to observe a small focused zone at any level of the heated zone.

The primary fragmentation behavior of 18 coals of different rank (including brown coal, bituminous coal and anthracite) was investigated. Therefore two coefficients were determined to characterize the fragmentation behavior: Fragmentation ratio (number of particles after experiment/number of particles before experiment) and fragmentation probability (number of particles where fragmentation occurred/total number of inserted particles).

Experiments were carried out at 1400°C for all coal samples while the focus of the camera optical system was set at the lowest possible position in reactor. At this height brown coals did not show any fragmentation phenomena, whereas anthracite disintegrated in many fragments. The fragmentation behavior of the bituminous coals differs. On the one hand there are some coal types which show nearly no fragmentation, on the other hand there are also coals that have a high fragmentation ratio.

On this experimental basis correlations of fragmentation coefficients and coal properties (proximate analysis, ultimate analysis, maceral composition, porosity) were made. Overall there is a tendency that fragmentation increases with increasing carbon content.

Furthermore the fragmentation process of intensively fragmenting coals, like anthracite, was observed. Therefore the focus of the camera optical system was altered and a particle tracking method was developed.

#### **Binding of SO<sub>3</sub> to Fly Ash Components: CaO, MgO, Na<sub>2</sub>O and K<sub>2</sub>O**

Benjamin Galloway, Erdem Sasmaz, Bihter Padak, University of South Carolina, USA

Oxy-combustion proposes to incorporate carbon capture and storage technologies into existing coal-fired power plants to lower carbon emissions. It does so by separating out the N<sub>2</sub> prior to combustion, resulting in a concentrated CO<sub>2</sub> as a final product that can be easily captured and stored. Sulfur oxide (SO<sub>x</sub>) emissions can be lowered due to high concentrations of SO<sub>3</sub> in the oxy-combustion flue gas resulting in sulfur retention on fly ash and ash deposits in the furnace. It has been shown that the extent of sulfur

retention is heavily dependent on the alkali and alkaline earth metal (AAEM) species in coal such as Na, K, Mg and Ca and the sulfur retention increases as the AAEM:S molar ratio increases. While higher sulfur retention on the ash particles reduces the emission rates, it creates problems utilizing the fly ash for cement and concrete production.

Although there have been previous experimental studies, the mechanism of sulfur retention on fly ash is not well understood. In this study, density functional theory (DFT) calculations were performed using Vienna *ab initio* Simulation Package (VASP) to investigate the binding mechanism for SO<sub>3</sub> on several metal oxides that compose fly ash, namely CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O. Energies and density-of-states were calculated for a variety of binding sites and adsorbate orientations to examine the binding mechanism and electronic interactions that occur between the surface and adsorbate. Results show that the SO<sub>3</sub> binding energy follows the trend i.e., K>Na>Ca>Mg. Calculations were also run where SO<sub>3</sub> was co-adsorbed with H<sub>2</sub>O to examine if its presence would facilitate oxidation to H<sub>2</sub>SO<sub>4</sub>. Results yielded the most energetically favorable structures for binding and provide a starting point for examining additional heterogeneous reactions between SO<sub>3</sub> and the other fly ash components.

#### **Research of Fuxian Coal Desulfurization and Ash Reduction by the Flotation Method**

Zhao Shiyong, Liu Meimei, Wu Peipei, Zhou Anning, Yang Zhiyuan, Xi'an University of Science and Technology, CHINA

High-sulfur coal in this research is the sample from Fuxian, Shanxi Province. It studies desulfurization and ash reduction research of Fuxian coal by the flotation method. This paper discussed the ash, sulfur, disseminated state of pyrite sulfur and floatability of sulfur in raw coal, and carried on the experiment of desulfurization and ash reduction by flotation. It investigated mainly ball milling, ultrasonic pretreatment, coal slurry concentration, collector dosage, blowing agent dosage, inhibitor dosage and different agents which affected the result of desulfurization and ash reduction. From the test of desulfurization and ash reduction, we can know the ash of raw coal is 33.32% and sulfur is 3.31%, but after ultrasonic pretreatment, the sulfur is 1.95% and the ash is 16.52%, so ball milling and ultrasonic pretreatment on raw coal are better than conventional flotation. The results show that it is beneficial to expand the way of desulfurization and ash reduction through proper ultrasonic pretreatment on high-sulfur coal.

### **SESSION 13 Clean Coal Demonstration and Commercial Projects: Gasification Projects**

#### **Linc Energy: Advancing Underground Coal Gasification (UCG) Technology to a Commercial Reality**

Paul Ludwig, Linc Energy Operations, Inc., USA

Linc Energy presents an update on its significant progress made in advancing UCG technology to a commercial reality. Linc's proprietary UCG technology is able to transform billions of tons of deep stranded coal around the world into valuable commodities and products.

Our presentation will be in three parts: a corporate update, a discussion of technical and environmental breakthroughs that are paving the road to UCG commerciality, and our learnings on the vital ingredients for a successful UCG project.

Linc has achieved several important milestones over the last 12 months. These include:

- Completion of the operating portion of its 14-year research, development, and demonstration program at its Chinchilla plant in Queensland after numerous important accomplishments.
- Receipt (expected by October) of our first US license to construct and demonstrate UCG technology, in Wyoming.
- Initiation of project development activities for two commercial UCG opportunities globally.
- Active support of our first commercial licensed opportunity with Exxaro in southern Africa.

The foundation of our progress towards commercialization rests on technical advancements and growing environmental permitting experience in diverse locales. We'll discuss:

- Our demonstration of safe and effective decommissioning practices.
- Learnings from our environmental license process in Wyoming.
- Progress on economic commercial design practices resulting from our UCG project development activities.

Finally, we have made substantial progress in recognizing the critical ingredients of a successful commercialization of UCG. These include:

- Market "demand" for products and the availability of plentiful unmined deep coal deposits.
- Presence of key geological and hydrological properties of coal deposits in the area.
- Solid project economics.
- Political will and support.
- Regional customers, suppliers, and partners.

#### **Update on the Kemper County IGCC Project**

Diane Revay Madden, DOE/NETL; Matt Nelson, Tim Pinkston, Southern Company, USA

The Kemper County Energy Facility is a lignite-fueled 2-on-1 Integrated Gasification Combined-Cycle (IGCC) facility incorporating the air-blown Transport Integrated Gasification (TRIG™) technology jointly developed by Southern Company; KBR; and the United States Department of Energy (DOE) at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. The plant is owned by Mississippi Power Company (MPC) and South Mississippi Electric Power Association (SMEPA), and has a net capacity of 524 MW with a peak net output of 582 MW with duct firing. Incorporating advanced emissions-control equipment, the facility is designed to produce marketable products of ammonia, sulfuric acid and carbon dioxide. At least 65 percent of the carbon dioxide will be captured and used for enhanced oil recovery (EOR), making the Kemper facility's carbon emissions comparable to those of a similarly sized natural gas-fired combined cycle power plant. The Kemper County project team is currently completing the last phase of construction for the plant and startup commissioning activities are underway. The facility's commercial operation date (COD) is scheduled to be fully operational in the fourth quarter of 2014. This presentation will provide both background and a status update for the Kemper County IGCC project.

#### **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

RTI has developed a warm syngas desulfurization process (WDP) that has been demonstrated successfully at both lab and pilot scale. Results from the lab and pilot tests have shown that the WDP technology has potential to significantly improve both the efficiency and cost of gasification plants. Because of the demonstrated WDP performance and anticipated benefits, RTI has negotiated a cooperative agreement with the U.S. Department of Energy for a 50-MWe 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. Construction on the project is now finished, and by the time of this conference the demonstration testing program should be almost halfway completed. The project scope also includes a sweet water gas shift (sufficient for 90% carbon capture conversion) coupled with carbon capture via an advanced activated amine system. This advanced activated amine system has enhanced capabilities for CO<sub>2</sub> capture, but has previously been excluded from use in syngas applications because of its relative non-selectivity between sulfur and CO<sub>2</sub> and some sensitivity to high sulfur exposure. Because of the selective upstream sulfur removal by RTI's WDP process, the CO<sub>2</sub> capture target can be achieved by this amine process without detrimental effects of higher sulfur exposure. Since the amine process is expected to provide high removal of any low level residual sulfur following the WDP step, the integration of these two processes is expected to reduce overall sulfur in the treated syngas to very low concentrations, suitable for rigorous syngas applications. These integrated processes are also expected to achieve syngas cleanup 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<sub>2</sub>S and COS from coal/petcoke derived syngas, operate for 5,000 to 8,000 hours, and capture up to 90% of any CO<sub>2</sub>. The results from this project will be used to establish performance criteria for stable commercial operation, including reliability, availability, and maintainability performance, provide extensive operating experience including startup/shutdown and operator training, and verify capital and operating costs. The results from the demonstration project will be utilized to update current performance and economic models. This presentation will provide an overview of these integrated syngas cleanup technologies, the status of the pre-commercial demonstration project and its performance to date, and updated economic comparisons with conventional syngas cleanup technologies.

#### **Texas Clean Energy Project Update**

Karl E. Mattes, Summit Power Group, USA

The Texas Clean Energy Project (TCEP or the Project) will be a first-of-its-kind integrated gasification combined cycle (IGCC) power plant sited in West Texas's

Permian Basin, a hub of energy resource development and sequestration activity. TCEP will integrate for the first time proven gasification and carbon capture technologies to achieve a carbon capture rate of ninety percent (90%). The Project will capture three million (2,500,000) tons of carbon dioxide annually for enhanced oil recovery (EOR) operations in the Permian Basin and ultimate geologic sequestration. The author will present a project status, technical and financial aspects of the project, and schedule going forward.

### Hydrogen Energy California: Project Update

Stefanie Korepin, James Croyle, Hydrogen Energy California, USA

The Hydrogen Energy California (HECA) project is an Integrated Gasification Combined Cycle plant with co-production of fertilizer and 90% carbon capture and sequestration. During 2011 Hydrogen Energy California LLC was purchased by SCS Energy California, LLC, an experienced power project developer with a successful track record. This presentation is an update on the project status and a discussion on the benefits and challenges of developing a Carbon Capture Utilization and Sequestration (CCUS) Project.

Supporting the project are the US Department of Energy (Fossil Energy), Mitsubishi Heavy Industries and Fluor. The US Department of Energy is providing funding to the project through an award made under Round 3 of the Fossil Energy Clean Coal Power Initiative (CCPI-3). Mitsubishi Heavy Industries is providing oxygen-blown gasification technology, the gas turbine/steam turbine/generator and will facilitate a portion of the project funding.

HECA will utilize Integrated Gasification Combined Cycle technology to produce synthetic gas from coal and petroleum coke that can then be separated into hydrogen for energy and fertilizer production and CO<sub>2</sub> for capture, utilization and sequestration. Over 90 percent of potential CO<sub>2</sub> emissions from the synthesis gas that is produced during steady state operations will be captured and used for EOR (approximately 3 million standard tons per year). This CO<sub>2</sub> will be compressed and transported via buried pipeline to nearby oil fields, where it will be injected underground and used for Enhanced Oil Recovery (EOR). The CO<sub>2</sub> EOR process involves the injection and reinjection of CO<sub>2</sub> into the oil fields to recover otherwise unrecoverable oil. During the process, the injected CO<sub>2</sub> becomes sequestered in a secure geologic formation. This process is referred to as CO<sub>2</sub> EOR and Sequestration. The CO<sub>2</sub> EOR and Sequestration process will employ existing, well-tested technology that minimizes potential risks and is protective of human health and the environment. As a result, the Project will provide low-carbon power, clean fertilizer and produce additional oil, while generating revenue for the state and creating hundreds of jobs.

This presentation will focus on the benefits of HECA including: 1) EOR, which offers a solution to CO<sub>2</sub> emissions associated with energy production from our abundant domestic energy sources. Safe implementation of CCUS/EOR on a large scale could significantly aid in climate change mitigation while at the same time improve US energy security, and production of other products in a low carbon footprint manner. 2) Poly-generation, which adds an additional revenue stream, making CCUS economically viable. 3) Economic development including thousands of union construction jobs and hundreds of permanent jobs. This presentation will also discuss some of the challenges that arise from developing a first-of-its-kind CCUS project in the US.

### SESSION 14

#### Coal Mining: Mine Reclamation and Mining Economics

#### Use of Flue Gas Desulfurization By-Products for Coal Mine Reclamation: Laboratory, Pilot, and Full-Scale Studies

Tarunjit S. Butalia, William Wolfe, Jason Cheng, The Ohio State University, USA

Unreclaimed coal mine lands present threats to human health, public safety, and the environment, such as disrupting natural streams, acid mine drainages (AMDs) discharge, dangerous highwalls, and hazardous habitats. In Ohio, it is estimated that about 1,300 miles of streams in the state have been impacted by AMD. Coal combustion by-products (CCBs), e.g., flue gas desulfurization (FGD) by-products, as backfill material can be an effective and economical approach to re-contour the original landscape of unreclaimed mine lands, eliminate dangerous highwalls, and abate AMD. In this study, the response of using FGD materials to reclaim mine lands is investigated in different scale settings, i.e., laboratory, bench, and full-scales. Currently, two full-scale reclamation projects of varying constructability and fill material combinations are being carried out at two unreclaimed mine lands near American Electric Power (AEP)'s Conesville and Cardinal coal combustion power plants. Approximate 1 million tons and 0.5 million tons of FGD by-products are to be placed at the Conesville Five Points and Cardinal Star Ridge demonstration sites, respectively. The changes of the water qualities of the upper-most aquifer systems underlying the reclamation sites are studied to assess the environmental response. The groundwater and surface waters around the reclamation sites are collected periodically

(monthly or quarterly) and analyzed for 34 parameters and constituents. Over 18-month worth of background water quality data were collected before reclamation began. The water monitoring data collected before and after reclamation started are analyzed for upper prediction limits (UPLs), Mann-Kendall trend test, principal components, and by geochemical modeling to detect and reveal any water quality changes. In the laboratory study, the effect of pH on the intrinsic leaching behaviors of the stabilized FGD materials under AMD percolation condition are investigated using protocols modified from USEPA methods. The partitioning of constituents in the liquid and solid phases as a function of liquid-to-solid ratio is also determined. A bench-scale mine highwall reclamation testing module, which has dimensions of 3 feet by 4 feet by 12 feet, is used to investigate the effectiveness of using stabilized FGD material for coal mine reclamation and AMD neutralization. A number of potential placement designs of stabilized FGD material against a mine highwall for AMD treatment are presented and tested in the module, which simulates the conditions similar to AMD penetrating stabilized FGD material during and after mine highwall reclamation under real-life scenarios. The module has pre-installed testing ports for water pressure measurement and leachate collection, which allows the detections of AMD flow within the mass of the fill as well as the change of AMD water quality along the flow. Results obtained from the laboratory- and bench-scale investigations are to be used in the design of a full-scale demonstration project, in which an AMD-producing unreclaimed coal mine highwall complex located at Cheshire, OH will be reclaimed. Results obtained from the laboratory, pilot, and full-scale studies will be discussed and demonstrate the potential impacts associated with coal mine reclamation using FGD by-products. The overall goal of these studies is to assess the potential of using high-volume CCBs in a manner that is economically viable and beneficial to the environment, the public's health and safety, and the generating industry.

#### Drillability Assessment of Rocks Based on Strength and Brittleness

Okan Su, Utku Sakiz, Ekin Koken, Bulent Ecevit University, TURKEY

Jumbo drills are commonly used in drilling and blasting method when the conditions are not suitable for mechanical excavation. They are used for opening blast holes and bolt holes in galleries and various types of tunnels. The performance of a jumbo drill is quite important to obtain maximum drilling rates. For this reason, drillability of rock is assessed in the laboratory to get an idea about its resistance to drill. It is put into consideration and evaluated carefully in order to reach maximum penetration rates in tunnels. Rapid and feasible drilling can only be achieved by successful assessment of rock drillability.

There are a number of factors based on both geologic and machine parameters affect the drilling process. The mechanical properties of the rock characterize the drillability and give us information about it. Besides, specific drilling energy (SDE), which is defined as the amount of energy to excavate a volume of rock, is a valuable parameter to identify and have an idea about the drillability of rocks. In order to increase the drilling efficiency and penetration rate of a drill, all these parameters should be evaluated and predicted prior to buying a rock drill in a mine or tunnel.

The first serious discussions and testing of specific drilling energy emerged during the 1960s by Teale (1965). He emphasized that the specific energy consumed during the drilling process of blast holes may be predicted accurately from penetration rate, drill bit diameter, rotational speed, and thrust force. He proposed Eq. (1) in which the energies in the thrust and rotary components are separately summed.

$$SDE = \frac{F}{A} + \left(\frac{2\pi}{A}\right) \cdot \left(\frac{NT}{u}\right) \quad (1)$$

where SDE is specific drilling energy F is force acting on the bit, A is area of cross sectional area, N is rotation speed, T is torque, u is penetration rate.

Hughes (1972) and Mellor (1972) later suggested that the specific drilling energy can be calculated by Eq. (2) since the uniaxial compressive strength was used as a predictive model of drillability by many researchers. Both of these equations can successfully be used in a tunneling project.

$$SDE = \frac{\sigma_c^2}{2E} \quad (2)$$

where  $\sigma_c$  is unconfined compressive strength, E is the secant modulus from zero load to failure.

This study evaluates rock properties for correlation of specific drilling energy with drilling rate index and Brazilian tensile strength. In order to achieve these objectives a number of samples were collected from tunnels and underground galleries at Zonguldak Hardcoal Basin in Turkey. They are mostly coal measure rocks such as sandstone, limestone, clay, siltstone, and conglomerate. Once the blocks were delivered to the laboratory, the entire blocks were cored in NX size. Then, uniaxial compressive and Brazilian tensile strength of rocks were determined. The UCS of the rock samples varied from 40-80 MPa and were classified as having medium-hard strength characteristics. The modulus of elasticity was also measured at a stress level equal to 50% of the axial stress-axial strain curve. Then, SDE was calculated by Eq. (2) in the light of the UCS test results obtained in the laboratory.

In addition to strength tests, the drilling rate index (DRI), which is based on two laboratory tests such as brittleness tests ( $S_{20}$ ) and Sievers' miniature drill tests (SJ), of the same rocks was determined since it has the best capability of predicting rock

drillability as an alternative method in the laboratory conditions. Then, the relationships between drilling rate index and strength tests was investigated. In addition, a correlation between drilling rate index and SDE was examined.

The specific drilling energy and the strength test results exhibited significant correlations with the drilling rate index. In that sense, an inverse linear correlation was found between the strength test results and drilling rate index. Thus, it can clearly be claimed that the strength properties of coal measure rock give preliminary idea about the drillability of rocks. On the other hand, a similar trend was also obtained from the curve between DRI and SDE. We found that the specific drilling energy decreases as the DRI increases. Therefore, it can be concluded that all test methods evaluated in the study provide reliable estimation of the drillability.

These results may provide vital information for evaluating the performance of rock drills and selecting drilling equipment, improving the productivity and penetration rates as well as saving drill costs.

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### GIS Analysis of Coal Values in Evaluation and Design of Model of Flexible Production at TKI Mines

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General Directorate of Turkish Coal Enterprises (TKI) corresponds to open coal quarries with a production of 43 million tons of run of mine coal countering 200 million cubic meter overburden material. 80 percent coal produced is sold to the thermal power plants and the remaining 20 percent is sold to the industry and heating sector. Environmental constraints of the coals of these markets, price and coal properties are different.

The demand of coal is increasing, especially in the industrial sector with environmental sensitivity. Existing reserves in accordance with market conditions, taking into account environmental factors necessitate the production of the coal in the most economical way. GIS (Geographical Information System) is a database containing basically the geographical coordinates which allows visual analysis.

Coal analysis values (thermal, sulfur, moisture, ash), environmental constraints and market conditions are associated with the GIS environment, thus the total weights of the domains of production matrix is created and TKI open pit coal reserves production model design is performed.

As a result of questioning existing data with necessary calculations and analysis, decision support phase is created to give answers to meet the needs of the users according to the coal production quality. Thus, using the coal analysis values of the reserves of the open pit mines of TKI, a flexible production model has been designed including the market situation.

### Acid Mine Drainage (AMD) Treatment Options for an Abandoned Coal Mine

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Characterization of environmental conditions related to legacy coal mining was conducted at a coal-fired power plant owned and operated by American Electric Power (AEP). An investigation was performed to assist in defining near-term treatment options and/or requirements during closure construction of a fly ash reservoir, where a network of sluice pipes conveyed water-entrained fly ash from the Plant to the reservoir for disposal. Sluicing and disposal of fly ash ceased in 1994, when flue gas desulfurization (FGD) units were installed at the plant.

Acidic streams (pH < 4) appear to coincide with known coal mine drift entries, auger borings, and air shafts that had previously existed along the highwall. Acid Mine Drainage (AMD) flow rates were measured continuously over a four month-long period. The impact of precipitation on AMD was assessed by comparing meteorological data with measured flow rates and water quality parameters. Following data collection, *AMDTreat* computer software was used to assess treatment options.

#### SESSION 15 Gasification: Underground Coal Gasification

### Africary Under Ground Gasification Project: An In-Depth Coal Characterization Study of the Theunissen Coal Reserve in South-Africa

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Africary has acquired the coal rights to the Theunissen coal field in South-Africa and is proposing to develop underground coal gasification (UCG) as a means of exploiting these deep and unutilized coal reserves. The current project, as it will be presented in this paper, will involve gasification of about 5 million tons of coal over 20 years under an area of about 100 hectares and will generate 50 – 60 MW, but Africary will apply for a mining right over the entire exploration right area of almost 300 square kilometres. If the current project proves to be commercially viable, gasification may be expanded to a larger area and the power generation capacity may also be expanded. Coal characterization, together with a fundamental understanding of the chemical and physical properties of coal are an important component in operating and optimizing any coal conversion technology. In both gasification and combustion, coal characteristics are the key input for stable and efficient operations. Coal characterization is not only important towards long term fundamental R&D, but a critical component also in day to day quality control of gasification and combustion operations, and more specifically for this study in designing and operating an Under Ground Gasification Process. Coal is a crucial and available feedstock for South Africa's unique electricity, synfuels and petrochemicals industry and a detail in-depth understanding of the coal composition and structure of a coal resource are necessary for efficient and effective utilization. A detailed knowledge of coal characteristics is essential to predict gasification behaviour when a specific coal source is to be gasified. The TUCG project is targeting coal in the Theunissen Coalfield, a middle Ecca coal deposit which is in a Karoo aged coal basin with a floor of volcanics (extrusives) of the Ventersdorp Supergroup in the north and in the south quartzites of the Witwatersrand Super Group. A total of four (4) coal seams have been identified however not all seams meet the minimum requirements for potential UCG exploitation in terms of seam thickness, depth, qualities and proximity to infrastructure. Seam 3 is the most widely distributed and economically significant developed coal seam and also most suitable for UCG, with a thickness ranging from 0.83m to greater than 5m and a depth ranging from 245 to 385 meters below surface in the target area. The coal quality, together with gasification behaviour, is suitable for UCG and the raw calorific value has an average of 20.3 MJ/kg. The raw volatile matter content has an average value of 19.2 % all on an air dried basis. The raw ash has an average value of 30.8 % on an air dried basis.

This paper will address an in-depth overview of the coal geology, coal characteristics and gasification behaviour of the coal for UCG purposes.

### Bloodwood Creek UCG Pilot 2011-2014

Burl E. Davis, Carbon Energy Pty. Ltd., USA; Cliff Mallet, Carbon Energy Pty. Ltd., AUSTRALIA

In April, 2011 Carbon Energy PL installed Panel 2 of their Keyseam UCG technology (a parallel UCG CRIP module) at their site at Bloodwood Creek, 50 km west of Dalby, Queensland Australia. The unit was operated until October of 2012 and generated 188,000 GJ fuel gas as feed to a 5 MW of electricity plant. This demonstrated the commercial applicability of fuel gas generated by the Carbon Energy Parallel CRIP UCG process. The Panel 2 module operation was terminated and the gasifier decommissioned, to verify effective rehabilitation can be achieved for local regulators. Exploratory wells have been drilled into the inactive cavity to obtain water and core samples to obtain information needed for the Rehabilitation Plan. Once Government approval of the rehabilitation plan is achieved Carbon Energy will initiate an Environmental Impact Statement for commercial development of a Synthetic Natural Gas plant to feed into the local gas network.

### Underground Coal Gasification in China

Feng Chen, ENN Sci. & Tech. Co.Ltd., CHINA

In this report, the Inner Mongolia Wulanchabu underground coal gasification demonstration project founded in 2006 is mainly introduced, the project was listed as the national "863 Program" by Ministry of science and technology in 2011. Lots of scientific achievements have been made in many aspects after more than 7 years of scientific research and experiments, such as: the design of underground gasifier is more reasonable, complete underground gasification technology system, detection and monitoring of the underground combustion zone, the underground gasification process to produce high-quality gas, and groundwater quality monitoring and pollution prevention. Under the support of national policies, the project has been allowed to build the first demonstration project to synthesize liquefied natural gas use the gas produced by underground gasification process (UCG-LNG) in China. The feasibility of the UCG-LNG project was analyzed, and finally, the research directions and contents of UCG technology in the future in China are introduced.

### Laboratory Studies of Coal Combustion Zone Evaluation Using AE Monitoring During Underground Coal Gasification (UCG)

Faqiang Su, Ken-ichi Itakura, Muroran Institute of Technology; Gota Deguchi, Underground Resources Innovation Network; Kotaro Ohga, Junichi Kodamac, Hokkaido University, JAPAN

Underground coal gasification (UCG) is a technique for the utilization of coal reserves, particularly at great depths or complicated geological conditions where mining is not economical. UCG involves the gasification of coal in the underground by injecting oxidants through an injection well and extracting the syngas through a production well. This process has only a modest environmental impact and produces an easily transportable product.

Due to the low permeability nature of the coal seams, the injection and production wells are linked by a channel, which can be developed with various linking techniques. The typical UCG model designed in our works consists of a coal block molded with heat-resistant concrete in a drum can and a typical linking-hole passing through the coal block. The configuration of these linking methods implies different technologies for adapting the different buried conditions of the coal seam, such as V-shaped, L-shaped, and Coaxial linking-holes. A UCG model experiment conducted using an artificial coal seam was also introduced in this report.

UCG demands precise evaluation of the combustion area in the underground coal seam. Especially, the monitoring of fracture activity in the coal seam and around rock is important not only for efficient gas production but also for estimation of subsidence and gas leakage to the surface. During UCG process, after creating a combustion reactor in an underground coal seam, air and oxygen flow through the injection well. Heat energy and gases are collected from the production well. As gasification progresses, the combustion reactor is moved along the linking hole. Using this process, the fracturing activity inside the coal seam serves an important role for enlargement of the gasification zone because the surface area oxidation increases continuously by coal cracking. For effective coal gasification, fracturing activity must be controlled. Moreover, excess fractures inside the coal seam and surrounding rock can induce gas leakage, underground water contamination, subsidence, etc. Therefore, monitoring and control of fracturing activity in underground areas constitute key technologies for efficient and safe UCG. During burning of the coal, temperatures inside the coal, contents of product gases and acoustic emission (AE) activity were monitored successively under the control of feeding gas (air/oxygen and steam) flow rate.

In the UCG experiments, AE source locations and moment tensor analysis were investigated to establish a crack distribution model. Results show that the combustion propagated inside the coal along the linking hole. Many AE events were generated during coal combustion. These AE generations seem to result from the crack initiation and extension around coal combustion area in the influence of thermal stress. AE activity was related closely to temperature changes inside the coal. Monitoring the AE during UCG process is a useful tool to infer the mechanisms of failure and to estimate the damage zone development. The crack distribution model constructed through three-dimensional calibration of AE sources and moment tensor analysis is expected to be useful to evaluate the gasification process, and to provide important data and parameters for developing the UCG simulation.

#### Underground Coal Gasification: Prospects for Carbon Capture and Storage

Alexey V Belov, Igor V. Grebenyuk, Far Eastern Federal University, RUSSIA; Nikolai N. Kinaev, Strategic Energy Consulting Pty. Ltd., AUSTRALIA

Despite the rapid developments in renewable energy sources, fossil fuels remain dominant in the global energy mix, and coal continue to be one of the cornerstones of energy supply. According to experts at the 2020 world consumption of coal will be approximately 6.4 billion tons a year, compared with the figures for 2011 to 5.5 billion tonnes. The realisation of "Current policies" scenario by 2035 may result in more than 40% increase of coal demand (up to 7.8 billion tonnes).

The "450 Scenario" analysis is based primarily on the pledges announced in association with the Copenhagen Accord and Cancun Agreements, alongside the rapid implementation of plans to remove fossil fuel subsidies announced by the G20 in 2009. Emission reductions in the energy sector on the scale and at the pace described in the "450 Scenario" would require introduction of modern Clean Coal Technologies.

Coal has met nearly half of the rise in global energy demand over the last decade, growing even faster than total renewable energy deployment. Whether the of coal demand continues to grow, remains constant or even decreases, will depend on a number of factors, such as: the strength of policy measures favouring lower-emissions energy sources; the deployment of more efficient coal-based power generation technologies, and, especially important in the longer term, the CCS deployment [2]. It is important to note, that coal can be seen not only as an energy resource, but also as the alternate source of hydrocarbons. In this context Underground Coal Gasification Technology (UCG) may play a noticeable role in emissions reduction and secure energy supply.

Underground coal gasification is one of the technologies with a potential to reduce emissions of greenhouse gases in the atmosphere. There are three possible ways of decreasing CO<sub>2</sub> emissions with the help of Underground Coal Gasification:

- Carbon dioxide storage in extinguished underground gasifiers;
- Power generation and/or polygeneration with pre-combustion CO<sub>2</sub> capture process in Underground Coal Gasification;

Using of carbon dioxide during gasifiers construction and operation.

UCG can play a significant role in the future energy mix in a carbon-constrained world. While UCG technology by itself does not have any noticeable difference in carbon footprint compared to the conventional IGCC power generation, it is readily available for CCS deployment. UCG can also deliver some additional benefits, such as

CO<sub>2</sub> storage in extinguished UCG gasifiers, partial CO<sub>2</sub> utilisation for the construction of underground gasifiers, and substitution of natural gas for CCGT plants. Overall effect of the usage of UCG (combined with CCS) could be a reduction of CO<sub>2</sub> emissions up to 5.5 billion tonnes per year. That is 17.3% of current global carbon dioxide emissions from natural fuel in Pacific area only.

#### An In Situ Simulated Laboratory Tests Using MicGAS™ Approach for Bioconversion of Deep Unmineable Coals from the Tongue River Basin Between North of Sheridan, Wyoming and South of Ashland, Montana

Shaban Kotob, Robert Andrews, Shinwoo Lee, Daman Walia, ARCTECH, Inc.; William Orem, U.S. Geological Survey, USA

In recent years with increasing environmental concerns from coal use, the demand for cleaner-burning natural gas is rapidly increasing while coal energy production through use of thermo chemical approaches in the United States continue to worsen on multiple fronts because of release of pollutants and green house gases. However, coal continues to be the source of lowest cost-by-weight carbon fuel available compared to oil, gas and organic biomass, and retains deep economic and cultural importance to many communities. According to the US Geological Survey estimate, there are one trillion tons of coals in Wyoming out of 9.5 trillion tons of deep coal resources in the US (including Alaska). The vast majority of these resources are not currently economically and/or technically recoverable. The MicGAS™ technology provides a novel approach for *in situ* bioconversion of stranded coal to methane or for enhancing methane production in depleted coal bed methane deposits. The objective of this research was to establish the feasibility for *in situ* simulated laboratory pilot tests using termite derived microbes (MicAN microbes) to convert collected core coal and formation water samples from a site near the Tongue River in Rosebud County, Montana to biogas.

Two core samples were collected from each of the four coal beds: Knobloch (145.9ft – 160.1ft), Calvert (167.1ft – 172.0ft), Nance (204.1ft - 205.1ft), and Flowers-Goodale (370.7ft-380ft). Data showed that at 5% Coal loading, Tongue River coal bed samples were amenable to degradation by MicAN microbes and biogas was produced with 68 to 82% methane. To further test productivity of biogas in four coal samples, and also to select the best performing coal for *in situ* test, simulated laboratory tests were set up in microbioreactors with ground coal loading to culture medium at a ratio of 2:1. Over 209 days and at the high coal loading and in medium prepared in formation water, Knobloch coal produced 78.8% methane, the highest gas volume produced when compared with the other coal samples. Based on the results obtained from the microbioreactor tests, Knobloch coal was selected and used in an *in situ* large scale simulated horizontal bioreactor test. Over 73 days, biogas was produced from degradation of Knobloch under simulated *in situ* laboratory conditions and the data was extrapolated and productivity of biogas was 414 scf/ton of Knobloch coal per year. Based on laboratory experiments, we conclude that MicGAS™ approach provides baseline information for *in situ* bioconversion of stranded coal or for enhancing methane production in depleted coal bed methane.

#### SESSION 16

#### Combustion: Oxy-Combustion and Chemical Looping - 3

#### Fe-Ni Bi-Metallic Carriers for Chemical Looping Dry Reforming of Methane

Amey More, Saurabh Bhavsar, Götz Vesper, University of Pittsburgh, USA

'Chemical Looping Combustion' (CLC) is an emerging clean combustion technology which offers an efficient and elegant route for fossil fuel combustion with inherent CO<sub>2</sub> capture based on the cyclic oxidation and reduction of an "oxygen carrier" (typically a metal) with air and a fuel, respectively. We have recently shown that this process can also be used for CO<sub>2</sub> activation by replacing air with CO<sub>2</sub> as the oxidant for the process, thus enabling the reduction of CO<sub>2</sub> to CO (which has many uses in the chemical industry) as an alternate pathway to carbon sequestration. We had identified Fe as the most suitable metal for the process due to its good reactivity with CO<sub>2</sub> at realistic process operating conditions. However, Fe shows poor reactivity with methane as a typical fuel for this process. Ni and NiO, on the other hand, is well known as an efficient catalyst for methane combustion, but cannot be oxidized with CO<sub>2</sub>. We hence hypothesized that a bimetallic Fe/Ni oxide would show combined good reactivity with both CH<sub>4</sub> and CO<sub>2</sub> in the reduction and oxidation half cycles, respectively.

Supported Ni, Fe, and Ni/Fe oxygen carriers with 40wt% metal loading were synthesized using a simple wet-impregnation procedure. Three different ratios of the Fe to Ni were studied for their performance. Thermo-gravimetric analysis (TGA) of the carriers combined with X-Ray Diffraction (XRD) gave insight into oxidation states, carrier conversions, and reaction rates were evaluated in fixed-bed reactor experiments. We found that bimetallic oxides can indeed show activity for both methane combustion and CO<sub>2</sub> reduction, albeit the individual rates of oxidation are lower than for monometallic Fe carriers, and rates of reduction are lower than for monometallic Ni



carriers. For comparison, physical mixtures of monometallic Fe and Ni carriers with the same metal weight loadings were prepared to isolate the oxidation characteristics of the individual metal oxides during the reactive processes. Remarkably, a significantly higher rate of carrier conversion obtained with the physical mixture suggested that the steps involved were quite different from those in case of a mixed oxide. The different behavior can be explained based on a complex synergistic reaction sequence between the two carrier materials. Overall, our study thus identifies a promising carrier material for an efficient chemical looping process for CO<sub>2</sub> activation.

### Kinetics of Pressurized Oxycombustion of Coal Using Thermogravimetric Analysis

Piotr Babinski, Marek Sciazko, Martyna Tomaszewicz, Jaroslaw Zuwala, Institute for Chemical Processing of Coal, POLAND

Recently, a great amount of attention has been focused on the carbon dioxide emissions from the power sector due to the significant impact of these emissions on the greenhouse effect. To reduce the emissions of greenhouse gases from fossil fuel-fired power generation, several technologies for emissions control are being extensively studied. Oxy-combustion of coal (in an O<sub>2</sub>/CO<sub>2</sub> atmosphere) instead of air combustion has been recognized as a promising option for existing power generation plants. The possibility of retrofitting existing boilers to enable combustion in an O<sub>2</sub>-enriched atmosphere can bridge the gaps resulting from the present high cost of oxygen and the lack of continuous large-scale operation of such units. On the other hand, in new power generation units the pressurized oxy-combustion of coal is a competitive technology, and the main advantages of this process are as follows: the increased net efficiency of power generation, the reduced size of the boilers and the reduced costs of the capture and compression of flue gas CO<sub>2</sub> for sequestration.

The focus of the present work was on evaluating the oxy-combustion kinetics of two different chars derived from Polish coals (subbituminous and lignite). The chars for the studies of the oxy-combustion processes were obtained via devolatilization of coal in a bench scale laboratory reactor at a temperature of 1273 K and at atmospheric pressure. The kinetics of the char oxy-combustion was examined using the TA Instruments TG-HP150s pressurized thermogravimetric analyzer at absolute pressures of 0.1, 0.5 and 1 MPa. The experiments were carried out at isothermal conditions and at a wide range of temperatures (773 – 1273 K). Gas mixtures that contained 20% and 30% of O<sub>2</sub> in CO<sub>2</sub> were used as oxidants. Additionally, at a temperature of 873 K the experiment was performed using 10% and 40% O<sub>2</sub> in CO<sub>2</sub>. Kinetic parameters such as the activation energy, pre-exponential factor and reaction order with respect to oxygen concentration were calculated by using the model fitting method and the isoconversional method. The influences of temperature, pressure and O<sub>2</sub> concentration were established. The results show a significant shift of the oxycombustion process from the kinetically controlled regime to the diffusion – controlled regime with increasing temperature and pressure.

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### Unsteady CFD Simulation of Hematite Reduction by Methane in a Bubbling Fluidized Bed

A. Konan, DOE/NETL/ West Virginia University; J. Fisher, Y. Liu, URS/DOE/NETL; J. Weber, E. David Huckaby, R. Breault, W. Rogers, DOE/NETL, USA

Energy production in a carbon-constrained environment requires the development of engineering technologies that minimize or eliminate the carbon footprint. Solutions exist provided that the engineering processes can capture the CO<sub>2</sub> produced when converting fossil fuel into electricity or other forms of energy. One such option is Chemical-Looping Combustion technology where a series of oxidation and reduction processes take place within the inter-connected system reactors circulating an oxygen carrying material. This process separates oxygen from air using a carrier material allowing oxy-combustion of the fossil fuel thereby facilitating CO<sub>2</sub> removal from the flue gas.

The present study focuses on the reduction stage of the Chemical-Looping Combustion process which occurs in the Fuel Reactor. Computational fluid dynamics simulations are performed of recent fluidized bed experiments at NETL. The simulations are performed using a customized version of the Eulerian-Eulerian solver, *compressibleTwoPhaseEulerFoam*, from the OpenFOAM finite volume toolbox/library. The kinetic theory closures of Simonin (1996) are used for the granular phase properties. Two reaction models for hematite reduction are examined: a four-step model (Cuadrat et al. 2012) supplemented by the water-gas-shift reaction model (Shi et al., 2008) and a two-step global model (Monazam et al., 2013 and Breault et al. 2014). The four-step reaction model assumes a spherical shrinking grain core where the reduced metal forms a shell around the un-reduced metal at the grain scale. The reactions are assumed to proceed in four step parallel steps: (1) partially oxidation of methane to form hydrogen and carbon monoxide, (2-3) full oxidations of hydrogen and carbon-monoxide and (4) a carrier-catalyzed water gas shift reaction. In

contrast, the methane is fully oxidized in the two-step reaction and H<sub>2</sub> and CO are not considered. Further, this model assumes the following processes in the carrier:

1. a fast step where oxidized iron is reduced in the surface region of the particle, which creates an O<sub>2</sub>-depleted layer around the particle;
2. a slow step which occurs by the diffusion of O<sub>2</sub> from the unreacted zone of the carrier particle towards the O<sub>2</sub>-depleted external layer.

The experiments were conducted using 1.5-3.0 kg of hematite (21-42 cm static bed height) in a 5.5cm bed which was fluidized with a mixture of 5-20% methane balanced by nitrogen and argon as tracer. The system operated slightly above atmospheric pressure (1.05 atm) at different operating temperatures between 700C and 900C. The gas compositions, which were measured using a gas chromatograph, are compared with computational predictions. Further analysis is performed of the flow and composition fields of the simulations at different operating conditions and with different carrier reaction models.

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### Effect of Oxyfuel Condition on Char Characteristics and Burnout

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Oxyfuel combustion is emerging technology for CO<sub>2</sub> capture and storage (CCS) in power generation field. Devolatilization and combustion study of three coals were carried out in a drop tube furnace (DTF) at 1673 K in different gas conditions such as N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub>. Char characteristics were measured using X-ray diffraction (XRD) and surface area analyzer by CO<sub>2</sub> adsorption. Under all the tested conditions, compared with combustion in air, the presence of CO<sub>2</sub> increased coal burnout due to char gasification with CO<sub>2</sub>. The effect of CO<sub>2</sub> on char properties was influenced by coal type such low volatile coal indicated small increase in the burnout. After treatment with 100% CO<sub>2</sub> in a DTF, high volatile coal showed a greater change in the carbon structure parameters and surface area of chars when compared to low volatile coal. The study has implications on coal selection for emerging oxyfuel combustion process due to their impact on char properties and hence on combustion performance.

### Redox Reactions Kinetics Study for Natural High Concentrated Fe-Based Oxygen Carriers

Ewelina Ksepko, Piotr Babinski, Marek Sciazko, Institute for Chemical Processing of Coal, POLAND; Evidou Antigoni, Lori Nalbandian, Center for Research and Technology Hellas / Chemical Process Engineering Research Institute, GREECE

The presented paper shows the results of a Chemical Looping Combustion (CLC) study. The CLC technology has emerged during the last decade and is considered as one of the most promising combustion techniques. Its most significant advantages are that a concentrated pure CO<sub>2</sub> stream may be obtained after water condensation without any energy penalty for its separation, while at the same time the NO<sub>x</sub> emissions to the atmosphere are highly reduced.

The objective of this work is to study the reaction kinetics during the two steps of CLC, reduction and oxidation, for selected naturally occurring materials used as oxygen carriers. A Fe-based ore, Krivbas ore from Ukraine, is selected and evaluated during this study. The elemental composition of the ore is measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The material has high concentration of active metal oxides mainly Fe (84.8 %) and to a lesser extent Mn. The concentration of inerts such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> is relatively small (~8%, and ~1% respectively), while the content of CaO and MgO does not exceed 0.5%. The melting temperature of the material is high (1550 °C), which is important for practical application.

The reactivity measurements are performed at isothermal conditions (800 to 950 °C) during multiple redox cycles using a Thermo-Gravimetric Analyzer (TGA). CH<sub>4</sub> in Ar and synthetic air are used for the reduction and oxidation reactions, respectively. The material shows promising reactivity in CLC reactions, and might be practically used as oxygen carrier material. The kinetic parameters such as the activation energy, the pre-exponential factor and the reaction model are determined for the reduction and

oxidation reactions. Models of the redox reactions are selected by using the model fitting method. Both fresh material as well as samples used in several redox cycles, are characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy combined with X-ray Microanalysis (SEM-EDS), in order to detect any structural or morphological changes and determine the stability of the ore in repetitive CLC cycles. Acknowledgement: This study was financed by The National Center of Research and Development Poland, project No. NCBiR/FENCO-NET2/2013 and the General Secretariat for Research and Technology Hellas, project No. 13FENCO-13-478A 'Minerals for Sustainable COst and energy efficient chemical looping combustion Technology'- MINERAL SCOUT.

### Slag Flow Modeling with Reactions in Oxy-Coal Combustors

Albio Gutierrez, Steven L. Rowan, Ismail Celik, West Virginia University, USA

Oxy-coal combustion with flue gas recirculation is a promising technology intended to reduce the anthropogenic emissions of CO<sub>2</sub> and other pollutants such as NO<sub>x</sub> and SO<sub>2</sub> into the atmosphere. This technology is being implemented in existing air based equipment, such as boilers and furnaces. Other unique application of oxy-coal combustion is the activation of chemical reactions due to the very high temperatures that can be generated with char/O<sub>2</sub>/CO<sub>2</sub> mixtures. This application entails an economical alternative to the electric arc furnace process for production of chemicals. In this application, the chemicals will be produced in the molten slag of the reactor. The reactor being designed will be used for the purpose of activating chemical reactions that occur at very high temperatures (namely the production of calcium carbide from char and lime). This reactor is an entrained flow reactor type with swirling flow for flame stabilization and flow of molten slag on the walls. In this work, a methodology for design is applied using a CFD model for turbulent combustion along with a model for slagging. The CFD model for turbulent combustion utilizes the Reynolds-averaged Navier-Stokes (RANS) approach for fluid flow, heat transfer, and turbulent-chemistry interaction. The multiphase character of the flow in the combustor chamber is considered using the Eulerian (gas phase) – Lagrangian (Particle phase) treatment. The interaction between continuous and discrete phase is taken into account by using source terms in the coupling equations for mass, momentum and energy. The slagging model is based on an integral approach of the boundary layer theory with modified properties for very high temperature conditions. The CFD model for turbulent combustion provides the inputs for the slagging model, such as boundary conditions and source terms. This methodology is being applied in the design of pilot scale reactors. Different O<sub>2</sub>/CO<sub>2</sub> atmospheres with different molar oxygen concentrations are taken into consideration. The validation process of the oxy-coal turbulent combustion phenomena is done using previous experimental measurements and CFD results. Results for the turbulent reacting flow field show a stable combustion process with a well-defined burner recirculation zone. Also, complete coal devolatilization and char burnout of approximately 97% are attained. Results also suggest that the gas temperatures required for initiation of calcium carbide production are obtained for O<sub>2</sub>/CO<sub>2</sub> oxidant mixtures with molar oxygen concentrations higher than 50%. Preliminary results for the slag flow model show that a steady liquid slag thickness and a growing solid slag thickness are attained. These values are in the same order of magnitude that the ones reported in previous work.

#### SESSION 17

#### Clean Coal and Gas to Fuels: Direct Liquefaction

#### Effect of Reaction Temperature on Hydroprocessing of Medium and Low-Temperature Coal Tar to Clean Liquid Fuels

Rui Wang, Xiaofen Guo, Donghui Ci, Pengxiang Song, Xin Cui, National Institute of Clean-and-Low-Carbon Energy, CHINA

As the world supply of crude oil is depleting and the pressing environmental requirement, coal tar is emerging as an alternative source of feedstock to the refiners for producing transportation fuels. Extensive studies are focus on the hydroprocessing of coal tar to produce clean liquid oils with ultra-low heteroatom content. At the temperature and pressure required for hydrotreatment, many undesirable reactions including dehydrogenation, polymerization, isomerization, and condensation would occur. The most important process variables, which generally affect the hydroprocessing performance, are temperature, pressure, hydrogen-to-oil ratio, and LHSV. In the present study, the bench scale hydrotreating of middle and low-temperature coal tar using commercial catalysts was performed. Clean liquid oil was obtained from coal tar via hydrotreating in three-stage fixed-bed reactor system. The effects of reaction temperature on hydrotreating performance was investigated when hydrogen pressure of 12 MPa and LHSV of 0.8 h<sup>-1</sup> and hydrogen to coal tar volume ratio of 1200 were kept constant. This work primarily aims to reduce heteroatoms (S, N and O) and produce high-quality liquid fuels under varied reaction temperature. The ceramic balls, protective catalysts and hydrofining catalyst combined with hydrocracking catalyst were filled in the first, second and three fixed beds (R1-R3),

respectively. As catalyst bed temperature (R2 and R3) increased from 260 to 380 °C, the density of product oil decreased and S and N content decreased in the feed from 0.2% and 0.62% to 14.6 and 5.5 ppm, while the molar ratio of H/C increased, indicating the increase of catalyst bed temperature improves the production of light oils in the certain range. When catalyst bed temperature was kept constant at 380 °C, the effect of R1 temperature on the product distribution of coal tar was also investigated. It is shown that the chemical properties are hardly changed when from 260 increasing to 320 °C including oil yield and heteroatom content, indicating that hydrogenation thermal reaction could not occur at this temperature in catalyst-free reactor. When further increasing to 380 °C, the S and N content increased two times to 30.3 and 10.8 ppm, respectively. The gasoline yield slightly decreased from 25.9% to 22.1% while the tail oil yield increased slightly from 10.8% to 13.1%. This indicates that conversion degree of coal tar to light oil decreased, resulting in decrease in the removal of heteroatoms and gasoline yield, due to the condensation reaction of C-C bonding in the absence of catalyst at high temperature. When protective catalyst (R2) temperature increased from 320 to 380 °C with the constant R1 and R3 temperature, the gasoline yield increased while residue oil yield decreased, and the degree of N removal was much higher than S removal. Gasoline (<180 °C) and diesel (180–360 °C) fraction were separated from the oil products and analyzed. As the catalyst bed temperature increased, the RON of gasoline and cetane value of diesel decreased but was still lower than the standard specifications. The results of distillate properties indicated that the raw middle and low-temperature coal tar could be considerably upgraded through catalytic hydrotreating to obtain fuels for catalytic cracking feed or directly used as fuels through the further optimization of upgrading process.

#### Direct Coal Liquefaction Technology and Economics

Eric Peer, John Duddy, Axens North America Inc., USA

AXENS North America, Inc. (AXENS NA) has a long history in direct coal liquefaction technology development and demonstration, with its origins dating back to the 1960's. Development of direct coal liquefaction technology was based on the commercial H-Oil @ Process and demonstrates the remarkable versatility of ebullated-bed reactor technology. In 2008 the first commercial scale direct coal liquefaction plant was started by Shenhua in China and Axens provided the basic engineering design and start-up services for this plant. Today this plant is operating at its design on-stream time and capacity, and has proven the reliability of DCL process technology and can be an economic and environmentally viable option for the production of transportation fuels. Axens coal processing technologies represent the best and most advanced coal liquefaction technologies available in the world today, and include the H-Coal Process (single and two-stage versions) and Coal/Oil Co-Processing. This paper provides a description of coal liquefaction technology options including the most suitable coal ranks, catalyst types, coal/oil co-processing and upgrading process options, and will illustrate economics for production of high quality liquid fuels today.

#### Effect of Extract-Containing Solvent Recycling in Degradative Solvent Extraction of Low-Grade Carbonaceous Resources

Ryuichi Ashida, Ryo Takahashi, Motoaki Kawase, Kouichi Miura, Kyoto University, JAPAN; Janewit Wannapeera, Nakorn Worasuwannarak, King Mongkut's University of Technology, THAILAND

The authors have recently proposed a novel method that not only dewater but upgrades low-grade carbonaceous resources such as biomass, peat, lignite, and sub-bituminous coals. The method comprises a treatment of the raw materials in non-polar solvent, such as 1-methylnaphthalene, at temperatures below 350°C, and subsequent separation of the upgraded samples into extract, residue, and gaseous product consisting of CO<sub>2</sub> and a negligible amount of hydrocarbon gases at the treatment temperature. The extract is further separated into solvent-soluble fraction, Soluble, and solvent-insoluble fraction, Deposit, at room temperature. The method can produce a large amount of Soluble which consists of ashless, carbon-rich, low-molecular-weight compounds. From the viewpoint of practical application of the proposed method, it is desired to reduce the energy required to separate the Soluble from solvent. In this study a treatment using the solvent saturated with the Soluble has successfully been proposed in order to omit the energy-consuming distillation process of the solvent by enabling solid-liquid separation of the Soluble and solvent.

#### Catalytic Cracking of Coal Pyrolysis Product for Oil Upgrading over Char Solid Heat Carrier

Jiangshan Ma, Xiaohong Li, Jie Feng, Wenying Li, Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), CHINA

Coal char can provide active surfaces for the decomposition of hydrocarbons. The fast pyrolysis of Shendong coal using coal char as the solid heat carrier was investigated in a fixed bed reactor to upgrade the liquid oil. Coal chars pyrolyzed from four different ranks of coals were chosen as the solid heat carrier in this study and quartz sand as the reference. For the solid heat carrier in pyrolysis, its activity and stability are an important factors. The recycle experiments of Shendong coal char were conducted to

investigate the stability of solid heat carrier. The results showed that all coal chars selected as solid heat carrier had catalytic cracking effect on coal pyrolysis. During pyrolysis process, tar yield decreased, while gas yield and light oil (hexane soluble) fraction in the tar increased. Moreover, the yield of light oil using low-rank coal char was higher than that using high-rank coal char. It is indicated that the cracking activity of low-rank coal char was superior to the high-rank coal char. The product distribution, gas composition and the char gasification reactivity changed little during the recycle experiments, which is demonstrated that the cracking activity and stability of Shendong char were relatively good as the solid heat carrier in coal fast pyrolysis.

#### **Study on Co-pyrolysis Char Properties of Lignite and Shendong Coal Direct Liquefaction Residue**

Lili Li, Yanli Xue, Xiaohong Li, Wenying Li, Taiyuan University of Technology, CHINA

In order to improve the tar yield and quality of conventional coal pyrolysis, pyrolysis of integrating hydrocarbon wastes-coal direct liquefaction resid (DLR) to lignite was put forward for utilizing organic matter and liquefaction catalyst in DLR. Experiments of co-pyrolysis of Shendong coal direct liquefaction resid and Hulunbeier lignite were conducted using a fixed-bed reactor under atmospheric pressure in nitrogen. Synchronous fluorescence spectroscopy, gel chromatography and thermogravimetric analysis were performed to explore the quality of tar, char gasification and combustion characteristics. The results showed that DLR had both positive and negative effects during co-pyrolysis. It can promote the evolution of volatile of lignite and meanwhile enhance the condensation reaction of volatiles, which can be controlled by adjusting the mixing ratio of DLR to lignite. The co-pyrolysis of DLR/lignite with ratio of 0.15 showed the highest tar yield, when the most pronounced interactive effect occurred. Under the optimal conditions, the average molecule weight of the tar was less than 2187 amu and tar was made up of 4-5 rings and more than 5 rings of heterocycle hydrocarbons. Combustion properties and CO<sub>2</sub> gasification characteristics of the co-pyrolysis char didn't improve. However, liquefaction catalyst was enriched in char and made the char have higher content of sulfur. It is suggested that DLR should be washed by solvent oil to remove liquefaction catalyst before co-pyrolysis with lignite.

#### **SESSION 18 Coal Science: General - 3**

#### **The Importance and State of Coal Industry in Turkey's Energy Policy**

Bilgehan Kekeç, Niyazi Bilim, Selçuk University, TURKEY

Coal which has widely reserve in the world has important position in energy raw materials and it has widely consumption area. Nowadays, the most important requirement of developed and developing countries is energy. Energy is a significant factor for economic development and social prosperity of countries. In this study, Turkey's energy situation, distribution of primer energy generation and consumption based on source and importance of coal production in Turkey were emphasized in terms of energy generation.

#### **Effect of Pretreatment Conditions on the Determination of Trace Elements in Coal by Use of Atomic Spectroscopy**

Tsunenori Nakajima, Kosei Haraguchi, Misa Taira, Hirokazu Takanashi, Akira Ohki, Kagoshima University, JAPAN

Recently, acid digestion assisted by microwave processing is popularly utilized for a pretreatment of the coal samples. It must be important to establish a proper protocol for coal in terms of the determination of trace elements by a joint-use of microwave assisted acid digestion (MW-AD) and atomic spectroscopy. In this study, the effect of MW-AD conditions on the determination of trace elements in coal by use of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) was examined. When MW-AD was carried out by using with or without HF condition, the recovery of tested elements was not affected by the HF addition in the MW-AD acid mixture. After the optimization of MW-AD operation temperature and time, the concentration of major and trace elements in two certified reference coals (NIST 1632c and SARM 20) was examined and the good recoveries for each element were obtained. In addition, the determination of ultra-trace elements in coal sample, such as As, Se, Cd, and Hg were investigated by use of flow injection ICP-MS (FI-ICP-MS) method.

#### **SESSION 19 Clean Coal Demonstration and Commercial Projects: Combustion Projects**

#### **Update to Cost and Performance Baselines for Fossil Energy Plants: Bituminous Coal and Natural Gas to Electricity**

Timothy Fout, James Black, DOE/NETL; Marc Turner, Booz Allen Hamilton, USA

The United States Department of Energy Office of Fossil Energy, in conjunction with its National Energy Technology Laboratory (NETL), conducts research, development and demonstration of advanced fossil-based power generation technologies. In the process of identifying R&D needs and evaluating the potential for improvement upon state of the art (SOA) technologies, it is often necessary to first establish a comprehensive baseline for performance and cost estimation. To this end, NETL has developed a set of studies titled, "Cost and Performance Baselines for Fossil Energy Plants." This year, an update was performed to Volume 1, "Bituminous Coal and Natural Gas to Electricity". In Volume 1, coal generation is evaluated for both integrated gasification combined cycles (IGCC) and pulverized coal plants while natural gas generation is evaluated for natural gas combined cycles (NGCC). All technology types are evaluated both with and without carbon capture and storage technology. The analyses were performed on a consistent technical and economic basis that accurately reflects current market conditions for coal and natural gas fueled plants. The cost and performance data were compiled from published reports, information obtained from vendor quotes and users of the technology, and data from designing and building utility projects.

This update includes more recent performance and cost information for several key process components including CO<sub>2</sub> capture, compression, and steam turbines. All environmental pollution control systems were updated to ensure meeting the latest regulations. This includes the addition of dry sorbent injection and activated carbon systems to address the required levels of Hg capture under the new Mercury and Air Toxics Standard. Along with other modifications to more accurately represent state of the art systems, costs were escalated to a June 2011 basis. Information to be presented during this paper will focus on the new technologies, processes and assumptions included in the study, along with the updated process performance and economic model results. Results presented will focus on the IGCC and PC cases. NGCC results will be highlighted for reference. Comparison will also be made with cases that examine CO<sub>2</sub> emissions limits of 1,100 lb CO<sub>2</sub>/MWh for new coal based generation.

#### **Four Years of Operating Experience with DryFining™ Fuel Enhancement Process at Coal Creek Generating Station**

Charles Bullinger, Mark Ness, Michael Briggs, Great River Energy; Nenad Sarunac, University of North Carolina at Charlotte, USA

Lignite and other low rank coals generally contain high amounts of moisture (sub-bituminous: 15 to 30%, lignites: 25 to 40% brown coals: 50 and 60%). The high moisture content causes a reduction in plant performance and higher emissions, compared to the bituminous (hard) coals.

Despite their high-moisture content, lignite and sub-bituminous coals are attractive due to their abundance, low cost, low NO<sub>x</sub> and SO<sub>x</sub> emissions, and high reactivity (high combustion efficiency).

A novel low-temperature coal drying process employing a fluidized bed dryer and using waste heat was developed in the U.S. by a team led by Great River Energy. The coal drying system at Coal Creek Station has been in a continuous commercial operation since December 2009. Four years of operating experience are described in this paper.

#### **WA Parish Carbon Capture and Enhanced Oil Recovery Project**

Anthony Armpriester, David Greeson, Petra Nova LLC, USA

Petra Nova Parish Holdings LLC (PNPH), a subsidiary of NRG Energy Inc. (NRG) plans to build and demonstrate a 240 Megawatt equivalent (MWe) slip stream post combustion carbon capture system (CCS) at NRG's WA Parish facility in Fort Bend County, TX for the intent of carbon dioxide enhanced oil recovery (CO<sub>2</sub>-EOR) and accompanying sequestration. The project has been designed to capture at least 90% of the CO<sub>2</sub> from a 240 MWe slipstream drawn from an existing coal fired electric generating unit that would otherwise be emitted to the atmosphere. The CO<sub>2</sub> would be captured using a proprietary advanced amine-based capture technology. The captured CO<sub>2</sub> would be compressed and transported via a new approximately 80-mile-long pipeline to the existing West Ranch oilfield in Jackson County, Texas.

Fully integrated carbon capture, utilization, and storage (CCUS) systems with multi-party involvement and first-of-a-scale technology are also inherently risky and face noteworthy challenges. These issues, coupled with an uncertain political and regulatory landscape have slowed the progress of many clean coal projects. However, Petra Nova has addressed many of the issues (both commercially and technically) that

are inherent to large clean energy projects. Through their development efforts, Petra Nova has pioneered and applied novel solutions to make this project environmentally friendly, technically efficient, and economically feasible.

The focus of this paper will be to update the status, progress, and next steps of the project development and execution, and will also touch upon some of the unique technical and commercial solutions that have helped sustain its progress. Technical considerations such as how capture system energy requirements will be met, understanding water use and discharge options, determining how to handle emissions and effluents, optimizing site arrangement and layout choices, and others may be explored. Lastly, some of the non-confidential commercial arrangements that align stakeholders with differing objectives toward a common goal will be presented.

This material is based upon work supported by the Department of Energy under Award Number DE-FE0003311.

### **Technical and Economic Analysis of Alstom's 550MWe Chemical Looping Combustion Steam Power Plant**

Wei Zhang, Glen D. Jukkola, Iqbal F. Abdulally, Herbert E. Andrus, Shin G. Kang, Alstom Power Inc., USA

Alstom's Limestone Chemical Looping Combustion (LCL-C™) is a transformational technology that has the capability to capture CO<sub>2</sub> from new and existing coal-fired power plants while maintaining high plant power generation efficiency. Steam power plants using LCL-C™ technology were designed in four different configurations in this study: (1) an atmospheric pressure LCL-C™ system using transport reactors for both the Oxidizer and Reducer reactors, (2) a LCL-C™ system with the Reducer reactor only operating in the circulating fluidized bed (CFB) mode, (3) a LCL-C™ system with an advanced ultra-supercritical (AUSC) steam cycle, and (4) a pressurized LCL-C™ system with an AUSC steam cycle. Alstom conducted a techno-economic analysis on 550MWe steam power plants with these arrangements. Detailed process models and the cost estimating methodology were developed with assumptions defined by the US Department of Energy (DOE) Quality Guidelines for Energy System Studies (QGESS). The design basis was chosen to be the same as the published DOE Supercritical Pulverized Coal (SCPC) plant baseline case to facilitate the comparison with other Carbon Capture, Utilization, and Sequestration (CCUS or CCS) technologies in the industry. This paper summarizes the design and modeling basis for each technology case, along with the environmental targets, economic criteria, and costing assumptions. The technoeconomic analysis results show that Alstom's LCL-C™ technology has the potential to remove at least 96% of the CO<sub>2</sub> with less than a 20% increase in the cost of electricity (COE) as compared to a SCPC plant without CCS. The results also show a less than 10% CCS energy penalty in the LCL-C™ plant, which is significantly lower than the typical 25% energy penalty from the DOE oxy-combustion SCPC case. This study has reinforced the favorable projected economics of LCL-C™ as a potential "game changing" breakthrough technology that can significantly reduce the cost associated with coal power generation with carbon capture.

### **Flameless Pressurized Oxy-Coal: The Top of Power Cost Competition for CCS, and Along the Transition to Near Zero Emission, it Moves to 50 MWth Pilot for Fully Exploiting its Potential**

Massimo P. Malavasi, ITEA Spa, ITALY

Flameless Pressurized Oxy-Combustion is a newcomer in coal CCS arena. ITEA and ENEL had been cooperating for five years to develop FPOC for coal fired CCS power production application.

Indeed ITEA-ENEL 350 MWe FEED study results in 2013, and relevant economics based on commercial figures, set FPOC cost of energy at the top of competition among CCS technologies. However, it marked also a deep gap between adopted commercial solutions and conceivable tailor made solutions fully exploiting FPOC potential.

Consequently, the 50 MWth intermediate scale pilot step became mandatory in the industrial development strategy, to materialize valuable performances like, "flexible fuel" including low ranking coals, "velox" at constant fumes temperature profile control to match daily cycling, 35% efficiency. The on-going design and erection plan of the 50 MWth pilot is here illustrated. A call to OEM leaders to participate to the development of solutions is addressed, to fill some of the gap left in the picture of an highly innovative technology.

The 50 MWth pilot project boosts also the development and industrial exploitation of FPOC interim solution, here examined, cost competitive with SC established non-CCS technologies and retrofitable to CCS, by addition of CO<sub>2</sub> compression only, along the transition to zero emission.

To further expand FPOC fundamentals, the experimental exploration of higher pressure was given FOA award in 2013. Both interesting experimental evidences, and theoretical analysis of cycle efficiencies up to 50 bar performed by MIT Department of Mechanical Engineering, are here presented. Worth of mention is the superb fumes residual ashes and SO<sub>3</sub> content, which contributes the feasibility ground to operating regions analysed by MIT.

## **SESSION 20**

### **Coal Mining: Safety and Mining Technology - 1**

#### **Development and Participation in the American National Standards Institute (ANSI) Technical Advisory Group to ISO/TC 82 Committee – Coal Mining**

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

The International Organization for Standardization (ISO) Technical Committee (TC) 82 – Coal Mining has been in existence since 1955 but little to no standards have resulted from this committee, largely due to the lack of participate of key countries that include the US, UK, an Australia. Now a renewed effort through ISO led by Germany, but also including significant contributions by Russia and China has created renewed interest in developing standards that meet the specific needs of international mining operations. This includes standardization of specifications relating to machinery and equipment used in opencast and underground mining for the extraction of solid mineral substances, but excluding the preparation and processing of the minerals; recommended practice in the presentation of plans and drawings used in mine surveying; methods of calculation of mineral reserves; and, terminology. This activity is being undertaken because standards are needed to ensure mining operations are done safely and with due regard for protection of the environment.

Supporting this effort will help ensure the United States maintains its rightful place as a global leader in the mining sector and that American norms, practices, and experiences are recognized and accepted in international standards that can be adopted into the U.S. The specific scope, which included four (4) main topics includes:

1. specifications relating to machinery and equipment used in opencast and underground mining for the extraction of solid mineral substances, but excluding the preparation and processing of the minerals;
2. recommended practice in the presentation of plans and drawings used in mine surveying;
3. methods of calculation of mineral reserves; and
4. terminology.

Most significant is scope of work item number 4, which is designed to integrate the existing US (SEC Guide 7), Canadian (CN 43-101), and Australian (JORC) methods for determining mineral reserves. Based on a submission by the German Institute for Standardization (DIN), TC 82 has been reconstituted and the resulting voting members of TC-82 now include:

- Germany (project Secretariat)
- China
- Finland
- Iran, Islamic Republic of
- Korea, Republic of
- Russian Federation
- South Africa
- Spain
- Sweden
- United Kingdom

The main focus of this presentation is to present the reasons for and solicit support for US participation in the TC-82 as a participating (P-Member) Nation.

#### **General Assessment and Estimations of Occupational Accidents and Disasters in Turkey Coal Mines**

Niyazi Bilim, Bilgehan Kekeç, Sertaç Dündar, Selçuk University, TURKEY

Mining sector is very important for all county economy and employment. However, this sector has very risks in respect to occupational safety and health. Coal mining has the most risk in all of the mining sector. Hence in this sector with most work accidents and occupational diseases are encountered in an intensive. Coal mining is a relatively dangerous industry. Employees in coal mining are more likely to be killed or to incur a non-fatal injury or illness, and their injuries are more likely to be severe than workers in others industry. Work accidents are the big issued in mining industry of Turkey, because it can be significant influences to mining operations or activities. The coal mining industry plays an important role contributing to the national economy and development in Turkey, otherwise the mine accidents are become a big issues or problems. Sectorial examinations in 2013, the mining and quarrying sector is the maximum work-related accidents (10.4%) as the sector emerges. Safety in coal mining in Turkey is a critical issue. The number of fatalities is unacceptably high. This paper presents statistical analysis of Turkey coal mine accidents in last decades and analyzes the reasons causing coal mining high risk from technical and others viewpoints. Also, we explained occupational health and safety in relation to improve safety performances or accidents prevention.

## Investigation of Spontaneous Combustion of Coal in Longwall

Hadi Ozdeniz, Selcuk University; Osman Sivrikaya, Adana Science and Technology University; Sezgin Berberoglu, Ozkar Mining Company, TURKEY

The risk of spontaneous combustion of coal is highly serious especially for underground coal mines. Coals react with oxygen from the moment they are produced and are subject to spontaneous combustion. This reaction is an exothermic reaction and coals give heat to the surrounding air. If the heat is not removed from the surrounding air, spontaneous combustion occurs and then flaming fire starts. In addition, in underground coal mine besides exothermic reactions, hazardous, explosive and flammable gases are released to the surrounding air. This situation causes interruptions in production, economical losses and environmental problems. In order to avoid these problems, production at the longwall should be closed and the contact of the coal with air should be prevented. In this study, the temperatures changes in the longwall in the spontaneous combustion condition were measured by temperature sensor placed inside the longwall. In addition, while the temperature recording was carried out for inner part of the longwall, the temperature of the exhaust air and concentration of some released gases (CO, CH<sub>4</sub>, O<sub>2</sub> and CO<sub>2</sub>) were measured. Graham's ratio was calculated and used to determine of spontaneous combustion with the concentration of released gases. The temperatures of the longwall were increased in time and the coal production of longwall was stopped. After cutting the air contact of coal, the temperature recording was continued. The temperature changing for the inner part of the longwall were observed continuously.

## Development of Moisture Tolerant Rock Dust for Improved Mine Safety

Dave Anstine, Neil Doidge, Imerys, USA

In damp or wet underground coal mines current rock dusts cake when wetted and subsequently dried. Concerns arose regarding this caking and its effect on the adequate dispersion of the rock dust with the fugitive coal dust and its ability to abate an explosion. Imerys responded to BAA (Broad Agency Announcement) #2012-N-14257 to investigate technologies that would render rock dusts more moisture tolerant and allow for easier dispersibility under damp or wet conditions. The objective of the project was to develop modified limestone-based rock dusts capable of effectively 1) dispersing in the NIOSH dust dispersion chamber after being wetted, then dried, and 2) inerting coal dust in the NIOSH 20-L explosibility chamber. The project was centered upon the development of a rock dust that was more moisture tolerant but still met the existing requirements of 30 CFR 75.2. Rock dust samples were developed, subjected to a procedure of wetting and drying, and then tested for dispersibility in the NIOSH dust dispersion chamber. Samples were also subjected to high humidity conditions for longer time periods and then tested for dispersibility in the dust dispersion chamber. The most promising samples were evaluated for their effectiveness in inerting Pittsburgh pulverized coal (PPC) dust in NIOSH's 20-L chamber. These samples when compared to conventional rocks dusts exhibited a significant improvement in dispersibility while demonstrating an equivalent explosion inerting capability. In addition to improved dispersibility and comparable inerting capabilities, the samples evaluated, met the existing requirements of 30 CFR 75.2. A larger sample was evaluated in the Bruceton Experimental Mine. The sample dispersed immediately after application and continues to disperse over time.

## SESSION 21 Gasification: Novel Technologies - 1

### Pilot-Plant Evaluation Gasification of Illinois No. 6 Coal with Aerojet Rocketdyne Compact Gasifier, with Syngas Upgrading by GTI Morphysorb Process

Jim Aderhold, Bruce Bryan, Andrew Kramer, Adam Burkhart, Gas Technology Institute; Steve Fusselman, Aerojet Rocketdyne, USA

The Gas Technology Institute (GTI) and Aerojet Rocketdyne (AR) have completed pilot-scale validation of improvements to the AR compact gasification system, through hot testing with Illinois No. 6 coal as the gasifier fuel. The coal-derived syngas was processed on the pilot-scale Acid-Gas Removal (AGR) system to reduce carbon-dioxide concentration in the syngas to less than two percent with Morphysorb solvent. This presentation will review improvements to the AR compact gasifier, the GTI AGR system, and the testing results. This work was done with support from the Illinois Clean Coal Institute (ICCI) and a grant from the Illinois Department of Commerce and Economic Opportunity (DCEO).

### Calcium Looping Catalytic Coal Gasification: Experiments and Systems Analysis

Nicholas Siefert, Hunaid Nulwala, DOE/NETL/Carnegie Mellon University; Dushyant Shekhawat, DOE/NETL, USA

First, we present experimental results from a fixed bed steam-coal gasifier in which a CO<sub>2</sub> sorbent (CaO) and coal gasification catalysts (KOH, NaOH, and CsOH) are mixed with the coal prior to gasification. The goal of this research is to capture CO<sub>2</sub> inside a coal gasifier [1-2], rather than using current methods to capture CO<sub>2</sub> outside of the gasifier [3]. This approach utilizes the exothermic CO<sub>2</sub> capture reaction to offset the endothermic steam-coal gasification reaction. The output of the gasifier is a fuel stream (syngas) with high concentrations of hydrogen and, depending on the pressure and temperature of the gasifier, high concentrations of methane. Outside of the gasifier, CO<sub>2</sub> is released and the CaO is regenerated from CaCO<sub>3</sub> by oxy-combusting unburnt carbon from the gasifier. The alkali hydroxides are used to speed up the reaction rates inside of the gasifier. Here, we present experimental data on both the kinetic rate of coal-gasification and the gas composition as a function of time during fixed-bed, batch experiments. Experiments include the following: (a) baseline experiments without CaO or alkali catalyst, (b) baseline experiments with CaO but no alkali catalyst, and (c) a series of experiments with CaO and alkali catalysts in pure or mixed compositions. We kept the cost of the catalyst fixed when adding pure or mixed compositions so that we could determine which alkali catalyst composition can lowest the leveled cost of electricity the most. In order to determine whether the addition of alkali hydroxide catalysts is beneficial to the CaO-looping gasification process, we have conducted a complete thermodynamic & economic analysis of an IGCC-CCS power plant with CaO-looping gasifier with and without alkali catalysts. To conduct the economic analysis, we determined capital and operating costs using cost estimates from NETL [3]. We calculate that the addition of alkali hydroxides can significantly lower the leveled cost of electricity from this CaO-looping power plant configuration compared with the case without the addition of alkali hydroxides.

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[2] Siefert NS, Shekhawat D, Litster S, Berry DA. Steam-Coal Gasification Using CaO and KOH for in Situ Carbon and Sulfur Capture. *Energ Fuel*. 2013;27:4278-89.

[3] Gerdes K. Current and Future Technologies for gasification-based power generation: Volume 2: A Pathway Study Focused on Carbon Capture Advanced Power Systems R&D Using Bituminous Coal. 2010;DOE/NETL-2009/1389.

## Fuel-Flexible Hybrid Solar Coal Gasification Reactor

Matt Flannery, Tapan Desai, Advanced Cooling Technologies, Inc., USA

Current power generation systems in the United States are based on combustion of fossil fuel technologies and emit carbon dioxide, which is costly to mitigate and has a negative impact on the environment. Coal gasification is a conversion process that utilizes vast, domestic coal resources to generate cleaner syngas for power generation and has gained significant attention due to its reduced carbon emissions. Carbon emissions reduction has motivated research into power generation from renewable resources, such as solar and wind. However, these technologies are more expensive than current power generation technologies, and are a long term goal to securing energy independence. Hybridizing solar energy from concentrated solar power towers, a renewable resource technology, to provide process heat for coal gasification, a fossil fuel based technology, will create an intermediate solution that reduces carbon emissions while maintaining power generation capacity.[1] Preliminary energy balance calculations indicate that producing the stoichiometric amount of steam required for the gasification reaction from solar energy, such as concentrated solar power towers, can reduce the energy required for gasification by 29%. Furthermore, through an innovative fuel-flexible gasification reactor, the remaining energy can be provided by low-carbon emitting fuels, such as natural gas, thereby reducing the carbon emissions of the gasification process by 60%. The fuel-flexibility of the reactor is supported by an allothermal gasification reactor wherein the combustion and gasification section are thermally linked by high temperature heat pipe. A prototype annular heat pipe with an integrated fluidized bed gasification reactor was fabricated to verify the feasibility of the design. Through gas chromatography analysis, this prototype demonstrated conversion of 88% of the input steam to hydrogen at 900 °C, with an effluent composition comprised of 1.3:1 H<sub>2</sub>:CO ratio. Therefore, through modeling and experimentation, the hybridization of solar energy and coal gasification demonstrated an intermediate solution that supports the transition between fossil fuel based power generation to systems based on more sustainable renewable resources.

## Catalytic Effect of Biomass Ash on Anthracite Coal Gasification

Weiping Ren, Zibing Zhao, Yuhong Qin, Jie Feng, Wenying Li, Taiyuan University of Technology, CHINA

Investigation on the catalytic activity of biomass ash to the gasification of anthracite coal was performed in details in the present study. Thermogravimetric analyze indicate that there is a synergetic effect between coal char and biomass char during co-gasification process due to the biomass ash catalytic effect and 40% is a needed additive amount to complete the gasification of a certain amount of coal char. The successive leaching treatment on biomass ash using de-ion water, NH<sub>4</sub>Ac solution and HCl solution shown that chemical forms of K/Na in biomass ash have little effect on

the catalytic properties of biomass ash compared with the content of K/Na. The mineral in coal char have “toxic” function on biomass ash. A little amount of CaCO<sub>3</sub> addition during the coal char preparation process can “shield” the deactivation of alkali metals in biomass ash due to the calcium salt can suppress the interactions of alkali metals with acidic minerals in coal during the co-gasification process.

**SESSION 22**  
**Combustion: Oxy-Combustion and Chemical Looping - 4**

**Improvements in Exergetic Efficiency in High-Temperature Oxyfuel Combined Cycle Systems**

Thomas Ochs, Rigel Woodside, Danylo Oryshchyn, DOE/NETL; Lauren Kolczynski, ORISE/DOE/NETL, USA

The National Energy Technology Laboratory (NETL) has started a program designed to improve the exergetic efficiency of the use of fossil fuels. This program will improve the efficiency of the transformation of chemical fuel energy to work products using advanced oxyfuel combustion to produce ultra-hot flames (3000K) that would melt or vaporize most materials. The use of the high temperature for power production gives the system an advantage related to the exergy available in the system. In a normal flame (2000K) the flame is diluted with N<sub>2</sub> and the energy stored in the N<sub>2</sub> and the rest of the combustion products considered to be a substantially lower quality of energy than that available in combustion products at 3000K. This advantage for the higher temperature flame allows the system to extract energy in a cascading manner from the high temperature source of the flame, in increments, down to the low temperature of the environmental sink.

Since the high temperature source can be problematic for any moving parts in the path of the flame, we turn to a method that does not require any physical impingement on the combustion products to extract energy. In this method, the flame is ionized and passed through a strong magnetic field to, directly, produce electricity through the process of open cycle magnetohydrodynamic (MHD) interaction. In open-cycle MHD the combustion products are seeded with an ion-producing material such as potassium. The ions are then sent between the poles of a powerful magnet. The motion of the ions is then converted to current using electrodes. Open-cycle MHD has been known for centuries and has been developed for decades. However, the technology to support economical open-cycle MHD (inexpensive computers, superconducting magnets, new monitoring methods, new materials, and new processes) have only recently become available.

At lower temperatures (2500K) a technology known as closed-cycle MHD shows promise of extracting even more exergy from the chemical potential of the fuel. In closed-cycle MHD the system operates in a non-equilibrium mode and can provide ions at a lower temperature than in an open-cycle system.

The combination of an open-cycle topping unit and a closed-cycle mid unit allows the system to continuously extract energy from approximately 3000K to 2500K in the topping unit and then from approximately 2500K to 1800K in the mid-range unit. The exhaust from the mid-range unit is the right temperature to be used in a third (bottoming) cycle employing conventional steam.

In each stage of this design the heat is transformed into work at the highest available temperature to provide the most efficient energy exchange in a thermodynamic cycle. The result is more work from each increment of chemical energy available. The use of pure oxygen for combustion provides high-temperature combustion products that are also amenable to capture and sequestration. When we join this combined cycle approach with the NETL integrated pollutant removal (IPR<sup>TM</sup>) process, the resulting system can achieve high efficiency while capturing nearly 100% of the CO<sub>2</sub> produced. When the system uses biomass as a part of its fuel, the high capture rate allows the power plant to scrub the atmosphere of CO<sub>2</sub>. This presentation reports on modern MHD technology, its potential for integration with standard steam power generation, and the potential of the combined system to integrate with an efficient CC process to capture nearly 100% of the CO<sub>2</sub> produced.

One of the unique advantages of high-temperature oxyfuel is the ability to directly retrofit coal fired power plants using natural gas. The radiation/convection heat transfer mode distribution of high temperature natural gas combustion is similar to that of a lower temperature coal combustion. This means that natural gas may be employed in the near term to reduce the CO<sub>2</sub> footprint of fossil fueled power production. By employing a range of combinations of natural gas and coal, one can economically meet incremental changes in EPA requirements without resorting to carbon capture and with the concomitant advantage of higher temperature flames. This combination of fuels allows power producers to prepare for scenarios where near total capture may be required – but without resorting to capture immediately. As EPA regulations change it becomes less capital intensive to go to greater carbon capture and eventual storage. It is also noteworthy that the approach of MHD research in the 1970s and 1980s was to use enhanced air (greater oxygen content than 21%). Thus, lowering the carbon footprint via MHD power is still possible using natural gas and even with a modest enhancement of combustion with oxygen.

There is a broad potential program in the area of high temperature oxyfuel combustion with oxy-coal combustion, fuel switching to natural gas, open-cycle MHD, closed-cycle MHD, and steam combined cycle.

**Experimental Characterization of the Effect of Dry Recirculation on a Swirled Self-Stabilized Oxycoal Flame**

Diego Zabrodiec, Anna Massmeyer, Johannes Hees, Tim Gronarz, Benjamin Gövert, Matthias Höfler, Andreas Ohliger, Martin Habermehl, Oliver Hatzfeld, Reinhold Kneer, Institute of Heat and Mass Transfer, RWTH Aachen University, GERMANY

This paper presents the results from detailed measurements and observations of the effects of dry recirculation upon the characteristic parameters and structure of a pulverized oxycoal swirled flame. The pulverized fuel swirl burner (100 kWth) used for this study was previously designed, developed and constructed at the Institute of Heat and Mass Transfer at the RWTH Aachen University. In the present study, measurements on the swirl burner were performed in a vertical pilot scale furnace. Operating limit conditions for O<sub>2</sub>/RFG and flame equivalence ratios were meticulously evaluated and fixed for the formation of stabilized flames under different thermal loads. Combustion chamber wall temperature at different axial burner positions and the concentration of major species in flue gas have been measured for the set of different studied burner operating conditions. Spontaneous emission of OH radicals was studied and relative concentration profiles were obtained as complementary data describing the pulverized flame structure.

The observed flame characteristics and the flame behavior under different tested operating conditions as well as the influence of recirculated flue gas are presented and discussed.

**An Experimental Investigation of Heat Transfer Behavior in Oxygen-Enriched Coal Combustion**

Adewale Adeosun, Akshay Gopan, Fei Xia, Bhupesh Dhungel, Benjamin Kumfer, Richard Axelbaum, Washington University in St Louis, USA

Oxy-combustion is a promising technology towards efficient capture of carbon dioxide from coal-fired power plants. For first-generation oxy-combustion technology, a large amount of flue gas is normally recycled to control temperature and heat transfer in the boiler. Several approaches are being explored to improve the plant costs and operation, including the reduction of recycled flue gas stream, resulting in a higher overall oxygen concentration, and fuel staging techniques. Increasing the overall oxygen concentration (or reducing flue gas recycling) is known to promote flame stability and fuel ignition and reduce the total gas volume; however, this can also result in a significant increase in combustion temperature. A key challenge associated with this approach is to maintain an optimal level of radiative heat flux, and not exceed the temperature limits of boiler tubes. In this study, the heat transfer behavior in an enriched oxygen combustion environment is experimentally investigated. A 1MW<sub>th</sub> oxy-combustion test facility was used for the study. The radiative heat flux, temperature and gas species profiles were obtained. The experiments are compared to modeling results obtained from computational fluid dynamics simulation.

**A Reduced Order Model for the Design of Oxy-Coal Combustion Systems**

Steven L. Rowan, Albio Gutierrez, Ismail B. Celik, West Virginia University, USA

Oxy-coal combustion is one of the more promising technologies currently under development for addressing the issues associated with greenhouse gas emissions from coal-fired power plants. Oxy-coal combustion involves burning the coal fuel in mixtures of pure oxygen (or oxygen enriched air) and recycled flue gas (RFG) consisting of mainly carbon dioxide (CO<sub>2</sub>). As a consequence, many researchers and power plant designers have turned to CFD simulations for the study and design of new oxy-coal combustion power plants, as well as refitting existing air-coal combustion facilities to oxy-coal combustion operations. While CFD is a powerful tool that can provide a vast amount of information, the simulations themselves can be quite time consuming and expensive. A reduced order model (ROM) for oxy-coal combustion has been developed as a supplement to CFD simulations. This Reduced Order Model (ROM) utilizes a combination of tools, including coal devolatilization and chemical equilibrium models, to carry out energy balance calculations taking the reactor as one large control volume. With this model, it is possible to quickly estimate the average outlet temperature and speciation of combustion flue gases given a known set of mass flow rates of fuel and oxidant entering the power plant boiler; as well as determine the required boiler inlet mass flow rates for a desired outlet temperature. Several cases have been examined with this model, and the results compare quite favorably to CFD simulation results.

**Numerical Study on the Effect of High Content of Steam to Oxy-Fuel Combustion of Pulverized Coal in Vertical Pilot Facility**

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

Steam-rich atmosphere (20-45% in volume) is found to be ordinary in oxy-fuel combustion of pulverized coal, especially for the wet recycle way which tends to feed flue gas without previous moisture removal. To explore how this high content of steam influences combustion behaviors, a numerical study is presented here in a vertical pilot facility. It is found that steam addition could increase or decrease the flame temperature than conventional O<sub>2</sub>/CO<sub>2</sub> combustion of pulverized coal which depends on the steam and oxygen concentration that is feed in, as the steam concentration increase from 20% to 50% in feed gas, flame temperature increase initially to a peak and then drop, the steam concentration that lead to the peak flame temperature is 20% at 25% oxygen concentration, 30% at 28% oxygen concentration and 40% at 30% oxygen concentration respectively; the steam addition can substantially enhanced bulk gas radiation, the radiative heat transfer is proportional to steam concentration at same oxygen concentration, and consequently lead to a lower flue gas temperature; if the input of steam increase, the homogeneous ignition is considerably delay, but it will be improved by raising oxygen concentration; NO<sub>x</sub> generation slightly reduce than in O<sub>2</sub>/CO<sub>2</sub> combustion as steam concentration increase at the same oxygen concentration, although the flame temperature increase in steam-rich condition.

**SESSION 23**  
**Clean Coal and Gas to Fuels: Catalysts**

**Preparation of Supported Mo-Based Catalyst and its Performance in  
Hydrolysis of Shenfu Coal**

An-ning Zhou, Yan-yan Lei, Na Liu, Xin-fu He, Hui-kuan Zhang, Jian-Guo Wei,  
Xi'an University of Science & Technology, CHINA

Mo-based catalysts with supporters of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> were prepared by impregnation method, and catalytic acidities were conducted by catalytic hydrolysis of Shenfu coal at 750 °C for 40 min. The results shows that the tar yields are much higher when the loading amount of Mo is 10% (wt.) for each supporter. The highest tar yield is up to 18.7% over 10%-Mo/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, while the highest water and gas yield are reached over 10%-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%-Mo/SiO<sub>2</sub>, respectively. The catalysts were characterized by XRD, BET, NH<sub>3</sub>-TPD and H<sub>2</sub>-TPR, and the results suggest that interaction of MoO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> enhances catalytic activity of the catalysts, the particle size of MoO<sub>3</sub> in Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> is moderate, and the dispersion of MoO<sub>3</sub> in 10%-Mo/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> is more uniform than other supported Mo-based catalysts.

**TGA Reactivity and Recyclability Studies of Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> Based Oxygen  
Carriers Using Steam for Chemical Looping Gasification**

Ankita Majumder, Liang-Shih Fan, Niranjani Deshpande, Mandar Kathe, The Ohio  
State University, USA

The chemical looping gasification (CLG) process is based on the high temperature cyclic reduction and oxidation (redox) reactions of metal oxide-based oxygen carriers in three separate reactors, known as the reducer, oxidizer and combustor. In the reducer, carbonaceous fuel is converted to carbon dioxide (CO<sub>2</sub>) and steam (H<sub>2</sub>O) by oxygen from the oxygen carrier particles. The oxygen carriers are reduced in the process. The reduced oxygen carriers are then partially oxidized using steam in the oxidizer to produce hydrogen (H<sub>2</sub>). This is then followed by the oxygen carriers' complete reoxidation with air in the combustor and recycling to the reducer. The oxidation reaction is highly exothermic and the heat generated can be used to run steam turbines and generate electricity. CO<sub>2</sub>, H<sub>2</sub> and heat are thus produced in three separate reactors with reduced downstream processing, resulting in increased energy efficiency, decreased cost and overall process intensification. The process inherently produces a sequestration-ready CO<sub>2</sub> stream.

Oxygen carriers play a crucial role in the successful operation of a chemical looping system as their physical and chemical properties dictate the fuel conversion efficiency of the system. Thus, it is essential that they have high oxygen carrying capacity and high attrition resistance. Oxygen carriers are expected to undergo multiple redox cycles while maintaining their reactivity and mechanical strength in order to improve the overall process economics for commercial viability.

This study investigates the performance of supported Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> based oxygen carriers with respect to H<sub>2</sub> production with steam oxidation in a CLG process. The two different oxygen carriers are subjected to 20 reduction and oxidation cycles under H<sub>2</sub> and steam respectively, in a Thermogravimetric Analyzer (TGA). These tests are used to study their oxygen transfer efficiency per cycle and their recyclability under steam oxidation. The TGA is used to study the impact of various reduction conditions on the steam oxidation behavior of the oxygen carriers. The reduction parameters studied include changes in temperature, pressure and reduction gas concentrations. In addition to experimental studies, this study also presents thermodynamic analyses of Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> in presence of steam, and the resulting overall process analyses in terms of theoretical system efficiencies. X-Ray Diffraction (XRD) is used to identify the various metal oxide phases formed in the reduced and re-oxidized samples. The

oxygen carriers are subjected to surface characterization to study change in surface morphology using Scanning Electron Microscopy (SEM) and the Brunauer-Emmett-Teller (BET) method. The samples tested here show excellent recyclability under the steam oxidation conditions with little to no drop in their reactivities over the 20 cycles. During every redox cycle, both the oxygen carrier samples are fully reduced and fully oxidized to the highest oxidation state thermodynamically possible. These preliminary tests serve to aid in the development of effective oxygen carrier particles for H<sub>2</sub> generation by the CLG process.

**SESSION 24**  
**Coal Science: General - 4**

**The Effect of Fixation of Acidic Wastes by Coal Fly Ash on the Properties of the  
Fly Ashes**

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Survey of Israel; Haim Cohen, Ariel University, ISRAEL; Xavier Querol, Oriol Font,  
Institute of Environmental Assessment and Waster Research (IDÆA) Consejo  
Superior de Investigaciones Científicas (CSIC), SPAIN

The most abundant fossil fuel for power generation in Israel in the last 30 years is the bituminous coal. The average coal consumption in the last decade was ~13x10<sup>6</sup> tons of coals, which produced annually ~1.3X10<sup>6</sup> tons of Class F coal fly ash. Ambient air quality standards used in Israel require a low content of S and P during the combustion process resulting in an ash, which is rich in alkali and alkali earth elements. The South African and Colombian fly ashes were chosen for this study, since they are the most abundant ashes formed in the utilities (>70%).

Recently it has been reported that Class F (very basic due to high CaO content) fly ash can be used as a scrubber and fixation reagent for acidic wastes (from the phosphate or the regeneration of used motor oil industries). Furthermore, the scrubbed product can serve as a partial substitute to sand and cement in concrete, while the produced bricks have proved to be strong enough for concrete standards.

The fixation process is resulting in changes in the structure of the fly ash particles. In order to explore the fixation mechanism, treatment of the fly ash with acidic (0.1M HCl) and neutral, ultra-pure deionized water (UPDI), aqueous solutions were performed. Several analyses (e.g. XRD, SEM, TEM and ICP) have examined the ashes prior and post treatment. It has been demonstrated that the fly ash particle's surface composition and crystallographic structure was changed appreciably, affecting the interactions with transition metal ions. Moreover, two possible modes of interaction between the fly ashes and the waste are suggested: (i) Electrostatic interaction of the fine precipitates to the surface anions and also of the metal cations (cations exchange mechanism) or (ii) coordination bonding of the surface anions *via* the oxygen atom to form surface complexes of the metal ions.

**Effects of Organic Liquids on Coking Properties of a High-Inert Western  
Canadian Coal**

Tony MacPhee, Louis Giroux, CanmetENERGY – Ottawa; Maria Holuszko, Ross  
Leeder, Teck Coal Ltd.; Melanie Mackay, Trillium Geoscience, CANADA

Early determination of coal quality during exploration stage is an important factor influencing decision making pertaining to its utilization. However, raw coal collected from drill core is usually loaded with ash and the quantity insufficient to be cleaned in a wash plant. In industrial practice, float/sink density testing is the standard laboratory method used for cleaning small mass coking coal samples. This involves the use of organic liquids to cover the density ranges needed (i.e. 1.3 to 2.0). However, research conducted in Australia revealed that exposing coal to organic liquids may negatively impact the quality properties of the samples, including coal fluidity and coke CSR. This finding suggested the routine use of organic liquids may impact the economics of Western Canadian coking coal exploration project. The Canadian Carbonization Research Association (CCRA) undertook a research program to examine the effects on coal and coke properties of exposing a High-Inert Western Canadian coal to various organic liquids. In this program, the effects of four commonly used organic liquids in float/sink density testing, perchloroethylene, bromoform, tetrabromoethane and white spirit, on coal and coke properties were examined. The influence of exposure time was also investigated. The main findings of this work will be presented and discussed.

**Influence of the Mechanical Properties of Coals on the Fragmentation Behavior  
of Coal Particles Under High-Temperature Conditions**

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Particle fragmentation phenomena are of tremendous practical interest for several energetic or non-energetic coal utilization processes, since the change of the particle

size distribution can strongly impact the flow behaviour of particles, carbon conversion rate and further important characteristics. But the direct determination of the particle size distribution in industrial-scale burners and gasifiers is complicated by the extreme process conditions (high temperature, high pressure, reactive gas atmosphere). Motivated by the existing demands, systematic experimental and theoretical investigations of the primary coal fragmentation, which takes place at fast heating-up of single coal particles under well-defined conditions in laboratory-scale reactors, were performed in the last years at the German Center for Energy Resources DER.

It is obvious that the mechanical characteristics of coals are definitely one of the major factors governing the fragmentation of coal particles. In order to provide a sufficient database for a detailed analysis of the relationships between the fragmentation of coal particles under fast pyrolysis conditions and the coal properties, as well as to promote a deeper understanding of the actual fragmentation mechanisms, we have investigated the mechanical properties of more than 20 coals of different rank, ranging from lignite to anthracite. Mechanical properties were determined 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 specimens. Coal particles of different size and geometrical shape were applied for the investigations.

The experimentally determined values were used for a multiple regression analysis between the mechanical characteristics and different coal properties (content of moisture, ash and volatile matter, carbon content, maceral composition, porosity, pore size distribution, microhardness, particle size). Additionally, the effect of the thermal treatment of the coal specimens on their mechanical properties was investigated too. For this reason, we have investigated the influence of the process parameters (temperature, heating rate, residence time) on the compressive strength and the elastic modulus of coal particles after the thermal treatment. Obtained data were used to establish correlations between the fragmentation intensity of coal particles, which was measured in different lab-scale reactors, and the mechanical properties of coals. Furthermore, determined values of the elastic modulus and the critical compressive strength were applied for the development and validation of numerical models of the thermally-induced stress distribution inside the coal particles. Direct optical observations of the crack propagation during the coal specimen breakage at the mechanical tests were used to derive information about the failure mechanism.

#### **Research on the Preparing of Coal Water Sully with Semi-Coke and Pulverized Coal**

Zhao Shiyong, Wu Peipei, Liu Meimei, Zhou Anning, Yang Zhiyuan, Xi'an University of Science and Technology, CHINA

This paper makes coal water sully (Hereinafter referred to CWS) with the abandoned semi-coke (less than 1 mm) and pulverized coal. Then examined what efforts the semi-coke may have to CWS properties (concentration, viscosity, stability) through the experiments. The study examined the properties of CWS that made by different raw materials, explored the best ratio of semi-coke and pulverized coal on making CWS, selected the best additive and the proper amount of additive and simply explored the mechanism of impact of semi-coke on coal water slurry concentration. The experiment indicated that the concentration of CWS will be low if the CWS is made by only semi-coke. The best ratio of prepared at a concentration of 60% of semi-coke and pulverized coal-water slurry is 3:7. The best additive is NBS-1B and the proper amount of additive is 0.7%. It is difficult for semi-coke to prepare a high concentration of CWS. It is because semi-coke has well-developed pore. It can improve the properties of CWS if we modify the semi-coke with some neutral oils and organic surface modifier. This CWS has met the requirements of the gasification of coal water slurry.

### **SESSION 25 Clean Coal Demonstration and Commercial Projects: Oxy-combustion and Industrial Projects**

#### **Port Arthur CCUS: Demonstration of CO<sub>2</sub> Capture and Sequestration of Steam Methane Reforming Process Gas Used for Large-Scale Hydrogen Production**

Anthony Zinn, DOE/NETL; Nile R. Bolen, Bob Hutchison, Air Products and Chemicals, Inc., USA

Air Products and Chemicals, Inc. (APCI) has designed and constructed a state-of-the-art system to concentrate the carbon dioxide (CO<sub>2</sub>) from two steam methane reformer (SMR) process streams for delivery of the CO<sub>2</sub> via pipeline for sequestration by injection into the Hastings oil field (near Pearland, TX) as part of an enhanced oil recovery (EOR) project. APCI has retro-fitted their two SMRs, located in Port Arthur, TX, using Vacuum Swing Adsorption technology to separate the CO<sub>2</sub> from the process stream, followed by a drying process and compression. The CO<sub>2</sub> capture facility is designed to convert the initial stream containing 15% - 20% CO<sub>2</sub> to greater than 98% purity for delivery to the pipeline. The technology removes greater than 90% of the CO<sub>2</sub> from the process gas stream used in the world-class scale hydrogen production

facility. Approximately 1 million tons per year are being delivered for sequestration and EOR, which results in additional domestic oil production.

This paper will provide background to the Port Arthur (CO<sub>2</sub> Capture, Utilization and Storage) CCUS demonstration project, as well as a current status update. The topics to be covered include objectives and scope of the demonstration program; a background/summary of the newly retro-fitted CCUS process at the Port Arthur site; approximate cost information per ton of CO<sub>2</sub> captured; recap of the monitoring, verification and accounting (MVA) program developed to verify sequestration; current status of project operations (i.e. demonstration period); and a projection on the amount of CO<sub>2</sub> emissions avoided due to the project.

#### **Illinois Industrial Carbon Capture and Storage Project**

Scott McDonald, Archer Daniels Midland Company, USA

The Illinois Basin is hosting several major carbon capture and sequestration projects. This basin, which underlies most of the state of Illinois, parts of Kentucky, and Indiana, ranks among one of North America's the best sites for potential storage of anthropogenic CO<sub>2</sub> emissions. Within this basin, the Mount Simon Sandstone, a major regional saline reservoir, is the target for sequestration because it has good permeability and porosity with overlying strata of impermeable shale. Because the regional thickness of this reservoir increases towards the center of the basin, the optimum location for maximum storage of CO<sub>2</sub> is in north central Illinois. Because of the excellent regional geology and access to industrial scale quantities of CO<sub>2</sub>, two projects are being conducted at the Archer Daniels Midland Company's (ADM) agricultural processing and biofuel production facility located in Decatur, Illinois. Both projects will demonstrate the ability to inject and store industrial scale quantities CO<sub>2</sub> emissions into the Mount Simon; safely, permanently, and economically for hundreds of years.

Illinois Basin - Decatur Project (IBDP), (Status- in Operation). This project is led by Illinois State Geological Survey (ISGS), under the Midwest Geological Sequestration Consortium (MGSC) Regional Carbon Sequestration Program, and is a large-volume, saline reservoir sequestration test that will inject approximately 333,000 metric tons of carbon dioxide (CO<sub>2</sub>) per year for three years.

Illinois Industrial Carbon Capture and Storage Project (IL-ICCS), (Status- under Construction). This project is led by ADM and will expand the sites CO<sub>2</sub> injection and storage capability to that of a commercial-scale operation. The project is scheduled for startup in the first quarter of 2015 and will inject up to 1.0 million metric tons per year over an operational period of approximately 2.0 years. ADM will integrate the IBDP compression and dehydration facilities with the new facilities constructed under the IL-ICCS project upon completion of IBDP injection operations in fall 2014. A significant benefit of these two complimentary projects is the unique opportunity to better understand the interaction between the CO<sub>2</sub> plumes and pressure fronts emanating from two injection wells in the same sandstone formation.

IL-ICCS project has the following objectives:

- Demonstrate an integrated system for collecting CO<sub>2</sub> from an ethanol production plant and geologically sequestering in a saline sandstone reservoir;
- Conduct required geologic site surveys, site characterization and modeling.
- Design, construct, and operate a new CO<sub>2</sub> collection, compression, and dehydration facility capable of delivering up to 2,000 metric tons of CO<sub>2</sub> per day to the injection site.
- Integration of the new facility with an existing 1,000 metric tons per day CO<sub>2</sub> compression and dehydration facility to achieve a total CO<sub>2</sub> injection capacity of 3,000 metric tons per day or one million tons annually.
- Design, construct, and operate a storage site capable of accepting up to 3,000 metric tons of CO<sub>2</sub> per day.
- Implementation of deep subsurface and near-surface monitoring, verification, and accounting (MVA) plans for the stored CO<sub>2</sub>.
- Develop and conduct an integrated communication, outreach, training, and education initiative.

The IL-ICCS project has leverage the knowledge and experience gained during the IBDP project. Site selection, reservoir modeling, MVA development, risk assessment, community outreach, engineering design, and facility construction are many of the areas in which the project team benefitted from the experience and lessons learned during the IBDP project.

#### **FutureGen 2.0 - Project Update**

Mark Williford, Ken Humphreys, Paul Wood, Chris Burger, FutureGen Alliance, USA

The FutureGen 2.0 program is comprised of two DOE-sponsored projects executed simultaneously under separate Cooperative Agreements with the National Energy Technology Laboratory (NETL). The Oxy-Combustion Large Scale Demonstration Project will retro-fit an existing 202MWe steam turbine generator and certain other legacy equipment with a new oxygen-fired boiler, air quality control systems (AQCS), and CO<sub>2</sub> compression/purification unit (CPU) to demonstrate CO<sub>2</sub> combustion capture technology with near-zero emissions of currently regulated air pollutants at utility



scale. Over one million tons per year of CO<sub>2</sub> will be captured per year at capture efficiencies approaching 98 percent.

Complementing the Oxy-Combustion Project is the CO<sub>2</sub> Pipeline and Storage Project, which will demonstrate permanent deep geologic storage of captured CO<sub>2</sub> in the Mt. Simon sandstone/saline formation. While the Oxy-Combustion Project will be the first one million ton per day CO<sub>2</sub> capture coal-fired power generation facility constructed world-wide, the CO<sub>2</sub> Pipeline Storage Project is likewise the first CO<sub>2</sub> deep geologic storage facility to be permitted by the US EPA, and will be the largest demonstration of CO<sub>2</sub> sequestration in the world.

This Pittsburgh Coal Conference presentation focuses on the FutureGen 2.0 Phase 2 Front End Engineering and Design (FEED) accomplishments to date, summarizes the Definitive Cost Estimate, explores challenges that have confronted the project, and plots the path forward to successful execution.

## SESSION 26

### Coal Mining: Safety and Mining Technology - 2

#### Gas and Dust Explosion Model for Methane Accidents in Coal Mines

V'yacheslav Akkerman, West Virginia University; Ali S. Rangwala, Worcester Polytechnic Institute, USA

Historically, accidental gas and dust explosions represent a hazard to both personnel and equipment in coal mining industry. In spite of the fact that the mining fatality/injury rates have tremendously reduced during the last century, the modern knowledgebase still does not provide an acceptable level of risk; and therefore it should be addressed from a fundamental viewpoint. Indeed, the coal-mining machinery has significantly increased the portion of small-size coal dust collected in intake and return airways; and the particle size provides a substantial impact in accidental explosions. Consequently, a computational model capable of quantifying the probability and associated hazards of spontaneous ignition, dynamics and morphology of a deflagration (flame) front, as well as the likelihood of a deflagration-to-detonation transition (DDT) event is highly needed.

The joint team of researchers from West Virginia University and Worcester Polytechnic Institute works towards the developing of such a model. The computational platform is based on a robust CFD code solving fully-compressible hydrodynamics and combustion equations in a turbulent environment. The capability of modeling laminar and turbulent burning velocities including the consideration of tiny dust particles is being incorporated into the solver. As a result, we provide a predictive scenario of methane explosion in a mining accident, in the presence of the coal dust. Specifically, we scrutinize the key stages of the flame evolution, namely, (i) initial quasi-spherical expansion of a centrally-ignited, embryonic flame, with the possibility of self-similar acceleration caused by the hydrodynamic (Darrieus-Landau; DL) instability; (ii) intermediate, so-called "finger-flame" acceleration that is devoted to the strongest acceleration; (iii) and the eventual, large-scale-based acceleration due to wall friction and/or in-built obstacles/roughness. As a result, we identify the key characteristics of these stages, such as the timing for each stage as well as the speed of flame spreading, and aiming to predict the expected pressure rise.

The thermal-chemical input parameters for the formulation are the unstretched laminar flame speed; the thermal expansion ratio (coupled to the equivalence ratio); and transport coefficients of the air/methane/dust mixture. The hydrodynamic input parameters are coupled to the size and configuration of a mining passage. Being initially laminar, the formulation is next combined with the analysis of turbulent burning in homogenous-gaseous and particle-gas-air environments. Specifically, the turbulent flame velocity is tabulated as a function of various flame parameters, discussed above, as well as the flow parameters (such as the turbulent intensity, integral and Kolmogorov length scales, etc.), as well as a function of the sizes and concentrations of the impurity particles. The particles typically intensify turbulent combustion, and this also provides a hint how multi-phase impurities and turbulence-instability interaction modify the conventional turbulent combustion regimes diagram.

While the majority of CFD models for turbulent combustion and explosion utilize empirical correlations between the laminar and turbulent burning velocities, and the parameters describing the turbulent flow (being thereby linked to particular configurations with experimental quantification of the associated phenomenological coefficients), the present research incorporate a turbulent flame speed model that is analytically developed from the first principles and should therefore work everywhere within its validity domain. The final model is aimed to eventually account for such state-of-the-art effects of turbulent combustion as flame-flow feedback, burning along the turbulent vortex axes, and turbulence-instability coupling. To complement the numerical modeling, we perform extensive experiments on turbulent methane-air burning by means of an ad-hoc Hybrid-Flame Analyzer. Specifically, extensive experimental data of laminar and turbulent burning velocity for gaseous and particle-air flames as a function of particle type, size, concentration, turbulent intensity and length scale are being generated to validate the computational platform.

#### Design and Implementation of an Innovative Spray System for Continuous Miners for Dust Control in High Mining Areas

Yoginder P. Chugh, Harold Gurley, Southern Illinois University Carbondale; Joseph Hirschi, Illinois Clean Coal Institute, USA

Over the last 12-months, the authors have implemented in cooperation with MSHA a spray system for continuous miners that are mining coal in 3.6 m to 4.2 m (12 ft. to 14 ft.) high mining areas with about 1.0 m to 2.0 m (3-6 ft.) of out-of-seam dilution mining. The design was guided and developed through CFD modeling studies. The challenges included low air volumes and velocity at the end of the line curtain, dust produced from out-of-seam dilution rock being very fine with 50% of the particles less than 10 micron, poor capture of aerosol through scrubber suction inlets, dust escaping through the sides of the loading pan in mining high areas, overloading of dust-laden air in the wet-scrubber, and dust rollback toward workers. The CFD modeling of airflows; improved line curtain installation, redesign and varying the spatial locations of spray systems as compared to low mining height areas were considered in developing engineering controls.

The developed spray system is an extension of the spray system currently being used by about 26 CMs operating in mining heights of about 2.4 m and successfully reducing dust exposure of CM operator (CMO), haulage unit operator (HUO), and workers downwind of the operating CM in the last open crosscut (LOXC) by about 30-50%, 15-30%, and 20-30%, respectively. A temporary implementation of the designed spray system in the field showed very promising results with reductions at the CMO, HUO, LOXC locations of about 50%, 30%, and 25%, respectively. Modification of the CM is planned within the next two months. The modified miner will be tested for its dust control performance in the field through sampling of different types of cuts with results included in the paper.

#### Development of a Novel Noise Measurement System for Coal Preparation Plants

Jun Qin, Manoj K. Mohanty, Pengfei Sun, Southern Illinois University; Joseph Hirschi, Illinois Clean Coal Institute, USA

Noise induced hearing loss (NIHL) continues to be one of the most prevalent occupational problems in the United States. The mining industry has higher prevalence of hazardous noise exposure than other major industrial sectors. For coal miners, 90% have been found to have hearing impairment by age 50. Many workplaces in coal mining industry are subjected to the high level complex noise. The current noise measurement guidelines and devices (e.g., conventional sound level meters) are developed based on the equal energy hypothesis (EEH), which states that loss of hearing by exposure to noise is proportional to the total acoustic energy of the exposure. However, the EEH does not accurately rate the complex noise which was often experienced in coal mining fields. Therefore, conventional sound level meters may not be able to accurately assess the complex noise in coal mining fields. In this study, a new waveform profile based noise measurement system has been developed for the evaluation of high level complex noise in coal mining fields. Pilot field measurements have been conducted in a wet coal preparation plant using the developed system. In addition, a wavelet transform based signal analysis algorithm has been modified and implemented to characterize the complex noise measured in the field. The preliminary results showed that the system successfully detected and recorded waveforms of complex noise signals in the coal mining field. The modified algorithm can decomposed the complex noise signals and display the detailed features in the time-frequency joint domain. The key parameters of complex noise can be determined, and the hazardous complex noise in coal mining fields can be identified.

#### Performance of Full Scale Welded Steel Mesh for Surface Control in Underground Coal Mines

Zhenjun Shan, Ian Porter, Jan Nemic, University of Wollongong, AUSTRALIA

Welded steel mesh has been widely utilised in underground coal mines for surface control for a long time. Previous studies on its behaviour were mainly conducted on relatively small sections of mesh in the laboratory. In this paper full scale pull tests on two types of welded steel mesh were performed in the laboratory, with the load-displacement response recorded. In addition to the laboratory tests numerical modelling was also completed. Weld shear tests together with tensile and bend tests on steel wires were also undertaken to provide the input parameters and other relevant information for the numerical models. It was found that the load-displacement curves generated by the physical tests and numerical models matched well. The platen used to pull the mesh was a dome like seat rather than the commonly used flat plate. The influence of the two types of platen on mesh behaviour was investigated numerically, the results showed that the flat plate yielded greater load at first wire failure but for all practical purpose a similar load-displacement curve.

**Kinetics of Powder River Basin Coal Gasification in Carbon Dioxide Using a Modified Drop Tube Reactor**

Ying Wang, David A. Bell, University of Wyoming, USA

Carbon dioxide gasification and coal pyrolysis rates were measured in a modified drop tube fixed bed reactor, accompanied with a rapid response, real-time gas analysis system. Rapid heating and fast pyrolysis of the coal sample is intended to approximate the injection of ambient temperature coal into a fluidized bed gasifier. Experiments were done from 833 °C to 975 °C and from 1 atm to 12 atm in a 4:1 mixture of CO<sub>2</sub> and argon. Reaction rates and carbon conversions were calculated based on the CO signal from a quadrupole mass spectrometer. The random pore model closely fit the experimental results and fitting parameters are listed. Results from the effects of temperature and pressure, pyrolysis conditions, and characteristics of chars (surface area measurements, scanning electron microscope images) are presented. Preliminary results for steam gasification are also presented.

**Particle Deposition Studies for Modeling Syngas Cooler Fouling**

Clinton R. Bedick, Nathan T. Weiland, West Virginia University/DOE/NETL, USA

In gasification systems, particle-laden syngas exiting the gasifier is cooled in a heat exchanger prior to particulate removal and additional syngas cleaning. Significant fouling of these heat exchangers often occurs, leading to reduced system efficiency and increased downstream temperatures, while outages for cleaning these coolers significantly contributes to reduced availability and reliability of the gasifier plant. Analogous studies on heat exchanger fouling of combustion boilers are of limited use in this problem, due to significant differences in geometry and fouling agents that are present in reducing atmospheres. A combined experimental and modeling program is outlined here for the purpose of better understanding the specific fouling mechanisms present in syngas coolers.

Particle deposition experiments are performed in a drop tube reactor under temperature conditions relevant to industrial syngas coolers. Based on fouling deposit data from industry, the current study focuses on iron sulfides, nickel sulfides, and aluminosilicate particles as the primary fouling agents. Injected particles are heated to gasifier temperatures in an upper heater, and are cooled in a lower heater to mimic particle time-temperature histories in industrial gasifiers. Particles are accelerated through a nozzle to a deposition coupon, where the particle impact process is monitored using high-speed video. Data on particle size, velocity, and stick/rebound characteristics are extracted from the videos, while a 1D model of particle thermal and kinetic processes, coupled with in-situ particle pyrometry, are used to determine particle temperatures upon impact. Energy balances are then calculated for individual particle impacts, and are related to particle capture statistics and rebound coefficients of restitution as a function of particle property data.

In tandem with the experimental effort, the test section of the drop tube reactor is modeled in OpenFOAM® for implementing and validating the semi-empirical deposition model against experimental results. Initial and boundary conditions of the OpenFOAM® model are taken from measurements on the experimental hardware, while Lagrangian particle tracking is implemented for particle/coupon impacts. The semi-empirical model derived in the experimental section is used to define friction and coefficient of restitution functions at the particle/coupon interface. The validated interface functions will be useful in CFD modeling of industrial syngas coolers, where design changes for reduced fouling can be investigated as a means to diminish the problems associated with syngas cooler fouling in existing and future gasification plants.

**Gasification Kinetics of Coal Liquefaction Residue and its Characterization**

Nitya Iyer, Moshfiqur Rahman, Arno de Klerk, Rajender Gupta, University of Alberta, CANADA

Direct coal liquefaction (DCL) is a technology for producing liquid products from coal. One of the byproducts from this process is coal liquefaction residue (CLR), which is remaining coal that was not converted to liquid products during the liquefaction process. The CLR is enriched in mineral matter and the organic content is more refractory. The objective of our work was to characterize the CLRs produced under different DCL operating conditions and to evaluate the performance of the CLR as a feed for gasification.

The feed to the DCL process was Canadian sub-bituminous coal valley (CV) coal. The industrial solvent employed during DCL was hydro-treated heavy aromatic hydrocarbons. Different CLRs were obtained from a DCL process, conducted at four different temperatures ranging from 300-450°C in an autoclave reactor (0.25L). The ultimate analysis of the CLRs exhibited direct correlation the coal liquid yield of the DCL process. The highest carbon value of 61.424 wt.% C was obtained at 300°C

liquefaction temperature (64.68% yield) as compared to 51.76 wt.% C for CLR at 450°C (79.51% yield). However, the volatile content exhibits a decreasing trend with increase in the liquefaction temperature. The lowest volatile content was ~15.003 wt.% accounted for by CLR obtained at the highest liquefaction temperature of 450°C.

Gasification kinetics of CLR was investigated under CO<sub>2</sub> at various temperatures 800, 850 and 950°C. The conversion values were obtained for gasification at 950°C. The highest carbon conversion of the in the CLRs of 51.82% was obtained at the liquefaction temperature of 450°C. This study, thus, aids in substantiation of the effect of gasification of CLR to produce syngas; as one of the “clean” pathways for optimization of the liquefaction process.

**Thermochemical Modeling of Coal Slag Formation and Related Corrosion of Various Refractory Materials Under Simulated Gasification Conditions**

Markus Reinmüller, Enrico Thieme, Mathias Klinger, Marcus Schreiner, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

The corrosion of refractory materials has been recognized as omnipresent in gasification or any other high temperature conversion of solid fuels. Besides abrasive particles and corrosive gases the liquid slag has been found to act as the most aggressive species. Consequently, the behavior of ash in high temperature range and its interaction with the refractory have to be understood in more detail.

In the present study corrosion tests have been performed with three reference ashes together with five particularly novel designed refractory materials, presented previously [1]. The simulated gasification conditions in the experiment have comprised a typical operation temperature of 1450 °C and a reducing atmosphere composed of 5 vol.% H<sub>2</sub> and 95 vol.% Ar. All ashes, which originated from hard coal, lignite, and for comparison also one from biomass, have been chosen due to their different chemical compositions, e.g. high content of alkali oxides and variations in their base to acid ratio. The oxide-based refractory materials have been produced from alumina, calcia, magnesia, and titania. Due to comparison reasons a commercial, in industry widely used chromium-zirconium oxide refractory has been tested at the same conditions.

Thermochemical calculations have been employed as a cost and time efficient way to study the interaction of ash and refractory. Those have been associated with the potential to predict the interaction for new kinds of refractories. In the literature stepwise modelling approaches have been favored (cf. ref. [2]). The corrosion mechanisms for refractories in contact with slags have been noticed mainly under combustion conditions [3], whereas, a lack of knowledge has been identified for the mechanisms under gasification conditions. Different calculation approaches, using the parameters of the experimental setup, have been employed to reproduce the slagging of the ashes as well as their subsequent infiltration and related corrosion. One of these approaches has been performed by similar masses of liquid slag and refractory in a single step with and without intrinsic gas cycling for the respective interaction [4]. A qualitative trend between the masses of mineral phases remaining in solid state at 1450 °C and the corrosion resistance has been obtained. Nevertheless, for this approach a subsequent evaluation of the complex interplay of residual phases has been required. This first approach has been followed by a second one for the contact zone varying from pure ash to pure refractory in composition steps of 20 wt.% [5]. From this model a more quantitative description of slagging and infiltration behavior has been reconstructed by means of the solid mineral content present at the respective composition. A good agreement of these results with the experimental data has been achieved. In addition, the composition ranges between slag and refractory relevant for corrosion have been identified from this model. In the present study a most recently developed model more focused on the progression of the slag infiltration will be presented and compared to the other approaches. For this model the mass-related compositions (ash to refractory) from 2:1 to 1:4 have been regarded. Main corrosive interactions have been recognized in this composition range. The consideration of the infiltration behavior and corrosion potential has to be mentioned as an advantage of this model - especially independent for multiple immiscible slag phases, which could result in a clearly different infiltration depth.

The different calculations have considered a multitude of effects in the interaction between coal ash and refractory material under simulated gasification conditions. From all of these modelling approaches a description of the corrosion potential at increased temperatures for coal ashes with high contents of alkalis and earth alkalis has been enabled. The results obtained by the new model have been related to those of the previous models and have been validated by the experimental studies. Predictions of the corrosion resistance of refractory materials will be facilitated from these calculations. Infiltration depth of the liquid slag and their related corrosion mechanisms have been identified under simulated gasification conditions. In addition, the results from calculations of the ashes of various composition and refractories may be partially transferred to the application of the same refractories in co-gasification of coal and biomass/residuals.

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**SESSION 28**  
**Combustion: Co-Firing and Flames**

**Catalyst/Support Interactions between Pt Nanoparticles and Amorphous Silica:  
Impact on Structure and Catalytic Activity for CO Oxidation**

Christopher S. Ewing, Michael J. Hartmann, Daniel S. Lambrecht, Joseph J. McCarthy, University of Pittsburgh; Götz Vesper, J. Karl Johnson, University of Pittsburgh/DOE/NETL, USA

Metal nanoparticles (NPs) play a key role in catalysis due to large surface-to-volume ratios and low-coordination active surface sites. These catalysts are typically immobilized on oxide supports to suppress sintering, which leads to catalyst deactivation and degradation of catalyst selectivity. An atomistic understanding of catalyst systems is essential to the rational design of improved catalyst systems. Catalyst activity and selectivity is highly dependent on shape and size of NPs as well as the nature of the oxide support. Despite significant advancement of experimental characterization techniques, a detailed understanding of the catalyst-support interface for very small NPs (~ 1 nm or smaller) is largely precluded by experimental investigations. Computational methods provide one means to overcoming this challenge. In previous studies catalyst supports have generally been either neglected or treated as highly ideal structures, however, oxide supports are often used in an amorphous state, exhibiting a wide range of surface sites. Due to its thermal stability and tunable porosity, and hence specific surface area, amorphous silica is widely used as a catalyst support, but is still poorly understood at the atomistic level due to limitations in both experimental and computational methods. We have developed and experimentally validated a method for generating realistic atomistic surface models of amorphous silica for a range of temperatures by simulating the process of surface dehydroxylation. Using these surface models, we have studied the effects of amorphous silica supports on small platinum NPs (13 atom cuboctahedral structures) with regards to their catalytic properties. Specifically, we have studied the impact of catalyst-support interactions on NP morphology and energetics. We find that the morphology of Pt clusters undergo significant restructuring that depends on the local structure at the Pt-Silica interface. This restructuring typically leads to significantly increased exposure of lower-coordination atoms than are present on the unsupported NP. Additionally, we observe a compressive Pt-Pt bond strain that increases with the number of bonds at the Pt-Silica interface. The energy of interaction generally depends on the number of bonds formed between Pt and silica, which is in turn a function of surface hydroxylation, and hence, pretreatment temperature of the silica support. Lower coordinated metal sites and compressive metal-metal bond strain are expected to affect the d-band center, and hence molecular binding energies. Thus, we are currently studying CO and O binding energies as well as the electronic structure via projected density of states for surface sites on selected Pt-silica systems. Furthermore, we are extending our analysis to larger systems (55 and 147 cuboctahedral structures) in order to elucidate the size dependencies of the above-mentioned catalyst-support effects.

**Pneumatic Transport of Torrefied Biomass**

Carlos Vilela, Michiel Carbo, Mariusz Cieplik, Arnold Biesbroek, Energy Research Centre of the Netherlands (ECN), THE NETHERLANDS

Direct co-firing of more than 10% of woody biomass is very difficult, without extensive hardware modifications, due to the physical characteristics of biomass. Torrefaction as a pre-treatment may be a solution to bring the biomass characteristics closer to those of coal. In this paper we will demonstrate how torrefaction can improve the morphological characteristics of biomass. The pulverized raw biomass particles are very fibrous and heterogeneous. Torrefaction in combination with pelleting generates particles with a homogeneous shape resembling that of coal particles. This paper will also demonstrate that particle morphology plays a dominant role during pneumatic conveying. Pneumatic transport tests results will be presented that show the improvement that can be achieved by torrefied biomass pellets. Among the materials tested at ECN eucalyptus torrefied at 280°C followed by pelletization was the most similar to coal. The flowability variable defined in this work has proven to be a good indicator of pneumatic transport behaviour with the particle shape as the crucial variable in this parameter.

**Synergy Effect of Biomass Co-Firing on NO<sub>x</sub> Reduction and Carbon Burnout  
with Air-Staged Combustion**

Yonmo Sung, Sangmin Lee, Xing Wang, Cheoreon Moon, Gyungmin Choi, Duckjoel Kim, Pusan National University, SOUTH KOREA

The effect of hybrid NO<sub>x</sub> reduction technology between fuel blending and air staging on gas emissions and combustion performances has been investigated. To investigate the combustion and emission characteristics of the blends with coals (bituminous and

sub-bituminous) and biomass, a pulverized coal fired furnace was used in this research. Influences of staged condition, primary zone air ratio, coal types, blending ratio of low-rank fuel on NO<sub>x</sub> emission were surveyed. For the single coals, low-rank coal was more favorable to reduce NO<sub>x</sub> emissions due to low fuel-N composition and oxygen deficiency in the primary zone. In co-firing biomass with coal, as biomass has a high volatile content, it could be successfully applied in NO<sub>x</sub> reduction method as the air-staged combustion. In addition, combustion performances of the carbon burnout and flame temperature increased by the biomass co-firing. In this research, it was revealed that the hybrid NO<sub>x</sub> reduction technology between air staging and low-rank fuel blending has shown the potential simultaneously for reducing exhaust gas emissions and enhancing combustion performances when the combustion of pulverized coal particles was incomplete. The air-staged combustion has a synergistic effect on biomass co-firing for NO<sub>x</sub> reduction and carbon burnout simultaneously. This conclusion would be very useful information for pollutant control in the existing thermal power plant using biomass blending technology.

**SESSION 29**  
**Clean Coal and Gas to Fuels: Catalysts and Solvents**

**Advances in the Study of Composite Catalysts in Direct Coal Liquefaction**

Yuanyuan Zhang, China University of Mining and Technology (Beijing); Ke Liu, Shenhua Research Institute; Xiaofen Guo, National Institute of Clean-and-Low-Carbon Energy, CHINA

Traditional Fe-based catalyst on direct coal liquefaction has been highly developed, which is nanometer grade and highly dispersed. The catalyst is also used in the industrial demonstration plant of coal liquefaction in Inner Mongolia. Compared with the Ni-, Mo-based catalyst, the Fe-based catalyst is weaker on hydrogenation, and high water consumption and environmental pressure should not be ignored. The studies show that the synergism has been found by using both kinds of catalysts. The paper is focused on this kind of composite catalyst. It is also investigated that the comparatively few research of this composite catalyst remained in laboratory stage, and some of the catalyst preparation is too complex to improve the available preparation process and scale-up of the catalyst. So the high activity and simple prepared catalyst has advantages in industrialization. This kind of composite catalyst should be a trend in future.

**Cu/SiO<sub>2</sub> Based Catalyst For Industrial Ethylene Glycol Production: Synthesis  
Methods And Scaling Up**

Tiberiu Popa, Maohong Fan, University of Wyoming, USA

For the synthesis of Ethylene Glycol (EG) from syngas using the Dimethyl Oxalate (DMO) route, an important step is the hydrogenation of DMO. Cu/SiO<sub>2</sub> based catalysts have the advantage of high selectivity toward EG and the intermediate Methyl Glycolate (MG), but the conventional methods used for catalyst's synthesis were hard to scale-up for industrial use. A quicker, safer (compared to ammonia evaporation) method of copper deposition was developed using ammonium carbonate as a precipitation agent. The results of various techniques for the preparation of Cu/SiO<sub>2</sub> are compared in term of catalytic activity, materials properties and ease of scale up.

**Influence of Potassium-Doping on Activity of Ni<sub>2</sub>Mo<sub>3</sub>N Catalyst in the Presence of  
Thiophene**

Lili Zhang, Jie Feng, Qi Chu, Kun Xu, Wenying Li, Taiyuan University of Technology, CHINA

Ni<sub>2</sub>Mo<sub>3</sub>N and promoted Ni<sub>2</sub>Mo<sub>3</sub>N-K catalysts were prepared by a one-step synthesis using ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O], nickel acetate [Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O] and the decomposition of hexamethylenetetramine without ammonolysis under an argon atmosphere at 650 °C. Their catalytic activities were evaluated by using benzene as an aromatic compound and thiophene as a sulfur poisoning model. The structure of fresh and used catalysts were characterized by temperature-programmed desorption of absorbed species. The evaluation results showed that the addition of potassium had few influence on the initial activity while greatly improved the sulfur tolerance of catalysts. The good sulfur resistance was due to the presence of potassium decoration hindering the adsorption of a part of thiophene on the Ni<sub>2</sub>Mo<sub>3</sub>N surface to protect the active sites for hydrogenation of benzene.

**The Study on Dewatering and Upgrading of Lignite Through Organic Solvent**

Bingbing Huang, Meng Liu, Yufeng Duan, Guilin Ma, Jian Li, Southeast University, CHINA

Lignites were dewatered and upgraded by two kinds of organic solvent (ethanol, n-hexane) under a high temperature and high pressure reaction kettle. Compared with the raw lignite, the experimental results show that the dewatering and upgrading treatment can effectively decrease the inherent water in coal, volatile and oxygen content, also increase the fixed carbon content and heating value, eventually make lignite rank elevate gradually. The mechanism of dewatering was discussed based on the strength of hydrogen bonds formed between coal and water and the change in the solubility of water in the solvent with increasing temperature. The physical and chemical properties of lignite, such as macerals, micromorphology, pore structure, have been performed comprehensive analysis and comparison between the raw lignite and upgraded lignite. The experimental results show that aromatic carbon structure increase gradually after dewatering and upgrading. Compared with the single heating effect of evaporation upgrading technology, the synergistic effect of high temperature and pressure dewatering and upgrading treatment make lignite rank elevate more significantly. Dewatering and upgrading makes the lignite pore size distribution gradually develop towards the microporous direction. And surface area and pore volume show different degrees of first increasing then decreasing trend respectively. The upgraded lignite whose micromorphology has also changed a lot, for instance, the surface becomes chiseled, the structure becomes more compact, and coal quality becomes dense up.

#### **Influence of Solvent Pretreatment on Pyrolysis of Hulunbeier Lignite**

Huijun Huang, Huiling Rong, Xiaohong Li, Jie Feng, Wenying Li, Taiyuan University of Technology, CHINA

To increase the tar yield and improve the quality of tar, Hulunbeier lignite coal was pretreated with three solvents (methanol, tetralin and tetrahydrofuran) before pyrolysis process. Pyrolysis reactivity of different pretreated coal samples and the distribution of pyrolysis products such as tar, char and gas were investigated by thermogravimetric (TG) analysis and fixed-bed pyrolysis device. TG analysis showed that the initial pyrolysis temperature of three pretreated coals were all lower than the raw coal, as well as their weight loss were higher than the raw coal. The pyrolysis conversion of the pretreated coals all improved. The tar yield of methanol-pretreated coal increased the most among the three pretreated coals. Promoting effect of solvent pretreatment may come from solvent swelling. Solvent pretreatment could loose the coal structure and expand the pore structure, which would benefit to the release of small molecules when being heated. Solvent pretreatment could also disrupt some non-covalent interactions of the coal molecules and reduce the cross-linking reaction of hydrogen bonds in the pyrolysis process.

#### **SESSION 30 Coal Science: General - 5**

#### **Modeling Thermal Stress in Coal Particles During Heating-Up in a Drop-Tube Reactor and in a Graphite Furnace Atomizer**

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Fragmentation of coal particles during pyrolysis, gasification or combustion influences the particle size distribution and hence the reaction rate. Therefore is it interesting which coal types show thermal stress-induced disintegration during heating-up. This investigation is closely related to two experimental setups which examine the primary fragmentation of coal particles during pyrolysis. Firstly a pressureless drop-tube reactor applies temperatures up to 1550 -1600°C for approximately 0.45 seconds. As a special feature the particle is tracked with a high-speed camera to detect the time of disintegration and the fragmentation count. The second one is an electrothermal evaporation device, that was used to generate temperatures typically during pyrolysis. Since there is no visualization during the experiment, this will be carried out as parameter study for several heating rates and final temperature, to find the critical values for the different coal types. Thereby the stress distribution inside the coal particles is modeled within linear elastic theory using ANSYS software. Special attention is considered to the transient thermal conditions in both experiments and is applied in the modeling. The stress distribution from numerical analysis at the time of fragmentation will provide critical strength values. The shape of the fragments could give some information about the failure mechanism. The final goal is an estimation for the fragmentation probability depending on coal type, particle size and heating rate.

#### **The Influence of K<sub>2</sub>CO<sub>3</sub> on Powdered Coals with Varying Swelling Properties during Devolatilisation**

Sansha Coetzee, Hein W.J.P Neomagus, John R. Bunt, Christien A. Strydom, North-West University, SOUTH AFRICA; Harold H. Schobert, Penn State University, USA

The understanding of coal's thermoplastic properties, and the ability to predict the plastic behaviour of coal, is important for many coal conversion processes. Both coal

swelling and agglomeration are undesired phenomena, which have a negative effect on operational efficiency specifically in the case of fixed bed and fluidised bed gasification technologies. Swelling results in the formation of chars with different structures, which consequently influence char combustion, gasification kinetics, as well as ash formation. In addition to influencing process efficiency, excessive swelling of coal particles may lead to various operational problems, such as build-up of oven wall pressure. Various pre-treatment methods, such as pre-oxidation and slow heating rates, have been found to modify the swelling and caking properties of coal. In addition to these pre-treatment methods, the use of additives like alkali and alkaline earth metal salts have been investigated extensively in order to determine the influence of these additives on the caking and swelling of coal.

The aim of this paper is to investigate the influence of K<sub>2</sub>CO<sub>3</sub> on the functional groups of three South African coals (with varying swelling/softening characteristics) during devolatilisation. The effect of K<sub>2</sub>CO<sub>3</sub> on the swelling and fluidity, and the rate of mass loss during devolatilisation, was also investigated. TWD coal is a medium rank-C bituminous, non-swelling coal (Free Swelling Index (FSI) 0), GG is a medium rank-C bituminous, medium-swelling coal (FSI 6.5), and TSH is a medium rank-B bituminous, high-swelling coal (FSI 9.0).

Raw coal, as well as char (with and without 10 wt.% K<sub>2</sub>CO<sub>3</sub>) prepared at different temperatures (with specific focus on the thermoplastic temperature range (350-600 °C)), were analysed using DRIFT spectroscopy, in order to determine the effect of the K<sub>2</sub>CO<sub>3</sub> additive and heat treatment on the functional groups of the coal. Analyses such as FSI, Gieseler fluidity and Dilatometry were used to determine the influence of 5 wt.% and 10 wt.% K<sub>2</sub>CO<sub>3</sub> on the plastic behavior of the coals. The influence of K<sub>2</sub>CO<sub>3</sub> (10 wt.%) on the rate of mass loss during devolatilisation was also investigated using results obtained from TG experiments (up to 900 °C, 3 °C/min). -212 µm coal samples were used for the DRIFT analysis and devolatilisation experiments, while the coal samples were prepared according to standard for the FSI, Gieseler fluidity and Dilatometry analyses.

The DRIFT spectra indicated that the aromatic/aliphatic C-H ratio increased with increasing devolatilisation temperature. From the DRIFT spectra it could only be concluded that for the GG and TSH samples, the addition of K<sub>2</sub>CO<sub>3</sub> catalyses the elimination of functional groups, in particular hydrogen bonds (dehydrogenation). The K<sub>2</sub>CO<sub>3</sub> only affects the functional groups of the coals which exhibit swelling/softening behaviour (GG and TSH), which may indicate alkali-coal interactions. Results also indicate that the use of K<sub>2</sub>CO<sub>3</sub> effectively reduces the swelling behaviour and fluidity of powdered coal, as measured by FSI, Gieseler, and Dilatometry. It was found that an increase in K<sub>2</sub>CO<sub>3</sub>-loading results in a decrease in swelling and fluidity. The TG results indicated that the addition of K<sub>2</sub>CO<sub>3</sub> decreased the maximum rate of devolatilisation, but did not alter the temperature at which the maximum rate of devolatilisation occurs. Upon comparison it was also observed that the temperature range for maximum rate of devolatilisation (for GG and TSH) coincides with the temperature ranges at which maximum contraction (dilatometry) and maximum fluidity (Gieseler) occur.

#### **System Overview and Preliminary Characterization of the High-Temperature and Pressure Entrained-Flow Lab-Scale Gasifier at CSM**

Madison Kelley, Jason Porter, Colorado School of Mines, USA

The Colorado School of Mines (CSM) currently houses a high-temperature and pressure 10-kW lab-scale entrained-flow gasifier, capable of operating at 1650°C and 40 bar. Detailed in this paper is a description of the physical gasifier and its primary components, its subsystems, and preliminary characterization results.

#### **Determination of Coal Ash Sintering Characteristics by Compression Strength Test at Different Atmospheres**

Ronny Schimpke, Steffen Krzack, Nico Bräutigam, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

Fluidized bed coal gasifiers are frequently confronted with the problem of bed defluidization because of strong ash particle agglomeration. The agglomeration tendency of the bed particles can be evaluated by the ash sintering characteristics. One opportunity for the characterization is the compression strength test on heat treated ash pellets produced under defined conditions. Preliminary tests were executed for the determination of optimum conditions for compression strength tests. Varied parameters are the pellet height to width ratio, the pellet heat treatment time at particular temperature and the strain rate during the compression strength test. Further test conditions like abort criterion, minimum number of test pellets per measurement point and sample preparation are discussed. The optimum conditions determined are a temperature dwell time of 24 hours with a minimum of six pellets. The pellet dimensions are 15 mm in diameter and height. The strain rate is set to 0.1 mm/s. The abort criterion of the strength test is set to 20 % in force loss and 33 % loss in pellet height. Extensive compression strength tests were done on ash from Rhenish lignite coke pretreated at different atmospheres and temperatures to determine sintering temperatures. The atmospheres chosen are oxidizing and reducing, both at ambient

pressures. The sintering temperatures are determined and compared with ash fusibility tests and high temperature X-ray diffraction analysis.

## SESSION 31 Carbon Management: Capture of Carbon Dioxide - 1

### Novel Sorbents for Oxygen Separation from Air

Elliot Roth, Sheila Hedges, Evan Granite, DOE/NETL, USA

A less expensive route for the production of oxygen would be of tremendous value in applications such as gasification, oxy-combustion, smelting, chemical production, welding, and in health care. A laboratory-scale packed bed reactor and thermogravimetric analyzer (TGA) were used to screen potential sorbents for the capture of oxygen from oxygen-nitrogen mixtures. An on-line electrochemical sensor, used in a continuous mode, monitors the oxygen concentration in the inlet and outlet streams of the packed bed reactor. The TGA was employed to determine temperatures of active oxygen capture and release to or from various gas streams. The capacities and breakthrough times of several novel sorbents were determined as a function of various parameters. The mechanisms of oxygen removal by the sorbents are suggested by combining the results of the packed-bed and TGA testing with various analytical results.

### Mixed Solid Sorbents for CO<sub>2</sub> Capture Technologies: Theoretical Predictions and Experimental Validations

Yuhua Duan, Dan C. Sorescu, David Luebke, Bryan Morreale, DOE/NETL; Keling Zhang, Xiaohong Shari Li, David King, Pacific Northwest National Laboratory; Xianfeng Wang, Bingyun Li, West Virginia University, USA; Jinling Chi, Lifeng Zhao, Yunhan Xiao, Chinese Academy of Sciences, CHINA

Carbon dioxide is one of the major combustion products which once released into the air can contribute to global climate change.<sup>[1-4]</sup> Solid sorbents have been reported in several previous studies to be promising candidates for CO<sub>2</sub> sorbent applications due to their high CO<sub>2</sub> absorption capacities at moderate working temperatures.<sup>[5-8]</sup> During the past few years, we developed a theoretical methodology to identify promising solid sorbent candidates for CO<sub>2</sub> capture by combining thermodynamic database searching with *ab initio* thermodynamics calculations.<sup>[7-15]</sup> The primary outcome of our screening scheme is a set of promising CO<sub>2</sub> sorbents with optimal energy usage. However, at a given CO<sub>2</sub> pressure, the turnover temperature ( $T_i$ ) of an individual solid capture CO<sub>2</sub> reaction is fixed. Such  $T_i$  may be outside the operating temperature range ( $\Delta T_o$ ) for a particularly capture technology. In this study, we demonstrate that by mixing different types of solids it's possible to shift  $T_i$  towards the required temperature range  $\Delta T_o$ . When we mix two solids  $A$  ( $T_A$ ) and  $B$  ( $T_B$ ) to form a new sorbent  $C$  ( $T_C$ ), the  $T_C$  is located between  $T_A$  and  $T_B$ . Assuming that  $T_A > T_B$  and the desired operating  $T_o$  being  $T_A > T_o > T_B$ , we have typically three scenarios to guide the synthesis of the mixing sorbent  $C$ :

- (1)  $T_A \gg T_B$  and the  $A$  component is active for capture CO<sub>2</sub>. In this case since  $T_A$  is higher than  $T_o$ , mixing  $B$  into  $A$  to form  $C$  will decrease  $T_A$  to  $T_C$  fallen into  $\Delta T_o$ . For example, Li<sub>2</sub>O is a very strong CO<sub>2</sub> sorbent. However, its regeneration process from Li<sub>2</sub>CO<sub>3</sub> only can occur at very high  $T_A$ . By mixing with a weak CO<sub>2</sub> sorbent (such as SiO<sub>2</sub>, ZrO<sub>2</sub>), the  $T_C$  and the theoretical CO<sub>2</sub> capture capacity of mixture can be decreased with decreasing the ratio of Li<sub>2</sub>O/SiO<sub>2</sub> or Li<sub>2</sub>O/ZrO<sub>2</sub>.<sup>[5-15]</sup>
- (2)  $T_A \gg T_B$  and  $B$  component is active for capture CO<sub>2</sub>. In this case, since  $T_B$  is lower than  $T_o$ , mixing  $A$  into  $B$  will increase  $T_B$  to  $T_C$  towards the range of  $\Delta T_o$ . For example, although pure MgO has a very high theoretical CO<sub>2</sub> capture capacity, its  $T_B$  is lower than the required  $\Delta T_o$  used in warm gas clean up technology and its practical CO<sub>2</sub> capacity is very low.<sup>[16-17]</sup> By mixing M<sub>2</sub>O (M=Na, K, Cs, Ca) or carbonates (M<sub>2</sub>CO<sub>3</sub>) into MgO, the newly formed mixing systems have higher  $T_C$  and capacity making them useful as CO<sub>2</sub> sorbents through the reaction  $MgO + CO_2 + M_2CO_3 = M_2Mg(CO_3)_2$ .<sup>[16-20]</sup>
- (3)  $T_A$  and  $T_B$  are close to each other. In this case, both  $A$  and  $B$  components are active for capture CO<sub>2</sub>, and the CO<sub>2</sub> capacity of the mixture is the summation of those of  $A$  and  $B$ . Currently, we are working on doping systems. For example, when doping Na (with  $T_B$ ) into Li<sub>2</sub>ZrO<sub>3</sub> (with  $T_A$ ), the  $T_C < T_A$ , while doping K into Li<sub>2</sub>ZrO<sub>3</sub>, the  $T_C$  is close to  $T_A$ .<sup>[21]</sup>

These results demonstrate that although one single material taken in isolation might not be an optimal CO<sub>2</sub> sorbent to fit the particular needs and to operate at specific temperature and pressure conditions, by mixing or doping two or more materials to form a new material, it is possible to synthesize new CO<sub>2</sub> sorbents which can fit the operating temperature needs for industrial applications.

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### Discovery of System and Materials Requirements for Solid Sorbent-Based CO<sub>2</sub> Capture Using Reduced Order Modeling

Justin Glier, DOE/NETL, USA

In recent years, climate change concerns have spurred research efforts to developing more cost-effective processes for efficient carbon dioxide (CO<sub>2</sub>) capture from large point sources of CO<sub>2</sub>, especially coal-fired power plants. Solid sorbents are believed to be among the most promising early-stage technologies for achieving that objective. Most of the work in this area has focused on the CO<sub>2</sub> adsorption/desorption properties of different types or classes of solid sorbent materials. Recent efforts have focused on proving the concepts developed at laboratory-scale operations to larger pilot scale units. Relatively little attention, however, has yet been paid to the interdependence between the solid and the overall CCS system employing such materials.

To better assess the potential advantages of solid sorbents for post-combustion CO<sub>2</sub> capture, this paper presents an integrated cost and performance model for a solid sorbent-based CO<sub>2</sub> capture systems. This newly developed model is used to provide systematic estimates of the plant-level performance, costs, and environmental emissions for a new, supercritical pulverized (PC) power plant employing post-combustion CO<sub>2</sub> capture. We estimate the material flows, electricity, and steam requirements of the new CO<sub>2</sub> capture system based on different solid sorbent materials, and assess the effects of the capture system design on the cost and performance of the overall PC power plant. We further employ sensitivity analysis to evaluate the effects on power plant performance and cost of variations in key sorbent and system design parameters, including the CO<sub>2</sub> removal efficiency, reactor vessel design, solid interaction with flue gas constituents, and other parameters of interest. In particular, this study systematically evaluates the effects of the solid sorbent's CO<sub>2</sub> carrying capacity on the plant energy penalties and the levelized cost of electricity production.

Results for two solid sorbent system designs are compared to cost and performance results for a current amine-based liquid solvent system, modeled using the Integrated Environmental Control Model (IECM, a well-documented and publically available model developed by Carnegie Mellon University for the United States Department of Energy's National Energy Technology Laboratory). Based on the results from a series of sensitivity analyses, the proposed paper further explores and prioritizes the R&D needs for integrated material and system designs, including pretreatment options, integrated heat exchangers, adsorber design, and regenerator design. The objective is to help determine which sorbent systems and design combinations are the most viable candidates for a solid sorbent-based CO<sub>2</sub> capture system.

### Post-Combustion CO<sub>2</sub> Capture Using Metal Organic Frameworks - Performance and Cost Analysis

Wenqin You, Hari Chandan Mantripragada, Edward S. Rubin, John Kitchin, Carnegie Mellon University, USA

Metal organic frameworks are novel solid sorbents, known for their superior CO<sub>2</sub> adsorption potential compared to other solid sorbents. MOFs are porous solid sorbents consisting of organic-inorganic hybrid networks. The nodes are made of metals (single ions or clusters), which are connected by organic linking groups to form 1-D, 2-D or 3-D coordination networks. Owing to their extraordinary surface areas and tunable pore surface properties, MOFs have received a lot of attention recently for separation of CO<sub>2</sub> from gas fuels, both in pre-combustion and post-combustion applications. There are hundreds of possibilities for materials that can be used in MOFs, each having different adsorption capacities and other properties. The CO<sub>2</sub>-adsorption capacity of MOFs increases significantly with pressure. As a result, pressure or vacuum swing adsorption (PSA/VSA) is considered more appropriate for regeneration than temperature swing adsorption (TSA). In a PSA process, CO<sub>2</sub> is selectively adsorbed on the sorbent at a high pressure and is released from the sorbent when pressure is

lowered. This purified CO<sub>2</sub> is compressed and transported to a geologic storage site for sequestration.

Thermodynamic models for CO<sub>2</sub>-adsorption on MOFs have been developed based using a Langmuir adsorption model fitted to data at different pressures and temperatures. A new simplified process model has been developed for post-combustion CO<sub>2</sub> capture using pressure swing adsorption and regeneration. This model can also be used for rapid adsorbent screening for CO<sub>2</sub> capture applications. The amount of adsorbent material needed to achieve at a given CO<sub>2</sub> capture efficiency and the energy required for CO<sub>2</sub> capture were calculated using the performance model. Preliminary results showed that, for a particular MOF (Mg-MOF-74), a single-stage PSA/VSA is not sufficient to achieve high purity and recovery of CO<sub>2</sub>. The model was extended to incorporate a multi-stage VSA unit and we found that a CO<sub>2</sub>-purity of around 80% can be achieved with two stages. In this paper, we will present case studies to understand the effect of different performance variables on CO<sub>2</sub>-purity and the amount of material and energy needed to capture a desired amount of CO<sub>2</sub> from a pulverized coal power plant. We will also compare different types of MOFs for their relative advantages and disadvantages. Preliminary cost models will also be developed with the results from the performance models to calculate the capital cost (\$/kW) and operating costs (\$/MWh) of the power plant. The results from this techno-economic analysis will be compared to a power plant with amine-based (MEA or advanced amines) CO<sub>2</sub>-capture technology, using the Integrated Environmental Control Model (IECM) developed at Carnegie Mellon University.

This work is supported under a contract from Stanford University's Global Climate Energy Project (GCEP).

### Effects of Coal Characteristics on Carbon Dioxide Ad/Desorption

Louis L.Y. Tsai, Y.R. Tseng, J.H. Shiao, National Central University, TAIWAN

Greenhouse gas emission contributes to global warming and abnormal weather conditions. In recent years, how to reduce carbon dioxide quantity in the atmosphere is an important environmental issue. Geological sequestration of CO<sub>2</sub> is considered to be an effective way of reducing greenhouse gas in the atmosphere. Possible sequestration sites include depleted oil reservoir, saline aquifer and unmineable coal seam. The purpose of this study is to evaluate the effects of coal characteristics upon the ad/desorption of CO<sub>2</sub>. A total of 27 coal samples were collected from the Western Foothill Belt of Taiwan. The experiment work was divided into three parts (1) Coal samples were crushed to < 250µm, and then placed in a drying oven at 50 °C for a day, put coal samples into a sample vessel and gradually increase the pressure to 800psi, and then progressively reduce the pressure. Adsorbed and desorbed CO<sub>2</sub> under various pressures were recorded. The CO<sub>2</sub> ad/desorption data were then analyzed by Langmuir Isotherms to calculate Langmuir Volume Parameter (maximum adsorption coal gas storage capacity, V<sub>L</sub>); (2) Besides traditional Proximate and Ultimate analysis, coal samples were made into pellets to measure their vitrinite reflectance and maceral composition under reflected light microscope; (3) Combined with all of the coal data, Langmuir Volume parameters can be correlated among various factors by SPSS. The results showed that adsorption of CO<sub>2</sub> exhibits a curved relationship with coal rank, positively correlated with vitrinite content, and negatively correlated with mineral matter content. Finally as for statistical factor analysis, the influence of characteristics among each other can be analyzed for 19 available sets of data. The results indicate V<sub>L</sub>, P<sub>L</sub>, average pore size, and moisture exhibit good correlation with ad/desorption of CO<sub>2</sub>.

## SESSION 32 Combustion: Combustors

### Critical Factors in Understanding the Mechanism of Ash Agglomeration in Fluidized Bed Systems

Aditi B. Khadilkar, Sarma V. Pisupati, The Pennsylvania State University/DOE/NETL; Peter L. Rozelle, United States Department of Energy, Office of Fossil Energy, USA

A simple mathematical model was developed to study ash agglomerate growth in fluidized bed systems. The model can trace the temporal evolution of ash particle size distribution in the system. It evaluates every possible two-particle collision for sticking based on the Stokes' criterion. Agglomeration occurs when there is viscous dissipation of the particle kinetic energy by the slag-liquid formed on ash particles. Several chemical and physical parameters such as fuel chemistry, ash surface properties, slag rheology and particle hydrodynamics affect agglomeration. An integrated model capable of making predictions based on both the fuel composition (chemistry) as well as the reactor configuration (physics), under a given set of operating conditions has been developed as a useful tool for the industry. It would help to predict and prevent agglomeration during combustion and gasification in fluidized beds, including advanced combustion technologies such as chemical looping combustion. The slag-liquid formation tendencies were studied through the use of FactSage™ thermodynamic equilibrium simulation software. Using this technique, the slag-liquid

formation tendencies for Pittsburgh seam coal were predicted under both combustion and gasification gaseous atmospheres and experimentally validated using TGA/DTA, XRD and Thermo mechanical analysis (TMA). The hydrodynamics were studied through the use of MFIX-Multiphase Flow with Interphase eXchanges, a computational fluid dynamics software. The kinetic theory of granular flow was utilized to calculate a distribution of collision frequencies for a given particle size distribution. Using this mathematical modeling approach, theoretical predictions of particle hydrodynamics and particle growth kinetics were made. The simulations were run for combustion and gasification of density-separated Pittsburgh seam coal fractions in a laboratory-scale bubbling fluidized bed reactor. This unique two-particle collision model tracks the changes in the number of particles and simultaneous changes in particle dynamics with time. It uses Eulerian methods to compute the hydrodynamics but at the same time considers particle-level variations in the system by modeling particle collisions. The use of Eulerian methods helps to decrease the computational demands over discrete element methods while the collision model helps to maintain accuracy.

The model has enabled the consideration of interlinked effects of particle hydrodynamics with particle size increase. Broadly, it also facilitates more accurate predictions through the mathematical integration of chemical and physical parameters that influence agglomeration.

### Burning Uncleaned Solid Fuels

George D. Dumbaugh, Kinergy Corporation, USA

The purpose of this presentation is to qualify a method of continuously and efficiently burning "dirty" solid fuels. Thus, the fuel cost is reduced and a significant savings is realized. Looking back on the many years of burning coal, the added cost of a Preparation Plant was always involved in the fuel's supply. From a request issued by the Department of Energy, and aligning with a reputable Boiler Maker, an improved Vibrating Stoker Grate has been developed. Delivered in 2006, and "started up" in 2007, it has been in productive use for 6 years. One of the most significant gains was the successful burning of "Run of Mine" (ROM) Coal. Other "dirty" solid fuels derived from waste, such as refuse coal (which includes culm, gob and silt), wood waste, wood bark, shredded rubber tires, municipal solid waste (MSW and RDF) can also be burned. Usually the Power Plant is paid to accept these waste fuels. The maintenance of this Vibrating Stoker Grate appears to be minimal. Consequently, its productive availability rating is about 95%. Thus, this important improvement deserves attention when compared to other Stoker Grates. If it is wanted to observe the Vibrating Stoker Grate that successfully burns ROM Coal, a visit to its installation in the southern part of Illinois can most likely be arranged.

### Anomalies When Burning Low Grade Coals in Bubbling Fluidised Bed Combustion (BFBC)

Rosemary Falcon, R L Taole, University of the Witwatersrand; D Brook, Babcock Engineering, SOUTH AFRICA

Southern Africa faces a short to medium term future of coal-dependent energy while renewable sources are developed to replace the ever increasing demand for energy in the region. Large scale coal-fired pulverized fuel power generation plants have been the mainstay supplying energy in South Africa for the past century. However, emerging trends are now flowing towards smaller scale independent power producers (IPPs) using fluidised bed processes, all of which is strongly supported by current national legislation.

In parallel with this development is the reduction in coal qualities in the country as better quality coals are being beneficiated for export purposes. In addition, over 2 billion tons of discard materials from past beneficiation processes lie largely unused, spread between the major coalfields of the country. Given such quantities of low grade coal, a number of parties are giving serious consideration to the development and implementation of smaller scale fluidised bed combustion power generation units throughout the region, using both discard as well as run-of-mine coals from poorer grade areas. Bubbling and circulating fluidised bed processes are on the drawing boards.

However, where BFBC units have already been installed in the region (both in Botswana and South Africa) certain unexpected coal-quality related problems have arisen which have led to less than efficient operations and, at times, serious outages with costly replacements of plant parts. These issues have been investigated and the research has shown that the temperatures at which the particles of low grade coals burn are significantly higher than was originally thought, and certainly higher than the average bed temperatures normally operating for fluidised bed processes. Furthermore, under certain operating conditions, slagging occurs, leading at times to full bed slagging when in outage mode, ash handling below the bed has been difficult and corrosion has taken place in specific quarters below the entry of air in bottom-sourced sparge pipes.

Given the significant trend towards the introduction of fluidised beds into South and southern Africa, the results of this research may be relevant to note, both by

### Numerical Study of Gas-Solid Fluidized Bed Dynamics with Distributor Design

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Stable and evenly distributed gas flow through the distributor plate is critical for successful operation of gas-solid fluidized bed reactors. More specifically, the distributor design must prevent poorly mixed and stagnant zones that could lead to particle agglomeration, and subsequently negatively impact the operation. Stability requirements for long-term process operations constrain the design. In the context of the Chemical-Looping Combustion, mitigating potential coking at the distributor and reducing high thermal stresses on the distributor plate suggest the use of bubble-cap type distributor designs. In other respects, the bubbling behavior induced by the distributor has an impact on the combustion efficiency of the reactor, because the bubble dynamics implies mixing. However, when too many bubbles are generated and/or the bubbles are too large relative to the bed, gas-solid contact can severely be limited allowing for increased bypass of the reducing gases.

The present effort uses computational fluid dynamics to examine the effect of several distributor plate configurations on the hydrodynamics of a cylindrical stainless-steel laboratory scale bubbling bed. This vessel, which is used to study the reactivity of particles in fluidized bed, is 5.5cm inner diameter and 1.4m high. For the current study, the reactor contains 1.5 kg of hematite which corresponds to a static bed height of 21cm. The diameter of the Geldart B-type particles that compose the bed ranges from 50 $\mu$ m to 600 $\mu$ m with an average of 234 $\mu$ m and a density of about 4701 kg/m<sup>3</sup>. The bubble-cap distributor plates consist of 4-6 1cm tall bubble caps each with an inner diameter about 0.6 cm and perforated with 3 holes. Porous and bubble cap distributors are modeled in this work. The influence on the number of bubble caps as well as the geometric resolution of gas jets from the holes is also investigated. The simulations are performed using a customized version of *compressibleTwoPhaseEulerFoam* solver from the OpenFOAM finite volume toolbox/library. This code is an implementation of the kinetic theory-based multi-fluid Eulerian model for gas-solid flow dynamics (Simonin, 1996; Syamlal et al. 1993). In the simulations, the bed material is considered to be mono-disperse.

The “bubbles” are identified from iso-surfaces which are extracted using ParaView from the time varying volume fraction field. Bubble statistical properties such as the distribution of the size, shape, rise velocity, rise angle and coalescence rate are calculated from the iso-surfaces and bubble trajectories. These statistical properties along with the flow patterns for each distributor design are discussed. Further, time-series analysis and statistical analysis of the bed height (PDF, expansion frequency) and pressure fluctuations (amplitude, auto-correlation, power spectrum, wavelet analysis) are performed to extract quantitative information about bed dynamics (see e.g. Sasic et al. 2006, Johnsson et al., 2000) and compared to the bubble properties.

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### Design of a Cyclone Combustor for MILD Combustion

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Moderate and intense low oxygen dilution (MILD) combustion technology was applied to reduce NO<sub>x</sub> emissions from the combustion of solid fuels. Horizontal cyclone combustors were designed and constructed in our laboratory to improve the mixing of the solid fuels with air. In our previous tests, the horizontal cyclone combustor showed more stable MILD combustion of the solid fuels than the vertical combustor. An external recirculation technique was applied to the cyclone combustor to better control the flow pattern inside the combustion chamber. The performance and stability of the MILD combustion were examined varying the geometric and operational parameters of the cyclone combustor. Based on the combustion test results, the cyclone combustor was redesigned. With the optimized design, the cyclone combustion demonstrated stable MILD combustion of solid fuels.

## SESSION 33 Gasification: Modeling - 2

### Numerical Simulations of Reacting Porous Char Particles Under Gasification Conditions

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This work is devoted to the numerical study of char particle gasification in different gasification atmospheres and under convective conditions. In particular, char reactions inside the porous particle were considered. For this, porous, 200 micron sized particles were represented by idealized two-dimensional and more detailed three-dimensional geometries, and were studied by utilizing a CFD approach. In 2D, the macropores were modeled as a set of tori with varying diameter and number, which allows a systematical variation of the char porosity and internal surface. To substantiate this approach, additional 3D simulations were performed. Therefore a mono-disperse packed-bed based on a DEM simulation was generated (Schulze et al. 2014). From this packed bed a sphere was extracted. The geometry was inverted afterwards, so the packed bed spheres finally represent the pore system of the particle. The aim of this work is to analyze the heterogeneous reactions inside and on the surface of porous char particles, and to derive sub-models for the gasification of such particles.

It is a well-known fact that during coal gasification the processes inside coal particles play a major role for the carbon conversion of these particles. Due to the small length scales and the bad accessibility of the pores it is barely possible to study in detail the physical phenomena inside char particles experimentally. Concerning numerical studies it is not feasible to resolve the real pore structure of char particles due to the complex inner geometry and the different length scales. Therefore most of the numerical studies are based on non-porous structures or use field quantities on basis of the grain or random pore model to represent the porosity. Recent works include also convective mass transport (Dierich et al. 2014). Such approaches are useful for studying the overall particle behavior of the particles under different conditions. With rising computational capabilities nowadays it is possible to resolve at least idealized macroscopic pore structures, which gives a more detailed insight into the convective and diffusive transport mechanism to the particle and into the inner pores.

Motivated by this fact, in this study the transport and reaction processes inside coal particles studied via macro-pore resolved particle CFD simulations. The main focus of the work is the analysis of the impact of porosity, surface-to-volume ratio and particle Reynolds number of a single porous particle moving in a gas stream on the carbon consumption rate. For the 2D axisymmetric approach, the particle geometries include three different porosities and three different surface-to-volume ratios. The more detailed 3D case was used for validation purposes and to get an understanding of the flow behavior inside the macropores. The used grid size varied between 300000 and 400000 cells for the 2D case and was about 5.1 million for the 3D case. The chemistry was modelled using a semi-global mechanism that included five species, namely H<sub>2</sub>O, H<sub>2</sub>, CO, CO<sub>2</sub> and N<sub>2</sub>. Two heterogeneous reactions (gasification- and Boudouard-reaction) as well as the homogeneous watergas-shift reaction were employed.

The results allow to analyze the convective and diffusive mass and heat transport within the porous particle. In dependence of the species distributions it was possible to localize the temperature range, in which the reaction system switches from a kinetically controlled to a transport controlled regime. While it is obvious that the carbon consumption rate scales linearly with the surface to volume ratio for the kinetically controlled regime, the mechanism for the diffusion regime is more difficult to describe. Here a correlation in dependence of the porosity could be found. It could be shown that Re has only a minor influence on the distinct species distribution inside the particle. Furthermore it could be seen that the Stefan flow inside the pores can reach values of more than 1 m/s, which can influence the species distribution inside the particle and the local species transport at the particle surface.

### A Reduced Order Model (ROM) of Entrained-Flow Gasifier Flyash and Slag Generation Rates

Ramalakshmi Krishnaswamy, John M. Kuhlman, West Virginia University, USA

Entrained-flow gasification shows significant promise as a component of an integrated gasification combined cycle (IGCC) power plant, where overall plant efficiency is increased significantly through use of two power generation paths: a conventional Rankine steam cycle, plus the syngas gas turbine cycle. However, the pilot IGCC facilities in the US have experienced significant development problems relating to relatively higher maintenance requirements and reduced plant availability, often due to fouling of downstream process equipment by flyash.

In the present work, two simplified Reduced Order Models (ROMs) of the partitioning of the solid material into the flyash or the slag have been developed for a slagging entrained-flow gasifier. The first model is an initial heuristic rules-based ROM, and the second is an improved higher-order ROM. The predictions of the production rates of flyash and slag by these two ROMs have been compared. Generally, similar trends are predicted by the two ROMs versus particle residence time. However, the second ROM

uses gasifier operating conditions (pressure and temperature time history) as inputs that directly influence the char gasification rates and iron minerals kinetics, making this ROM easier to use, and potentially more directly useful.

Three physical models were added in the second ROM: (1) a flowing slag film model<sup>1</sup> which is used to compute the slag particle residence time, and then used to compute the sulfides conversion, (2) a simplified  $FeS \rightarrow FeO$  minerals chemical kinetics model<sup>2</sup>, and (3) a Langmuir-Hinshelwood char gasification kinetics model<sup>3,4</sup> that includes an effectiveness factor<sup>5</sup> to account for pore diffusion and mass diffusion. These three physical models have been coupled with the simple minerals partitioning model from the original ROM spreadsheet. In this solids partitioning model, the probability that a particular ash particle reports to the slag or exits the gasifier as flyash is based on whether or not that particle size-density fraction has final weight percentages of unconverted carbon and sulfides that are below assumed transition values. That is, for assumed carbon and sulfides transition values of ( $C_{trans}$ ,  $S_{trans}$ ), respectively, if  $C_{end} < C_{trans}$  and  $S_{end} < S_{trans}$ , then the particle size-density cut reports to the slag. Otherwise the particles report to the flyash. This same decision process is used in both ROMs.

As an example of the predictions from the second ROM, the effect of a 200K reduction in gasifier operating temperature at a constant operating pressure of 26.9 atm has been studied. For this magnitude of temperature reduction, the wt% of total solids reporting to the slag is reduced by 9%, while the wt% of total sulfides remaining in the slag is predicted to increase by a factor of 2.5. The wt% of combustibles reporting to the slag is predicted to be very small for both operating temperature profiles. In the flyash, the same operating temperature reduction is predicted to increase the flyash generation rate by 20%, while the mass of unconverted carbon leaving the gasifier in the flyash is predicted to increase by 36%.

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### Modeling High Viscosity Slag Flow in Coal Gasifiers Using a Volume of Fluid Approach

Konrad Uebel, TU Bergakademie Freiberg, GERMANY

The flow behavior of molten slag in entrained flow gasifiers has a major impact on the stability of operation and thus on availability and reliability. The ash content of coal feedstock forms a homogeneous solid/liquid slag layer on the cooled gasifier refractory lining and other cooled areas during gasification process. In constricted areas with smaller vessel diameter, such as in the transition piece between gasifier and heat recovery or cooling devices, slag can cause plugging of the system when gasifier outlet temperature falls below ash melting temperature or viscosity of the slag increases above 25 Pas for a longer time period.

Today, in industrial scale gasifiers it is nearly impossible to measure or monitor slag flow in detail and for every location. Therefore, providing a detailed and accurate numerical model to describe slag flow behavior is of great interest and importance.

First of all the flow of the molten high viscous slag needs to be described accurately. Second, the melting and solidification process has to be considered in order to predict the slag layer thickness in entrained flow gasifier or downstream units and possible plugging. Therefore, temperature dependent slag properties like viscosity, thermal conductivity, specific heat or surface tension and other material properties have to be determined in experiments and included into the model.

In this work, a numerical model to predict slag flow and melting/solidification behavior using a Volume of Fluid (VOF) approach with open-source software OpenFOAM is presented and compared to experimental data.

First, the accuracy of the modeled slag flow is investigated using a small-scale experiment. Silicone based viscosimetry fluids for calibration purposes with different normed viscosities are used to show the ability of the model to predict viscous behavior in a range up to 30 Pas. Here, the fluid flow down a 45-degree ramp through a defined opening out of an open supply tank is investigated. The flow behavior is documented and analyzed with a video system and compared to numerical model. Various parameter studies are carried out to analyze the impact of mentioned material properties to shape, flow velocity and time.

Second, a fixed-grid method solidification model was implemented. It was validated against an experiment of melting gallium from literature. The volume fraction of liquid in slag is determined using the melting temperature. In solidified areas a damping source term added to the momentum equation is used to freeze the velocity field. The enthalpy of fusion is represented in the temperature equation using the latent heat of fusion for the material. To be able to resolve the interface between gas and slag an

adaptive mesh method is implemented and can be used if grid resolution is not sufficient.

The functionality of the model and results of slag flow are shown. Both investigations show a good agreement between the numerical model and experiment.

### Direct Numerical Simulation of Reacting Char Particles in Turbulent Environments

Andreas Richter, Michele Vascellari, Stefan Buhl, Christian Hasse, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

In this work, the interaction of chemically-reacting pulverized coal particles and the turbulent gas flow around the particles is numerically studied. The processes inside pulverized-coal reactors feature a distinct multi-scale behaviour, which necessitates the usage of so-called sub-models, which describe the interaction between solid particles and gas phase. Hence, the quality of numerical simulations depends directly on the accuracy of the underlying sub-models. In these models, the heat and mass transfer is modeled based on Nusselt number and Sherwood number correlations for spherical or non-spherical particles. The relations typically implemented are developed under the assumption, that non-reacting particles moves at a constant velocity in a quiescent fluid. Effects of a non-quiescent gas flow around the particle are in general neglected in such models.

In the present work a chemically-reacting pulverized coal particle, which is embedded in a turbulent flow field, is considered. For this different calculations are performed using different positions inside an experimental-scale entrained flow gasifier. The positions correspond to the oxidation zone close to the coal injection, and to characteristic positions within the gasification region. An evaluation of these data revealed that for the BYU reactor the Kolmogorov length scales are larger than the particle diameters. In order to study the interaction between coal particles and such large-scale turbulent structures in detail, direct numerical simulations of the chemically reacting gas flow around the coal particle were performed. For this, the domain around an isolated particle was discretized. An isentropic turbulent field was generated based on the turbulent kinetic energy and the dissipation rate resulting from the reactor simulations, and was used as inflow boundary conditions for the single-particle calculations. The coal particle was assumed to be spherical and non-porous and consists of carbon only. On the particle surface, heterogeneous reaction such as the carbon oxidation reaction, the Boudouard reaction and the gasification reaction were present, whereas the homogeneous reactions around the particle are modeled base on a reduced GRI mechanism. This mechanism consists of 24 gaseous species and involves 104 homogeneous reactions. Since all turbulent length scales are resolved directly (DNS), no turbulence model was applied.

In this paper, we discuss the impact of large-scale turbulent structures on global reaction characteristics such as the overall carbon consumption rate and the averaged particle temperature. If necessary, correction terms for the Nusselt and Sherwood are proposed, which can be used to increase the quality of sub-models used for reacting particles.

### Simulation of Coal Gasification in Fluidized Bed Coal Gasifier

Fengli Zhang, Wenying Li, Xuecheng Ho, Jie Feng, Taiyuan University of Technology, CHINA

In the work, we develop the model of a fluidized bed coal gasifier by using CHEMKIN 4.1 software. In the simulation, which considers mass/energy balance, hydrodynamic and reaction kinetics, the fluidized bed was divided into distinct sections: a dense region at the bottom of the bed which is replaced by a PSR in the simulation, and a dilute region at the top replaced by a PFR where most homogeneous reactions occur in gas phase. The results of the simulation have been found to be in good agreement with the experimental data in the literature, which verified the validity of the model.

#### SESSION 34

#### Combustion: Power Plant Support Studies

#### Supercritical Carbon Dioxide (CO<sub>2</sub>) Indirect Power Cycles Incorporating Fossil-Fuel Heat Sources

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The U.S. Department of Energy (DOE) provides a worldwide leadership role in the development of advanced fossil fuel-based energy conversion technologies, with a focus on electric power generation with carbon capture and storage (CCS). As part of DOE's Office of Fossil Energy, the National Energy Technology Laboratory (NETL) implements research, development and demonstration (RD&D) programs that address the challenges of reducing greenhouse gas emissions. To meet this challenge, FE/NETL is interested in evaluating advanced power cycles that will maximize system



efficiency and performance, while minimizing carbon dioxide (CO<sub>2</sub>) emissions and the costs of CCS.

Supercritical CO<sub>2</sub> (SCO<sub>2</sub>) Brayton power cycles have the potential to increase system efficiencies due to use of recuperators that reduce cycle heat rejection and operation near the CO<sub>2</sub> critical point which reduces the recompression load. These cycles can be used as topping or bottoming cycles in various fossil-fuel electric power generation plants. Cases presented are formulated based on coal combustion processes that can be employed as heat sources for the SCO<sub>2</sub> cycle. The analysis estimates the thermodynamic and economic performance of the integrated system. The approach is first to evaluate the cycle potential on its own merits, second to compare it to conventional and advanced steam cycles to determine if the SCO<sub>2</sub> cycle has potential to be a superior cycle, and third to identify technology gaps for promising SCO<sub>2</sub> cycles.

The indirect SCO<sub>2</sub> configurations considered are based on recompression cycles which are the type most commonly proposed by industry and research organizations. Such configurations are estimated to have power cycle efficiency greater than 50% for turbine inlet temperatures above 700°C. An analysis objective is to understand the rationale behind this choice and to explore variations that include reheat, intercooling, and parametric changes. Additionally, possible integrations between the coal combustion and CO<sub>2</sub> capture processes and the SCO<sub>2</sub> power island sections are considered for performance improvement.

#### **Elemental Mercury Absorption in Systems Employing Oxidized Mercury Absorbents**

Nicholas R. Denny, Bruce Keiser, Wayne Carlson, Nalco Company, USA

Recently there has been some debate on the cause of elemental stack mercury emissions in plants equipped with wet flue gas desulfurization (WFGD) scrubbers. It has been reported that elemental mercury has been observed to be absorbed across a WFGD scrubber even though theory would suggest extremely limited solubility or absorption. This is Part 1 of a study to determine the effectiveness of various components in a WFGD system to absorb elemental mercury and limit mercury re-emission. Many papers have been written on the effect of chemical reduction of oxidized mercury to volatile elemental mercury as a cause. This phenomenon has been termed mercury re-emission and it has been widely demonstrated in commercial applications. A recent hypothesis suggests that high stack flue gas elemental mercury concentrations imply a lack of absorption of elemental mercury by the WFGD liquor. Rather, saturation of scrubber liquor with elemental mercury is the reason for stack emissions. Further it has been proposed that removing the elemental mercury from solution will minimize elemental mercury in the stack. This paper will discuss this elemental mercury saturation hypothesis and mercury re-emission based on recent experimental studies.

#### **Ash Removal Characteristics Evaluated by Fouling Tests Using 1.5MW<sub>TH</sub> Pilot Plant**

Miki Shimogori, Takahiro Marumoto, Mitsubishi Hitachi Power Systems, JAPAN

The goal of this study is to propose a method to determine optimum soot-blowing operation to operate coal-fired boilers without problems due to ash fouling in bank areas. For this purpose, ash removal characteristics have been evaluated by a series of fouling and soot-blowing tests conducted at a 1.5MW<sub>th</sub> pilot plant. The pilot plant was equipped with a test section simulating a tube bank with a soot-blower nozzle. In this study, the effects of tube bundle types (bare tube, rectangular finned tube, longitudinal finned tube) and coal types (PRB coal, high sodium and high sulfur coals) on ash removability have been investigated.

#### **Research on Charging and Removal of PM<sub>2.5</sub> in Both DC and Pulsed Electric Field**

Jian-ping Jiang, Zhong-yang Luo, Dong Zhou, Hao Chen, Dong-hui Sha, Meng-xiang Fang, Ke-fa Cen, State Key Laboratory of Clean Energy Utilization (Zhejiang University), CHINA

The particulate matter whose aerodynamic diameter is less than 2.5 μm (PM<sub>2.5</sub>) from flue gas of the power plant has already become a major type of air pollutions in China recently. ESPs are one of the most common particle control devices at power plants, but the particle collection efficiency in terms of number concentration for PM<sub>2.5</sub> is low mostly due to insufficient particle charging. Pulsed corona discharge has been considered to be an efficient technology for the large numbers of high energy electrons and other active species generated in the pulsed electric field.

In this dissertation, the removal of PM<sub>2.5</sub> using pulsed corona discharge and DC corona discharge has been investigated both theoretically and experimentally. In the theoretical study, the charging characteristic of fine particulate in both DC and pulsed electric field is investigated using the unipolar charging models. Both field charging and diffusion charging are calculated in different electric fields. In the experimental study, both the charging characteristic and removal efficiency of PM<sub>2.5</sub> has been studied in negative DC electric field, positive DC electric field and pulsed electric field

using the electrical low-pressure impactor (ELPI) in a laboratory-scale reactor with wire-plate electrode configuration.

The results showed that the particles are positively charged in positive DC electric field, while negatively charged in negative DC electric field. In pulsed electric field, particles with the diameters smaller than 0.2 μm are positively charged, while the larger ones are negatively charged. Furthermore, the amount of charges is much more captured by large particles than smaller ones. Experimental results show that particle removal efficiency in negative DC electric field is much larger than that in positive DC electric field. Particle removal efficiency has a very significant improvement using pulsed corona discharge combined with DC corona discharge than DC corona discharge.

### **SESSION 35 Gasification: Low Rank Coal**

#### **I-MILENA Gasification Technology for (High Ash) Low Rank Coal**

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The use of domestic (high-ash) low rank (sub-bituminous and lignite) coal reserves contributes to the security of energy supply, and therefore high-ash coal is expected to remain as a key energy source in several countries (e.g. India, Turkey, Greece) for at least the next 30-40 years. However, the use of high-ash coals for energy production, currently performed mainly via combustion processes, poses a number of technical and economic challenges, e.g. low efficiency and environmental issues. Gasification is an attractive option, since it allows a more efficient, more environmentally friendly conversion of the coal. In particular, gasification for power production (IGCC) or synthesis of Substitute Natural Gas (SNG) offers high efficiency, reduced emissions and potential for the implementation of CO<sub>2</sub> capture. With this background, the OPTIMASH project aims at the optimization of the operating conditions of IGCC technology based on high-ash coals.

The Energy research Centre of the Netherlands (ECN) has modified its biomass gasification set-up to make it suitable for high to very high-ash (> 35% wt.) coal and other low rank coal. The modified gasifier is called the i-MILENA. The i-MILENA is an indirect gasifier where gasification of the solid fuel is separated from the combustion of the remaining char and tar. The i-MILENA gasification technology has a high cold gas efficiency and high methane yield, making it very suitable for application in combination with gas engines, gas turbines and the production of Substitute Natural Gas (SNG).

In this work, the status of the development of the i-MILENA technology is presented. Gasification tests using Indian high-ash sub-bituminous coal and German lignite as feedstock have been carried out in the 25-kW i-MILENA gasifier coupled to the OLGA tar removal system in order to assess the overall performance of the process. Two methods for sulfur removal have been implemented: in-bed sulfur capture using a commercial calcium-based additive, and downstream low-temperature sulfur capture using an iron oxide sorbent. Results of the tests have proven that high-ash coals can be gasified in the i-MILENA gasifier with an overall complete conversion (white-grey fly- and bottom ash), thus making ash disposal easier. The gas contains some tars which are removed by the OLGA tar removal technology that was developed by ECN. The OLGA system is able to remove tars according to expectations. Moreover, the addition of calcium-based sorbents during i-MILENA gasification has shown that sulfur capture is possible. Under conditions tested, emission of gaseous sulfur compounds was reduced by 46-55% by using an in-bed calcium sorbent. The i-MILENA technology is relatively simple due to the atmospheric operation of the gasifiers, the production of a N<sub>2</sub>-free syngas without the need for an air separation unit, and the carbon-free residue that is produced. Steam consumption is relatively low, because the required conversion in the gasifier is relatively low. The disadvantage of the atmospheric operation of the gasifier is the need for gas compression, but because of the high heating value of the gas the compression energy is much lower than would be required for a syngas containing no hydrocarbons. The lack of competing proven technology, especially in the medium scale range (1 - 500 MWh), offers a good opportunity for the further development and demonstration of the technology for (high ash, >35 wt% ash) low rank coal.

#### **Hydrolysis of Tar-Rich Brown Coal Using a Pressurized Drop Tube Reactor**

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

Novel and innovative technical routes have to be investigated owing to the worldwide raising demand for chemical feedstock or fuel from the crude oil processing to guarantee the security of energy supply in the 21st century. In this context coal has been denoted as one of the most important energy and carbon carrier. Due to its extensive consumption in the last decades, a tendency towards an increasing demand for the additional utilization of low grade resources like ash-rich or low-rank coals has been recognized. The hydrogenation of coal in direct or indirect way has been noticed

as an opportunity to use coal as a chemical feedstock supplier, which has provided a replacement of crude oil or natural gas. Three main pathways, which have been characterized as more or less wellknown, have been found present to produce chemical material or transportation fuel. The first and oldest one is coal hydrogenation in sump phase reactor by means of a catalytic reaction. A second one is coal gasification with subsequent Fischer-Tropsch synthesis.

Whereas, the third process route is the hydrolysis of coal, which is the core of the present study. Based on this background, hydrolysis investigations in a pressurized drop tube reactor using a pulverized tar-rich brown coal from Central Germany expecting high yields of liquid product have been carried out. In this procedure high heating rates have been realized, which might possess relevance for fluidized bed or entrained flow processes. The equipment has enabled the sampling and analysis of all products and as a result of this the mass balances for the pyrolysis product distribution as well as product composition could be compiled.

The effects of volatile residence time for different temperatures from 400 to 800 °C at 25 bar and 60 bar gauge pressure have been carried out in the present study. Moreover, the pyrolysis product yields (char, gas, tar/oil, and reaction water) and gas composition as well as the char and tar/oil properties have been determined for the treatment under elevated total and hydrogen partial pressures, which have been supplied by a hydrogen/argon atmosphere with a H<sub>2</sub> content range from 0 to 100 vol.%. An extensive characterization of the produced chars has comprised conventional ultimate and proximate analysis, HHV determination, XRF analysis of inorganic matter, BET surface area, true and apparent density, particle size distribution, and SEM micrographs. For the tar/oil fraction a comprehensive gas chromatography has been combined with mass spectrometry (GCxGC-MS) as well as ultimate and proximate analysis besides HHV determination. The gas composition has been instantly recorded by an online mass spectrometer.

The obtained results have improved the understanding of brown coal hydrolysis as a function of the parameters temperature, volatile residence time, and total as well as hydrogen partial pressure. In addition, the results have provided a fundamental basis for prediction of quantity and quality of liquid product just as well for the modeling of pyrolysis or gasification processes using process simulation or fluid dynamics software. The achieved information might contribute to a future utilization of (low-rank) brown coal in gasification or pyrolysis plants to produce chemical products, which will be prospectively required due to the raising demand.

#### Simulation of Ash Deposition Behavior in an Entrained Flow Coal Gasifier

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Fly ash deposition is an important phenomenon associated with ash/slag handling and discharge in the entrained-flow coal gasification process. Fouling and slagging inside the gasifier may cause reliability and safety problems because they can impose strong negative effects on the gasifier wall in the way of heat transfer and chemical corrosion. For these reasons, this chapter focuses on investigating the ash deposition mechanism inside of a two-stage entrained-flow gasifier. The computational model is developed in order to simulate the gasification process with a special effort spent on modeling ash formation, fly ash, and ash deposition. The Eulerian-Lagrangian approach is applied to solve the reactive thermal-flow field and particle trajectories with heterogeneous reactions. The governing equations include the Navier-Stokes equations, twelve species transport equations, and ten global chemical reactions consisting of three heterogeneous reactions and seven homogeneous reactions. The coal/ash particles are tracked with the Lagrangian method. The effects of different coal/ash injection schemes and different coal types on ash deposition have been investigated. The results show that the two-stage fuel feeding scheme could distribute the ash throughout a larger gasifier's volume and, hence, could reduce the peak ash deposition rate and make the ash distribution more uniform inside the gasifier. Gasification of a coal with high ash content results in a high ash deposition rate, low syngas higher heating value (HHV), and low carbon conversion rate. Almost 48% of the un-reacted char will deposit on the wall before it completely gasifies. A char recycling scheme is needed to increase the carbon conversion rate if a high-ash coal is used for gasification.

#### SESSION 36 Coal Science: General - 6

#### Review of Recent Industrial Applications of Fly Ash Geopolymer Concrete

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Geopolymer concrete has been receiving increasing acknowledgement as a viable and effective solution for some of the construction industry's greatest problems, such as durability in corrosive and high temperature environments and ecological benefits.

This paper presents an overview of the recent progress made in the field demonstration of geopolymer technology in various case scenarios in the United States and abroad, as well as the opportunities of utilization and the challenges to overcome for the future.

Recent EPA issued evaluations and historical cases of the use of alkali activation technology will be discussed as well.

#### The Reduction of Swelling of Large Coal Particles through Impregnation with K<sub>2</sub>CO<sub>3</sub>

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The understanding of coal's thermoplastic properties, and the ability to predict the plastic behaviour of coal, is important for numerous coal conversion technologies. Both coal swelling and agglomeration are undesired phenomena, which have a negative effect on process efficiency specifically in the case of fixed bed and fluidised bed gasification technologies. In addition to influencing process efficiency, excessive swelling of coal particles may lead to various operational problems, such as build-up of oven wall pressure. Various pre-treatment methods, such as pre-oxidation and slow heating rates, have been found to modify the swelling and caking properties of coal. In addition to these pre-treatment methods, the use of additives like alkali and alkaline earth metal salts have been investigated extensively in order to determine the influence of these additives on the caking and swelling of coal.

Thus far, the reduction of coal swelling through additive addition has mainly focused on small particles and powders (< 500 µm). The aim of this paper is to investigate the influence of K<sub>2</sub>CO<sub>3</sub> on the swelling propensity of large coal particles (20 mm) from three South African coals. The three coals selected were two medium rank-C bituminous coals (TWD and GG), and a medium rank-B bituminous coal (TSH).

Mercury submersion was used to determine the volume of single 20 mm coal particles, before and after devolatilisation, in order to determine the volume swelling ratio of each particle. The K<sub>2</sub>CO<sub>3</sub> was added by means of solution impregnation; coal particles were submerged in a 5 M K<sub>2</sub>CO<sub>3</sub> solution for 24 hours. Single coal particles (raw and impregnated) were devolatilised in a Carbolite AFT furnace, at a rate of 7 °C/min and a nitrogen flow rate of 6 NL/min. The devolatilisation temperature for each coal was selected based on the average maximum swelling temperature of 20 mm coal particles, as previously determined. The devolatilisation temperatures used were: 445 °C for TWD coal, 422 °C for GG coal, and 419 °C for TSH coal.

The volume swelling ratios (SR<sub>v</sub>), which were defined as the ratio of the particle volume after devolatilisation to the particle volume before devolatilisation, were determined for the raw and impregnated coal particles. It was found that impregnation with K<sub>2</sub>CO<sub>3</sub> reduced the average SR<sub>v</sub> (determined for five 20 mm particles) of GG and TSH coals from 3.0 and 5.7 to 1.8 and 2.5, respectively. Thus, the addition of K<sub>2</sub>CO<sub>3</sub> through solution impregnation reduced the average SR<sub>v</sub> for GG and TSH by 40 % and 56 %, respectively. Results also showed that the average SR<sub>v</sub> for the TWD coal remained unchanged after devolatilisation, even with the addition of K<sub>2</sub>CO<sub>3</sub>. This can be attributed to the fact that the change in volume of the TWD coal particles were possibly due to fragmentation, and not the swelling phenomenon as observed for GG and TSH coal.

#### Analysis of Hydrophobicity of Carbonaceous Solids and Their Effect on the Slurry Rheology

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Carbonaceous solid-water slurry rheology is greatly affected by the surface properties of the solids used, especially the degree of hydrophobicity. In order to understand the effect of hydrophobicity on viscosity of carbonaceous solid-water slurries, highly hydrophobic carbonaceous solids such as pet-coke and bitumen water suspensions were studied. The results for these highly hydrophobic slurries were compared with a hydrophobic anthracite-water slurry and a non-hydrophobic Illinois#6 coal-water slurry. Yield stress values of petcoke, bitumen, anthracite and Illinois#6 water slurries were compared for different size ranges. Higher yield stress values signify greater aggregation of solids in the suspension. It was found that for any particular size-range, petcoke and bitumen slurries had yield stress values higher than anthracite slurries and much higher than Illinois#6 coal-water slurry. For petcoke and bitumen-water slurries, it was observed that -20 micron size particles were highly hydrophobic and hydrophobicity decreased with increase in particle size. Yield stress value for -20 micron sized particles was 90 Pa whereas for slightly higher size range (+53 microns to -75 microns) the yield stress value was 30 Pa. Anthracite and Illinois#6 coal-water slurries were found to have the same yield stress values for all size ranges signifying the same degree of hydrophobicity. Degree of hydrophobicity of each sample was further confirmed by contact angle measurements. Hydrophobic force was calculated for each sample based on the contact angle measurements and correlated with the yield stress values.

Since the existing semi-empirical models do not take into account the aggregation behavior of such complex carbonaceous solids water suspensions, viscosity predictions for such complex slurries by these models are highly inaccurate. In this work a degree of aggregation was calculated based on the yield stress values which when incorporated into Simha's viscosity model, predicted the viscosity of such aggregating suspensions accurately.

## Fly Ash Geopolymer Concrete Mix Design Software

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Geopolymer concrete is one of the most promising alternatives for fly ash utilization, since it provides an opportunity to use fly ash sources that do not have the characteristics required to be used as addition for Portland cement (OPC) concrete.

However, the creation of geopolymer concrete volumetric mix designs based solely on guidelines such as ACI 211.1 is a complex process with often unpredictable results. The Geopolymer Mix Design Software accounts for the contribution to compressive strength and slump associated with geopolymer design parameters like activator solution concentration, fly ash composition, curing conditions, and others.

Among the capabilities of the software is the ability to provide recommendations of use for a particular fly ash source, considering restraints such as project location and final concrete properties such as high corrosion or thermal resistance. The software utilized a growing database of nearly seventy fly ash stockpiles from across the world.

## Mercury Contents in Various Low-Sulfur Bituminous Coals from Different Countries: Relationship to Coal Properties

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One hundred and two kinds of coals from different countries were analyzed for Hg by an automatic mercury analyzer (AMA) based on an official method (heat vaporization atomic absorption spectrometry); the majority of those coals were bituminous coals with relatively low-sulfur content. Those coals are supplied in a powdery form as standard samples by a Japanese organization and called "SS-coals". Since the sample amount of coal used in the AMA measurement is usually small, the particle size of coal may greatly affect the measurement; however there have been no systematic studies on the matter. Some of the SS-coals showed a great deviation in data (relative standard deviation (RSD) is high) in the determination of Hg. For the determination of other trace elements, those coals did not show such a deviation in data. The unique character of Hg observed in the determination was discussed with the possibility of localization of Hg in coal body at a microscopic level. The content of Hg in coal (bituminous coals) somewhat correlated with that of ash (or Al) rather than that of sulfur. Also, it was found that the coals of low ash contents and those of high inherent moisture tended to have low Hg contents.

### SESSION 37

#### Carbon Management: Capture of Carbon Dioxide - 2

### Hydrophobic Solvents for Precombustion CO<sub>2</sub> Capture: Experiments and Systems Analysis

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PDMS (Polydimethylsiloxane) is an inorganic, hydrophobic polymer with the general chemical formula  $\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$ . PDMS can selectively separate CO<sub>2</sub> over H<sub>2</sub>. However, its CO<sub>2</sub> solubility and selectivity is lower than the physical solvent analyzed in the Bituminous Baseline Studies by NETL, Selexol® (UOP LLC). Selexol is a polyethylene glycol, di-methyl ether (PEGDME.) It has high CO<sub>2</sub> and H<sub>2</sub>S solubility and selectively over H<sub>2</sub> in syngas streams; however, this solvent is completely water miscible, which requires that the syngas to be cooled from 200°C down to temperatures of 40°C or below in order to condense out the water before the CO<sub>2</sub> absorber. The syngas then needs to be re-heated to approximately 200°C before it can be expanded and sent to the hydrogen fueled gas turbine at an IGCC-CCS power plant. In order to reduce the cooling and re-heating demand, NETL/ORD is synthesizing novel hybrid materials that combine the relatively high CO<sub>2</sub> solubility of PEGDME with the hydrophobic nature of PDMS. In addition, a high molecular weight solvent, such as PDMS-PEGDME, has a low vapor pressure, which results in low solvent slip at elevated temperatures. Here, we present experimental results from a pressurized, continuously stirred reactor in which we measure the CO<sub>2</sub> and H<sub>2</sub> solubility as a function of pressure and temperature, and we compare this solubility data with solubility data of both PEGDME and PDMS separately. We also present our experimental results on the viscosity, heat capacity, density, and surface tension of the PDMS-PEGDME solvent, and compare with data collected using PEGDME or PDMS. We used the experimental data to model the PDMS-PEGDME hybrid solvent using the PC-SAFT method in AspenPlus, and we built a thermodynamic and economic model in AspenPlus to compare the leveled cost of capture CO<sub>2</sub> from an IGCC power plant using either PEGDME or PDMS-PEGDME. We will present a comparison between the solvents on both the operating and the capital costs at an IGCC-CCS power plant.

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### Analysis of CO<sub>2</sub> Market Possibilities for Power Plants with Carbon Capture Using CTUS-NEMS

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The United States Department of Energy (DOE) Office of Fossil Energy (FE), in conjunction with its National Energy Technology Laboratory (NETL), conducts research, development and demonstration (RD&D) of advanced fossil-based energy conversion technologies, with a focus on electric power generation with carbon capture and storage (CCS).

The Capture Transport Utilization and Storage (CTUS)-National Energy Modeling System (NEMS) was developed by NETL in an effort to quantify the economic and environmental benefits of its RD&D activities in the areas of carbon capture, utilization, and storage. The model is an enhancement to the Energy Information Administration's (EIA) National Energy Modeling System (NEMS), which is used in the preparation of the Annual Energy Outlook (AEO), via integration of the CTUS sub-module into the NEMS model. The enhancement adds the capability to represent physical and economic interactions in a CO<sub>2</sub> market, composed of a network of sources, transport links, and storage reservoirs. The sources consist of representations of power plants with carbon capture technology (new and retrofits), industrial sites capable of capturing CO<sub>2</sub>, and natural CO<sub>2</sub> reservoirs. Each of the nodes in the CO<sub>2</sub> market network is given the ability to respond to external forces, such as demand for CO<sub>2</sub> from an enhanced oil recovery (EOR) market, as well as carbon policies. The transportation network is composed of dedicated and trans-shipment pipelines, which can deliver CO<sub>2</sub> from an individual (or combination of) source(s) to multiple storage reservoirs, while minimizing transportation system costs. Finally, the available storage reservoirs are a representation of both saline sequestration and EOR sites. The model was successfully integrated into EIA's NEMS system, and it is now part of the code used to generate the AEO 2014.

The modeling enhancements work by tapping into the information streams passed between NEMS modules during execution. By tapping into the NEMS information streams new cost data is introduced for consideration by the model. The cost of carbon retrofits is based on the FE/NETL Carbon Capture Retrofit Database (CCRD); this cost is modified by the use of multipliers to model a wide array of future technology improvements. The cost of saline storage is based on the FE/NETL CO<sub>2</sub> Saline Storage Cost model.

The integration of the CTUS model into NEMS permits a user to not only obtain direct results from the deployment of CO<sub>2</sub> related infrastructure, but also the indirect impact of the deployment of such technology on the U.S. energy markets. For selected scenarios, results show that there is an increase in the construction of new coal power plants with carbon capture equipment which take advantage of the opportunity offered by the availability of a market for the sale of the generated CO<sub>2</sub>. Also, there is a corresponding increase in the production of oil from enhanced oil recovery sites. For instance, when a CO<sub>2</sub> tax policy is implemented, the model shows a substantial increase in the production of oil from EOR sites due to the widespread availability of CO<sub>2</sub> from new and retrofitted coal and natural gas power plants. Goals from NETL's Research and Development program were also modeled under different policy scenarios. These goals demonstrate the potential reduction in plant costs with a resulting increase in new plant deployments, retrofits, and oil production.

The CTUS-NEMS model provides a new tool to identify economic opportunities for the advancement of CO<sub>2</sub> management in the power and industrial sectors. This model provides a comprehensive view to the possible future energy and carbon markets that will develop around the capture, transport, storage, and utilization of CO<sub>2</sub>.

### Capture of Carbon Dioxide with Magnesium by Reactive Milling

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Capture of carbon dioxide by magnesium by reactive ball-milling is in the present investigation. XRD patterns analysis indicates that 0.1 MPa CO<sub>2</sub> cannot react with Mg without carbon as milling aid, but it can be done on the surface of small particles to yield MgO and crystalline carbon of graphite structure by ball milling over 1.5 h with carbon from anthracite coal carbonization as grinding aid. With the progress of reaction, MgO layer on the surface of Mg particle hinders the reaction of CO<sub>2</sub> with the Mg in the particle core. The anthracite coal stripping away the MgO layer by milling, exposes the virgin Mg surfaces to CO<sub>2</sub>, decreases the particle size and speeds up the rate of the overall metal-oxide transformation.

**SESSION 38**  
**Shale and Coal Bed Gas: General - 1**

**The Study on Reservoir Properties and Geological Factors of Deep Coalbed Methane**

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This article comes from "development technology and equipment research for deep coalbed methane" which is a National Science and Technology Major Project of China. Chinese deep coalbed methane resource is very abundant, coalbed methane resource of 1000 ~ 2000m deep accounts for 61% of the total amount. Deep coalbed has special geological conditions and reservoir properties, such as high temperature, high crustal stress and low permeability, that means development techniques suitable for shallow coalbed methane cannot be directly applied to deep coalbed methane, so the research of deep coalbed methane is necessary. We investigated major deep coalbed methane zones at home and abroad, and took Shizhuang North block in Qinshui Basin of China as the main study area. We carried out comparative studies of reservoir properties and geological conditions between deep and shallow coal seam, a conclusion was drawn that deep coal seam reservoir properties and geological conditions have a step -type or logarithmic variation with increasing depth. A critical depth BP neural network model for deep coal seam was established, can determine critical depth with mechanical parameter, reservoir parameter and production parameter. We carried out research about geological factors influencing deep coalbed methane reservoir properties; Crustal stress is one of the main factors affecting the output of deep coalbed methane well. Based on the three-dimensional geological model for coal seam of Shizhuang North block, we drew the stress pattern by simulating the paleostress field and present stress field. We obtained the overall distribution of the stress of Shizhuang North block. Crack, porosity, permeability quantitative prediction method is established which is of great importance to find high permeability deep seam zone, and to achieve a breakthrough of deep coalbed methane well.

**Use of Abandoned Mine Drainage in Flowback Water Reuse for Hydraulic Fracturing**

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Flowback water generated during shale gas extraction is of great concern due to its high total dissolved solids (TDS), naturally occurring radioactive materials (NORM) and organic matter. Acid mine drainage (AMD) is a water source that is often located in the vicinity of gas wells and can be mixed with flowback water to reduce the fresh water use for hydraulic fracturing and truck traffic associated with water transportation to the site. Co-treatment of AMD water and flowback water provides an opportunity to manage these wastewaters and relieve the pressure on fresh water resources. AMD water typically contains several hundreds to several thousands mg/L of sulfate ( $\text{SO}_4^{2-}$ ) while flowback water has high levels of dissolved barium. Once AMD and flowback are mixed, barium sulfate (barite) will precipitate, which necessitates removal of suspended solids prior to use of this water for hydraulic fracturing. Membrane filtration and coagulation/flocculation are two potential alternatives to fulfill this treatment objective.

The use of AMD would alleviate demand for fresh water by the gas industry, reduce environmental impact of AMD, reduce the cost of water transportation for hydraulic fracturing, reduce the greenhouse gas emissions by the gas industry and reduce the cost of wastewater treatment prior to reuse for hydraulic fracturing. However, this approach has never before been tried by the unconventional gas industry and barriers to implementation range from technical issues to regulatory concerns. Technical issues include compatibility with fracturing chemicals, potential for excessive scaling and biological growth in the well, and management of solid waste that would be generated by mixing these water sources. Regulatory issues include liability for perpetual AMD treatment that is implied by current regulations. These issues will be discussed together with potential solutions based on original studies and review of the literature.

**Comparison of Environmental Impacts of Coal Bed Methane and Shale Gas Energy Extraction Operations**

Stephen C. Smith, Steptoe & Johnson PLLC, USA

Coal bed methane operations and hydraulic fracturing of shale gas both produce natural gas from the extraction of subsurface energy resources. Both operations generate air, water and solid waste emissions and are subject to numerous environmental regulations due to the environmental impacts. This paper will explore the similarities and differences in the environmental impacts by evaluating various aspects of the operations such as the area impacted (including surface footprint, impoundments, haul roads, additional surface needed for gathering/distribution lines, subsurface impacts, temporal impacts); air emissions (including greenhouse gases); water issues (including recycling/reuse, water demands/water quality, treatment and disposal, naturally occurring radioactive materials); solid waste management;

operational issues (including onsite power, potential for spills, ignitions, explosions, noise, lights, neighbor relations); regulatory (including ownership interests/consents, permitting, zoning, bonding, reporting, reclamation) and the economics of coal bed methane versus hydraulic fracturing of shale gas.

**Gas Processing & Risk Mitigation for CBM & Shale Gas**

Joseph S. D'Amico, D'Amico Technologies Corp., USA

The Appalachian Basin has been a historic cost effective source of abundant energy for America for the past 150 years. It is rich with Carbon in all of its phases starting with solid coal, then natural gas, and within the last 5 yrs shale gas along with its rich natural gas liquids.

Gas quality of CBM is typically lower than 1,000 Btu due to the mixture of non-calorific gases such as carbon dioxide ( $\text{CO}_2$ ) and nitrogen ( $\text{N}_2$ ) etc. In recent years, with the advent of Shale Gas, we are faced with the opposite challenge of high BTU gas being much greater than 1,000 Btu (Typically > 1,100 Btu and approaching 1,300 Btu). In the past we developed unique gas separation technologies to reject the non-calorific gas from CBM in order to make pipeline quality natural gas. For today's Shale Gas, we are developing new gas separation technologies to reject and recover the heavy hydrocarbons (NGLs) for the purpose of selling the NGLs and selling pipeline quality natural gas (<1,100 Btu).

Rejecting and recovering Shale Gas NGLs using the physics of high pressures and cold temperatures is no guarantee that you will have pipeline quality natural gas to sell nor is there a guarantee that you will have Y-Grade NGLs to sell. Large cryogenic based natural gas processing plants can achieve both objectives including fractionation of the NGLs, but not without the benefit of size to achieve economic success. They are typically > 100 MMCFD and larger. What do all of the producers do that have CBM and/or Shale Gas at < 50 MMCFD and < 10 MMCFD? This paper will provide unique cost effective solutions for both CBM and Shale Gas at flow rates < 50 MMCFD.

The paper will also provide Risk Mitigation strategy and solutions when dealing with low Btu CBM and high Btu Shale Gas. Transmission Gas Pipelines and NGL liquid transporters (Both truck and rail) are wrestling with these issues now. Yes, we are all in the volatile natural gas business where close attention is paid to prevent fire and explosions and this paper will cover that. There is an additional and silent risk among us called "Corrosion". Once a rupture occurs in a pressurized pipe or vessel, then it and the exposure to risk is not so silent. This paper will address CBM and Shale Gas corrosion issues and will provide non-destructive forensic type of tests that can inexpensively be done in a pro-active manner to mitigate risk and maximize production.

Lastly, a brief review of what America should be doing with its new found wealth of natural gas, from a globally experienced scientist's point of view.

**SESSION 39**  
**Gasification: General - 2**

**Cadmium, Phosphorus and Antimony Adsorption on Copper-Palladium Alloy Films**

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The adsorption of phosphine, cadmium and antimony on copper-palladium alloy films at 288°C was studied by scanning electron microscopy with energy-dispersive X-ray methods (SEM-EDX) characterization. The composition spread alloy film (CSAF) coupons were exposed to cadmium, phosphine or antimony in nitrogen in a small flow reactor. Trends for cadmium, phosphorus and antimony uptake as a function of alloy composition are being determined. The results have potential consequences for the design of sorbents for the capture of phosphorus from fluid streams, and for the stability of palladium-copper alloy membranes employed for hydrogen separation from coal-derived syngas.

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## Characterization of Coal and Biomass Chars from High Temperature Pyrolysis in CO<sub>2</sub> Atmosphere

Aime Hilaire Tchapda, Sarma Pisupati, The Pennsylvania State University, USA

Understanding the initial stage of solid fuels conversion is essential to predicting their subsequent chemical and physical transformations; with relevance in the design, modeling and improvement of commercial and lab scale solid fuels thermochemical conversion systems. In this regard, Coal and biomass chars produced during pyrolysis in an entrained flow reactor in CO<sub>2</sub> atmosphere at 1300 °C, 1400 °C, and 1500 °C were characterized using various analytical techniques.

The conversion level of the two fuels in the entrained flow reactor is significantly different, varying from 50 to 64% for coal and 87 to 91% for biomass and increasing with the operating temperature. This level of conversion is directly related to the particle densities as coal chars display a vertical parabola trend, meaning that chemical and physical transformations are still taking place. Biomass chars on the other hand display an increasing linear trend which suggests that these chars are approaching their optimum structural changes. This hypothesis is confirmed by the BET surface area measurement, which indicated a very close value for all biomass chars. The BET surface area of coal chars increased slightly from 1300 °C to 1400 °C but dropped significantly at 1500 °C. A plausible justification of this observation is the coalescence of the pore structure, typical to entrained flow reactor chars. This hypothesis is substantiated by the SEM images of coal char showing visible structure collapse at 1500 °C.

Coal chars generated at 1400 °C and 1500 °C have comparable reactivity to CO<sub>2</sub> at 800 °C and 900 °C, significantly lower than the reactivity of coal char generated at 1300 °C. A similar trend is found with biomass chars suggesting that the deactivation of reactive sites for heterogeneous reactions is initiated after 1300 °C.

## Modeling and Experimental Investigation of Internally Circulating Gasifier for High Ash Coals

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The reduction of capital costs is the most important step towards general economic competitiveness of coal gasification technologies compared to alternatives such as conventional coal combustion or oil/natural gas based processes. Besides improving existing gasification technologies, the development of new gasifiers seems promising. Here, the focus is on both the reduction of investment and operation costs as well as suitability to low-quality coals (low grade, high ash).

The present work focuses on the experimental investigation and modeling of a novel Internal Circulating (INCI) gasifier invented by researchers at IEC, Technical University Bergakademie Freiberg, Germany [1]. This gasifier combines multiple flow regimes to provide high carbon conversion rates, high cold gas efficiency and syngas yields at comparatively low construction costs and operating costs, especially for the conversion of high-ash coals.

The system is characterized by a fast-fluidized bed with induced kidney shaped recirculation cells. These help to increase the particle residence time and protect the walls from high temperatures in the center of the gasifier. Oxygen is added as gasification agent leading to local temperatures above the ash fluid point. Resulting formation of ash agglomerates leads to an internal separation mechanism of fresh fine-grained feedstock and (partially) converted bigger agglomerates. Due to their size, agglomerates are no longer fluidized and fall downwards. In the lower section of the gasifier, the agglomerates form a moving bed. Secondary gasification agents are added from below the moving bed in order to post gasify the agglomerates. Thus complete carbon conversion can be achieved, whilst the outlet temperatures at the top are below ash fluid temperature.

A 15 kW lab scale unit was erected at the IEC to demonstrate the INCI gasification principle. The unit consists of a 6 m tall ceramic tube with an inner diameter of 0.15 m and electrically heated walls. First investigations were designated to a particle free, inert gas flow through the heated reactor tube. PIV and temperature measurements are compared to numerical simulations. The simulation shows a very good agreement with measured velocities and temperatures and allows for a more detailed analysis of the flow structure inside the gasifier. Thus, the effect of wall temperature or initial flow velocities on the size and shape of the induced recirculation cell can be investigated numerically.

Accordingly, reactive and particle laden two phase flows were investigated experimentally and in terms of numerical simulation. A coke obtained from German brown coal (hearth furnace coke, HOK) is gasified using oxygen as primary gasification agent and an oxygen-carbon-dioxide-mixture serves as secondary gasification agent. The experiment demonstrates the feasibility of the patented claims. Thus, the targeted outlet temperatures, formation of a recirculation cell and the post gasification of agglomerates in a moving bed are proven. Moreover, results from accompanying CFD simulation are in accordance with experimental results and allow for investigation of additional parameters that are not accessible through measurement techniques, such as radial velocity profiles, local particle distribution or size and shape of the recirculation cell.

References:

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## Poison Resistant Water-Gas-Shift Catalyst for Coal Biomass Gasification

Girish Srinivas, Steven C. Gebhard, Jeff Martin, Mike Looker, TDA Research Inc., USA

Co-feeding biomass with coal in a gasification-based synthetic fuels plant has the potential to reduce carbon dioxide emissions by 50% or more. Gasifying mixtures of coal and biomass to produce syngas is an excellent way to minimize the uncertainty associated with a biomass-only synfuels plant caused by interruptions in the biomass supply and to reduce CO<sub>2</sub> emissions. When biomass is plentiful, more is used, and when there are biomass shortages, more coal is used. By using agricultural waste, competition with arable land is eliminated. This feedstock flexibility ensures that a coal-biomass to liquids (CBTL) plant can operate continuously.

Catalytic processes are used to produce synthetic fuels from co-gasified coal-biomass, including adjustment of the H<sub>2</sub>/CO ratio using the water gas shift reaction. Because H<sub>2</sub>S is produced from sulfur in the coal, a sulfur-tolerant (sour) water gas shift (WGS) catalyst is used. Unfortunately, existing commercial, sour shift catalysts are poisoned by the contaminants in syngas that is unique to gasifying coal-biomass mixtures. Thus, developing a poison-resistant sour shift catalyst will advance coal-biomass-to-liquids (CBTL) technology as well as carbon-free integrated gasification combined cycle (CF-IGCC) power generation.

TDA Research Inc. (TDA) has developed a sour water gas shift catalyst that resists poisoning by contaminants found in syngas produced when mixtures of coal and biomass are gasified. Our catalyst has been tested in a laboratory scale fixed bed microreactor where we conducted poisoning studies using KCl, NH<sub>3</sub>, As, Hg, Fe, Ni, P and SiO<sub>2</sub>. We measured catalytic activity as a function of temperature, space velocity and steam-to-carbon monoxide ratio. Several leading commercial sour shift catalysts were tested for comparison. Our catalyst exhibits activity as good as low temperature Cu/ZnO *sweet* shift catalysts below 250°C, is resistant to poisoning between 200°C and 350°C, and significantly outperforms benchmark commercial sour shift catalysts that have been similarly poisoned.

We report on recent work investigating the effects of catalyst poisons on the performance of our new low temperature, poison-resistant, sour WGS catalyst. We are currently scaling up the catalyst synthesis (in several stages with testing and characterization at each stage) to produce 50+ kg batch with our industrial catalyst partner. The catalyst will be tested at the Power Systems Development Facility (PSDF) in Wilsonville, AL. The PSDF is part of DOE's National Carbon Capture Center and is operated by Southern Company, located at their Wilsonville, AL power plant. Field test using real coal- and coal-biomass-derived syngas is key to convincing customers of the activity, durability and cost effectiveness of our new sour shift catalyst.

## SESSION 40

### Combustion: Mercury Removal Research In China

## Capture and Oxidation of Elemental Mercury on Raw and Modified Mineral Sorbent in Low-Rank Coal Combustion Flue Gas

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Mercury released from coal fired boilers accounts for more than one third of the total amount of global anthropogenic activities mercury emissions every year. Mercury can be volatilized from fossil fuels at temperature as low as 150 °C and it is cyclic in flue gas or fuel gas. The release of mercury and some toxic trace metals/metalloids into the environment have an adverse effect to human health and throughout the ecosystem. Activated carbon injection is one of the leading mercury removal approaches which can remove mercury effectively from flue gas using conventional particulate matter controller. However, the application of activated carbon sorbents is limited by huge cost, lack of products for low rank fuels and for reduced impact on power generation fly-ash in concrete manufacturing. Accordingly, none post-combustion technology is financially and technically suitable for injection upstream of hot side ESP's or in hot gas clean-up streams in gasification systems. Therefore, it is important to developing an advancing "concrete compatible" sorbent that provides improved mercury removal performance without deterioration of quality of fly-ash. In this study, elemental mercury sorption of non-carbon based mineral sorbents which derived from waste paper recycling processes was investigated. A series of experiments was carried out using a laboratory-scale vertical fixed-bed reactor at temperatures from 200 to 750 °C. Samples were exposed to simulated low rank coal combustion flue gas (CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O), supplemented with SO<sub>2</sub>, NO, HCl and NH<sub>3</sub> that contained elemental mercury vapor. In order to improve the mercury removal, several chemical promoters were employed. Raw mineral sorbents were modified with manganese salts (MnCO<sub>3</sub>) and chlorine (CaCl<sub>2</sub>) impregnation, respectively. Sorbents were characterized by X-ray diffraction

(XRD), accelerated surface area and porosimeter (ASAP) using the N<sub>2</sub> isotherm adsorption/desorption method, scanning electron microscopy (SEM) and X-ray fluorescence spectrometry (XRF) to determine changes of morphologies and mineralogy before and after tests. Results indicate that thermal treatment and appropriate particle size range can enhance mercury capture performance which attributes to chemical changes during mineral activation and increasing proportion of mesopore in sorbents. It is shown that both of manganese salts and chlorine could improve elemental mercury removal efficiency observably. The probably reason is that elemental mercury can be oxidized by chlorine and manganese oxides to form mercury oxide or chloride which could be adsorbed on sorbent surface. It is shown calcium/iron-/aluminum-based sorbents could be a primary sorbent for mercury removal that provides both improved utility profitability in a wide range of temperatures and enhanced overall impact on utilization of fly-ash.

#### **Elemental Mercury Adsorption Characteristics and its Kinetics Over Biomass Chars**

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Four kinds of biomass (called peanut shell (PS), corn stalk (CS), wheat straw (WS) and wood chips (WC)) chars were prepared by pyrolysis, impregnation with solutions of KCl, KBr and KI, and steam activation. The mercury adsorption was carried out in a fixed-bed reactor with a quartz tube to study the effects of biomass species, pyrolysis temperature ( $T_p = 573\text{--}1173\text{ K}$ ), superficial velocity ( $V = 9554\text{--}31847\text{ h}^{-1}$ ), impregnation reagents (KCl, KBr, KI) and steam activation on elemental mercury ( $\text{Hg}^0$ ) adsorption characteristics. The results indicated that the mercury adsorption capacity of unit mass of pyrolyzed biomass chars shows the pattern of decrease first and then increase with increasing adsorption temperature, and biomass chars pyrolyzed at 873 K behaves the best adsorption characteristics. Mercury adsorption capacity of pyrolyzed char impregnated with solutions of KCl, KBr and KI was enhanced significantly. Steam activation can further improve the pore structure and promote the mercury adsorption. The mercury adsorption capacities of the same biomass are ordered as: all-modified char > impregnated char > steam activated char > pyrolyzed biomass char. The maximum mercury capacity of all-modified biomass char (PS873-KI(3%)-A) at  $T_a = 413\text{ K}$  and  $V = 19108\text{ h}^{-1}$  is  $29.14\text{ }\mu\text{g/g}$ . The kinetic parameters during mercury adsorption process were obtained by pseudo-first order model, pseudo-second order model, Fick's intra-particle diffusion model and Elovich model based on fitting the mercury adsorption curves.

#### **Experimental Study and Modeling for In-Duct Mercury Capture by Sorbent Injection**

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In order to evaluate mercury capture performance of raw and bromine treated activated carbon, and investigate the influences of particle size, temperature, inlet mercury concentration, residence time, and sorbent feed rate on in-duct mercury capture efficiency, experimental studies on mercury capture by sorbent injection were carried out in an entrained flow reactor. The results show that in-duct mercury capture efficiency of bromine treated activated carbon is higher at 120°C compared to raw activated carbon. This is owing to the increase of active site (Br) on activated carbon surface that improves chemisorption at higher temperature. Reducing sorbent particle size or increasing inlet mercury concentration can both speed up film mass transfer rate of mercury from gas to surface of the sorbent and rise intraparticle diffusion rate of mercury from surface to internal pores, which then improves mercury capture efficient. Longer residence time is beneficial to the mercury deposition on the inner pores. Due to sorbent residence time is far less than the adsorption equilibrium time, so mass transfer during mercury adsorption progress is recognized as adsorption rate controlling step. Higher temperature reduces physisorption ability leading to mercury removal capacity lowered. Increase of sorbent feed rate results in higher mercury capture, but reduces the mercury accumulative adsorption capacity per unit quality of sorbent. A comprehensive mathematical model, based on mass balance equation, mass transfer model and surface isothermal adsorption model, was established for predicting mercury capture efficient by sorbent injection. Sensitivity analysis of the model parameters was also conducted. The simulation results indicate that the model is capable of forecasting the mercury capture efficient and a good agreement between the modeled curves and the experimental data is obtained. So the mathematical model can be used to provide assistance in analyzing mechanisms for process of sorbent injection. The sensitivity analysis points out that sorbent feeding rate, particle size, adsorption constant K and sorbent residence time exert dominant impacts on mercury capture.

#### **Investigation into Mercury Removal with Different Sorbents Injection in Simulated and Coal-Fired Flue Gas**

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Mercury and its compounds have been brought into global focus for their heavy damages on both environment and human health. Coal burning remains one of the most significant anthropogenic sources of mercury emissions to atmosphere, roughly one quarter of total anthropogenic amount. Activated carbon draws attention to its feasibility of adsorbing Hg effectively in flue gas injection demercuration, but its high cost prevents its large-scale application in coal-fired power plants especially in China. Agricultural biomass residues are kinds of waste with high carbon content, which are potential precursors to develop low-cost and high efficient sorbents for mercury removal. In this work, the demercuration performance of rice husk char and a kind of activated carbon was investigated in both simulated and coal-fired flue gas. Both of these two kinds of sorbents were modified by low concentration ammonium halide solutions. The addition of halogen was found to enhance the fixed-bed mercury removal efficiency up to 80%~95% even after 2 hours. The simulated flue jet experiments results demonstrated that the mercury removal levels in excess of 90% were achievable at the residence time 2 seconds and the C/Hg ratio greater than  $9 \times 10^4$ . Lastly, these newly developed modified sorbents were tested in a bench scale coal-fired circulating fluidized bed facility to verify the mercury removal behavior by injecting them into a coal-fired flue gas duct. High mercury removal efficiency (82.05%~90.45%) was achieved, and a co-removal rates of 30.62%~36.07% and 9.8%~38.25% for SO<sub>2</sub> and NO<sub>x</sub> respectively. It has been shown that ammonium bromide modified biomass-based sorbents possesses as high mercury removal efficiency as commonly used activated carbon.

#### **Experiments on Mercury Removal by Plasma Enhanced Calcium-Based Sorbent**

Jun Zhang, Yufeng Duan, Chun Zhu, Qiang Zhou, Min She, Weixin Zhao, Southeast University, CHINA

Mercury emission from coal combustion has been ranked the fourth biggest pollutants following dusts, SO<sub>2</sub> and NO<sub>x</sub> in China. The non-thermal plasma has been known as functions to oxidize gaseous elemental mercury at low temperature effectively. A new method was proposed in this paper of combining plasma with calcium-based adsorbent to capture both elemental and oxidized mercury concurrently in flue gas. Experimental studies on mercury species transformation and adsorption in simulated flue gas by plasma enhanced calcium-based sorbent were carried out in a bench fixed bed reactor. The effects of plasma treating, input energy, plasma and calcium oxide interact to removal elemental mercury were investigated in a wire-cylinder non-thermal plasma reactor energized by AC power. Voltage and current of non-thermal plasma were measured through oscilloscope, high voltage probe (1000:1) and current probe. Results showed that calcium-based adsorption capacity to mercury was increased remarkably thorough non-plasma strengthened. The removal efficiency of elemental mercury was greatly depended on input energy at which an optimal input energy brought up to 80% efficiency. O<sub>3</sub> play an important role in oxidation elemental mercury rather than O under non-thermal plasma process. Therefore, the main mercury speciation were Hg<sub>2</sub>O and HgO<sub>3</sub> rather than HgO.

#### **SESSION 41 Gasification: General - 3**

#### **Influence of HCl, H<sub>2</sub>S and H<sub>2</sub>O on the Release and Condensation of Heavy Metals in Gasification Processes**

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The influence of HCl, H<sub>2</sub>S and steam on the release and condensation of Zn, Cd and Pb was experimentally investigated. The experiments were conducted in two different setups. The condensation behavior (temperature and speciation) of the heavy metal vapors was investigated in a heated flow channel reactor housed in a furnace with a gas cooling zone. Experiments on the release of the inorganic vapors were carried out in a heated flow channel reactor coupled to a Molecular Beam Mass Spectrometer (MBMS) in order to analyze the gas in-situ. The results of the experimental investigation were compared with "Scheil Gulliver Cooling" calculations performed by Fact Sage 6.3. A better understanding of the gasification process and a new insight into the optimization of the process to reduce the trace metal emissions was achieved.

#### **The New HITECOM Reactor for Single-Particle Conversion: Numerical and Experimental Studies on the Interactions Between Measuring Unit and Reacting Particle**

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For a sophisticated modeling of coal gasification and combustion a more detailed understanding of the conversion process of single coal particles is necessary.

Experimental results available in literature are typically based on drop tube and TGA measurements. The disadvantage of the drop-tube reactor is that only integral values can be measured. The TGA on the other hand has the disadvantage that the gas flow to the probe is not well-defined and cannot be varied independently.

For a more detailed insight into the thermo-chemical processes of reacting particles it is necessary to estimate the local distribution of main gas species and the temperature around reacting particles. To overcome these limitations the test reactor HITECOM (High Temperature Conversion Optical Measurement) is currently developed within a joint project of the TU Bergakademie Freiberg and the Friedrich Schiller University of Jena. The reactor allows for time-resolved and spatial-resolved in-situ measurements of single coal particle conversion at defined flow conditions. The reactor is designed for temperatures between 800 and 1400 °C, pressures of 1-40 bar and particle Reynolds numbers between 10 and 150. The HITECOM reactor is a plug flow reactor with electrical heating and a gas preheating unit. Inside the reactor a single coal particle is fixed in a centered position. Four optical ports around the particle allow for spatial and time-resolved measurements of the species distribution and the temperature via LIF, Raman and FS-CARS laser measurement techniques. Furthermore a thermogravimetric analyzer is installed, which enables the direct measurement of the carbon conversion rate.

An open question during the development of the reactor was the design of a robust but flexible particle fixation in the reactor, especially under the presence of large flow velocities. Different solution strategies have been tested experimentally utilizing a model reactor under conditions close to the final HITECOM reactor. In this work different types of fixings were compared against each other regarding stability, influence on the flow field and practicability during the experiments. It could be shown that a simple rod in combination with an adhesive may be the most convenient fixing method.

In order to estimate the interaction between the fixation and the boundary layer of the reacting particle, direct numerical simulations of the reacting particle together with the fixing have been carried out. For this, the Navier-Stokes equations coupled with the energy and mass conservation equations have been solved. The heat conduction within the particle and the rod was considered. Additionally the gas phase radiation was taken into account by the usage of the P-1 model. As a first step the gas phase was assumed to consist of CO<sub>2</sub> only, so only the Boudouard reaction takes place at the particle surface. The simulations revealed, that the particle fixation influence the flow and temperature field around the particle and reduces the reacting surface, which leads to a reduced carbon conversion rate up to 25%. To overcome this influence correction formulas have been developed to predict the char conversion in a correct way.

#### Results on Experimental Investigation and Modelling of Slag Viscosities with Consideration of Partial Crystallization

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The Viscosity of a slag is a vital parameter when operating slagging gasifiers. Slag viscosity is dependent on the composition of the slag constituents, the temperature, and the gas atmosphere of the gasifier.

Several viscosity prediction models are available in literature for completely molten slags. Within the gasifier, the slag undergoes several changes in structure and composition. Also, partial crystallization is observed. Solid particles within the melt will change the slag behavior from Newtonian to non-Newtonian. This results in dramatic differences between predicted and measured viscosity. Classical models will fail under these circumstances.

A solution to this problem is the consideration of epitaxy, slag composition change due to crystal separation, shear rates, and the influence of oxygen partial pressure. Numerous techniques are available to introduce above parameters into an improved viscosity prediction.

In this work, particle formation and atmosphere influence to the slag is described by the thermodynamic equilibrium software FactSage™. The rheological behavior due to particle influence and differing shear rates is introduced by the equation of Einstein-Roscoe. A systematic investigation of a natural slag system is carried out to validate the predicted viscosities. Viscosity measurements under high temperatures and reducing/oxidizing atmospheres are conducted in a wide temperature range to investigate the formation of particles due to crystallization. The Newtonian behavior is tested by applying several rotational velocities. The onset temperature of crystallization and the formed solid phase are compared to the thermodynamic equilibrium calculations, TDA and quenching experiments with XRD evaluation. Results of the investigated slag systems and differences between modelled and measured slag parameters will be discussed. The discovered relationships will be used to improve the viscosity prediction under industrial process conditions.

#### Effects of V<sub>2</sub>O<sub>5</sub> Oxidation on the Viscosity of High Iron and Vanadium Slag

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Petroleum coke is an attractive solid fuel because of its high heating value, low ash content and low price as compared to coal. However, the high sulfur content can pose a

problem when used as a combustion fuel. The gasification process which emits much less SO<sub>x</sub> is a more suitable process for petroleum coke utilization.

In gasification, vanadium rich ash can cause operational problems such as slag accumulation inside the gasifier. The deslagging of the accumulated slag can be achieved by oxidizing V<sub>2</sub>O<sub>3</sub> to low temperature-melting V<sub>2</sub>O<sub>5</sub>. The rate of oxidation of V<sub>2</sub>O<sub>3</sub> was measured, and the effects of V<sub>2</sub>O<sub>3</sub> oxidation on the slag viscosity were investigated. The oxidation rate of powder V<sub>2</sub>O<sub>3</sub> under air was fast that, when heated at 20 °C/min, the oxidation was completed below the melting point of V<sub>2</sub>O<sub>3</sub>.

For coke and coal mixtures, the slag viscosity increased with the higher coke contents and with reducing conditions. A coke ash of high concentrations of Fe and V and a bituminous coal ash rich in CaO were used. For 80:20 and 90:10 coke:coal mixtures, the temperature of critical viscosity under the oxidation conditions were lower by 50°C and 36°C, respectively, than those under reducing conditions. SEM/EDX analyses showed that vanadium in the cooled slag was present as a component in a minor crystalline phase and in the glassy phase.

#### SAXS Measurements of Pore Development During Steam and CO<sub>2</sub> Gasification

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A fundamental understanding of the chemical and physical changes occurring during gasification is extremely important for the design of coal gasifiers. The gas-solid reaction rate is dependent on how the physical char structure changes as conversion progresses, and has been studied in detail for activated carbons and numerous coal chars using gas adsorption techniques. The gas adsorption techniques give accurate volumes for the macro-, meso and micropores, with the use of mathematical models that calculate average pore size, pore size distribution and other structural parameters. The results obtained from Small Angle X-Ray Scattering (SAXS) analysis allows direct measurements of pore structure (including closed pores) over a very wide pore size range. The pore development during carbon conversion (for both combustion and gasification) has been studied using Small Angle Scattering (SAS) but pore development during steam and CO<sub>2</sub> gasification has not yet been directly compared using SAS.

In this study we compare pore development during steam and CO<sub>2</sub> gasification of a Witbank Seam 4 char as measured using the SAXS beamline at the Australian Synchrotron, Melbourne. The sample was scanned (3 x 6 scanning map) using two camera positions to probe the pore size between 0.25 - 145 nm. Chars were prepared in a nitrogen atmosphere controlled furnace at 1000 °C and a holding time of 1hr. The chars obtained for 75 µm, 2 mm and 20 mm particles were gasified (using CO<sub>2</sub> or steam) to specific conversions (0%, 10%, 25%, 35% and 50%) using two gasification temperatures (850 and 1000 °C for CO<sub>2</sub>, 800 and 950 ° for steam).

##### Char results:

The char pore size *distribution* of the 75 µm and 2 mm particles is found to be identical over the entire Q-range. The 20 mm particles show a greater pore *fraction* below 12.5 nm than the 75 µm and 2 mm sizes did. From the absolute intensity data it is observed that, although the pore *distribution* of the 75 µm and 2mm will be similar, the *number* of pores for the 2 mm particle size was greater per unit volume over entire pore size ranges. A further increase in the 20 mm pore amount (pores < 12.5 nm) is observed when compared to the 2 mm particles.

##### 75 µm results:

The intensity increases over the entire Q-range as the conversion increases. The char structure appears to be modified on all pore size scales, even at the smallest observed here (~0.25 nm radius). Both the normalised intensity of CO<sub>2</sub> and steam follow a similar trend: an initial change in the pore size *distribution* is seen up to 25% conversion with the pore size *distribution* unaffected for higher conversions. There is no change for the pore size *distribution* above 25 nm pore size, with all the changes taking place below 25 nm. Different pore size distributions are observed for the CO<sub>2</sub> and steam converted chars at pore sizes below 25 nm, with steam-reacted chars showing greater normalised intensities. The increased attack at small pore sizes by water could be due to deeper penetration of the water molecules into the pore structure when compared to CO<sub>2</sub> molecules. When comparing the steam and CO<sub>2</sub> char normalised and absolute intensities at the different gasification temperatures, it is observed that the pore development is independent of temperature over temperatures and the pore size range examined, suggesting char gasification rates are chemically controlled.

##### Particle size comparison:

Similar trends are observed for the steam and CO<sub>2</sub> gasification of 2 mm particles as for the 75 µm. The intermediate pore *fraction* (0.8 to 25 nm and 0.6 to 25 nm, respectively) increase is not as pronounced for the 2 mm when compared to the 75 µm, and even less distinguishable for the 20 mm particles. This shows a decrease in selective attack of pores in the intermediate *fraction* as particle size increases. There is also a shift in the lower limit of the intermediate pore *fraction* from 0.8 to 2.5 nm for the 20 mm particles. The same decrease in micropore *fraction* is seen for both the large particles size fractions, with an increase in micropore *fraction* depletion observed with an increase in particle size. The decrease is also more pronounced for the 20 mm steam gasification at 800 °C when compared to 20 mm CO<sub>2</sub> gasification. This work

demonstrates the nature of insights that can be obtained using SAXS studies of gasified chars.

**SESSION 42**  
**Coal Science: General - 7**

**Rare Element Systematics of Coal Ash from Major U.S. Sources**

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Rare elements such as Ga, Ge, Sc, Y, and the lanthanide rare earth elements (REE) have a wide range of applications in electronics, high performance permanent magnets, batteries for hybrid and electric vehicles, and generators for wind turbines, among others. Substitutes for rare elements in these applications, if available, are generally much less effective alternatives [1, 2]. Conventional sources of REE include bastnaesite-bearing carbonatites, such as at Bayan Obo, Inner Mongolia, China, the world's largest deposit, and at Mountain Pass, California, currently the only U.S. producer. Globally, monazite-bearing placers are the next most important type of deposit, but production of REE from monazite in the U.S. is unlikely due to its high thorium content and resulting concerns over radioactivity [2].

Chinese dominance in the world market has spurred exploration for new REE sources, including unconventional sources such as coal ash. Detailed studies of REE distribution in coal ash are limited but show that REE are highly refractory and, as a result, are strongly retained in the ash fraction during coal combustion [3]. Whole coals generally show chondrite-normalized REE patterns with moderate abundances, moderate light-REE enrichment and modest negative europium anomalies, similar to patterns for associated shales, and for shales in general [4, 5]. Recent work confirms that REE, like many other trace elements, are concentrated in finest grain-size fractions of coal fly ash [6]. Most previous work on coal and coal ash as possible sources of rare elements has concentrated on a limited number of widely scattered examples showing anomalous enrichment [7, 8]. In this study, we provide new and existing concentration data for coal ash derived from some of the most widely used U.S. coals. Understanding chemical properties and element transformations in going from coal to coal ash are especially important. This will better define how REE and rare elements occur in coal ash and help determine their potential extractability.

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**Low-Cost Recovery of Rare Earth Elements From U.S. Coal Ash**

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Rare earth elements (REE) have become a critical resource in both US civilian and military applications. While more abundant than many other minerals, REEs are not sufficiently concentrated in the earth's crust to make them easily exploitable economically. The United States was once self-reliant in domestically produced REEs, but over the past 16 years has become 100% reliant on imports, primarily from China, because of lower-cost operations. A survey of the USGS COALQUAL database indicates that REE are commonly found in domestic coal supplies in concentrations greater than their crustal averages, and suggests that the US produces over 40,000 tons of REE in coal mining alone, largely from Appalachian coal mines. Combustion of this coal used for electrical power generation concentrates the REE by a factor of 8-10. Thus coal ash, normally considered a waste product, represents a significant U.S. domestic resource for REE production. In order to make REE production economically competitive, however, further concentration of REE from the ash is needed prior to chemical extraction. Physical Sciences Inc. (PSI) and the University of Kentucky/Center for Applied Energy Research (UK/CAER) investigated several ashes from utilities to develop physical separation processes for enriching the rare earth element content. The processes included particle sizing, floatation, and other methods. We showed that an *extractable* REE enrichment factor of up to ~X5 can be achieved

using physical separation approaches. Further enrichment by purely physical processes may be limited due to the morphology of the source materials, and how the REE are tied up within the morphology of the constituents. Therefore, selection of coal with high starting REE content becomes important, bringing into consideration the geochemical origins of the coal. Our paper will discuss the rationale and results for various enrichment approaches investigated.

**Lanthanide-Bearing Coals in the Central Appalachians: Resource or Illusion?**

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The availability of lanthanide, or rare earth (REE), elements has become a critical issue as the demand for the elements for electronics, optics, and other end uses has risen. While no coal in the Central Appalachians has a Yttrium + REE (REY) content of ore-grade deposits, some have ash-basis concentrations within an order of magnitude of the concentrations at, for example, Mountain Pass, California. Furthermore, if the coal is mined for power production, the REY are concentrated in the fly ash at the power plant, a fine material requiring less processing than mined rock. In eastern Kentucky and West Virginia, the Fire Clay coal is the most promising REY resource owing to an influx of REY associated with a volcanic ash fall deposit, or tonstein, within the coal. The Fire Clay coal has been extensively mined and, as with many Central Appalachian coal resources, a century or more of mining has depleted the reserves. Resource investigations of the Fire Clay in eastern Kentucky indicate that while only 40 % of original Fire Clay coal resources >28-in. (71-cm) thick remain, more than 92 % remains in coal that is <28-in. (71-cm) thick. This pattern (few thick-coal resources, abundant thin-coal resources) is common to most, if not all, of the major mineable coal beds in central Appalachia. In addition, the REY resources are not concentrated at one location but, instead, are distributed among unmined coals, spoil piles at existing and previous mine sites, and in ash ponds or landfills at power plants throughout the southeastern US. Overall, while the promise of REY from coal is intriguing, that promise eventually will be weighed against the reality of the economics of recovery.

**Consideration of the Variability of Coals from the Botswana Karoo Basin Using Coal Petrography**

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As noted in a publication by Hower et al. (2012) there is limited published data on many of the Permian coalfields in sub-Saharan Africa, especially in the area of coal petrology. The Botswana coalfields form part of the Permian Karoo Supergroup, and the Karoo Basin covers an area of 550 000km<sup>2</sup>. In this study, 5 sets of coals from 5 different coalfields in Botswana were analysed petrographically and chemically. Botswana, with a comparatively small population in a large, relatively arid country, primarily relies on South Africa to make up the significant shortfalls in its electricity supply. There is currently only 1 active mine (Morupule Colliery) supplying 1 active pf power station (Morupule coal-fired plant, 132 MW) in Botswana. However, extensive exploration is underway, with plans to significantly increase power generation by 2017 (estimated at 57% per annum) by the expansion of the pf power station (underway), installation of circulating fluidized beds (CFB) currently on hold due to complications of combusting the coal), underground coal gasification (unlikely as seams are relatively shallow), and coal bed methane (significant exploration happening). Botswana may have coal reserves of over 200 billion tons, but limited information is available about the quality of the coal, and whether the coal is suitable for the different conversion technologies currently on offer. Unfortunately, there have already been instances of failed technology due to incomplete understanding of the coal.

The polished blocks were analyzed using a Leica DM4500P petrographic microscope fitted with an automated point counting stage and Petrog software for the maceral and abnormal condition analysis, the former in accordance with ISO 7404 - 4, at a magnification of x500 under oil immersion. The abnormal condition analysis was conducted following in-house development, and publications by Wagner (2007). Reflectance analyses were conducted at CAER using a Zeiss microscope. Micrographs (photographs) were taken using an Axiovision digital camera attached to the microscope. The intention of the analysis is to quantify abnormal features, such as extensive fissuring and cracking, mineral alteration, heat affect, and so on.

Results from the 1<sup>st</sup> set of coal samples (not cores) showed extremely high inertinite contents, and extremely low vitrinite contents. Rank determination was difficult due to the very low vitrinite content. Based on two samples (and only 50 readings) the mean random vitrinite reflectance values obtained were 0.45 and 0.47 % RoVmr, placing these coals in the Low Rank A / sub-bituminous coal category. Results for the Tuli area, an isolated coalfield on the eastern border, show very high vitrinite contents (over 80% generally) with low rank (Medium rank D). The liptinite content can be considered to be typical of southern African coals, and did not appear to have been affected by weathering (hence physical weathering rather than oxidative weathering). Secretinite is highly apparent in many samples, with a range of reflectance values. Funginite has been considered, but not definitely as yet; funginite has not been reported for southern African Permian coals. Many samples were highly fissured or



cracked or discoloured, all signs of the impact of water *in situ*, most likely following coalification. Epigenetic carbonate minerals were very prevalent. Attempts regarding stratigraphic correlations will be made.

#### Precious Metals in the Lincang Ge Ore Deposits, Yunnan, China

Shifeng Dai, China University of Mining and Technology, CHINA; Vladimir V. Seredin, Russian Academy of Sciences, RUSSIA; James C. Hower, University of Kentucky Center for Applied Energy Research, USA; Colin R. Ward, University of New South Wales, AUSTRALIA

Previous studies showed that high-Ge coals are enriched in precious metals (Zhuang et al., 2006; Seredin, 2007; Dai et al., 2012). In this study, three coal bench samples and host rocks including quartz metasomatite, carbonate metasomatite, clay, coaly sandstone, granite, and argillized granite, as well as coal combustion products (fly ash and slag) were collected for precious metal determination. The concentrations of Au and Pt-group elements were determined in low temperature ashes (< 150°C) derived from coal and host rocks. The determination procedure included: (1) Sample chemical digestion using acid decomposition and fusion with sodium peroxide and subsequent transference of the material into hydrochloric acid solution; (2) Sorption concentration of the precious metals from the hydrochloric acid solution by means of organic reagent (Polyorgs IV); (3) Incineration of the reagent and its transference into hydrochloric acid solution; and (4) Determination of Pt, Pd, and Au concentration by ICP-MS.

The results showed that the precious metals are highly enriched in the coal and host rock samples. Gold particles were detected in the fly ash derived from the high-Ge coals. The sum of Au, Pt, and Pd in the coal LTAs are 740 – 1150 ng/g. The precious metals can be concentrated in the upper, middle and lower portions of the coal seam section. The clay sample, which has been subjected to hydrothermal solutions, contains as high as 9840 ng/g Au, 740 ng/g Pt, and 70 ng/g Pd. The carbonate metasomatite sample of hydrothermal origin contains 230 ng/g Au, 130 ng/g Pt, and 590 ng/g Pd. The concentration of Pt in the argillized granite is up to 200 ng/g.

The highly elevated concentrations of precious metals are attributed to hydrothermal solutions that captured precious metals from magma chamber during its long-term circulation in the coal basin and deep underground along basin faults. The Lincang coals are enriched not only in Ge and W, but also in Be, U, and Nb, indicating that the hydrothermal solutions are alkaline N<sub>2</sub>-bearing water mixed with volcanogenic CO<sub>2</sub>-bearing chloride-sulfide volcanogenic solution. The origin of high concentrations of precious metals in the Lincang ore deposit was also evidenced by their high concentrations in the pyrite of epithermal origin in the Wulantuga Ge deposit, Inner Mongolia, China.

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#### SESSION 43

##### Carbon Management: Storage of Carbon Dioxide - 1

#### An Economic Evaluation of the Cost to Develop a Hypothetical Class VI Compliant Commercial Sequestration Site

Wayne Rowe, Schlumberger Carbon Services, USA

Over the past decade there have been numerous publications describing the methodology and cost of developing a site for the geologic sequestration of anthropogenic Carbon Dioxide. Many of the publications are based on early, small scale pilot projects, testing numerous siting concepts, monitoring technologies and experimental well construction techniques. Additionally, few include the impact of the recent issuing of US Environmental Protection Agency Class VI Underground Injection Control regulations. This paper draws on the knowledge gained from executing numerous CCS projects as well as preparing, submitting and gaining approval of actual UIC Class VI permits; to perform an economic evaluation of the cost to develop a hypothetical Class VI compliant commercial sequestration site. The evaluation uses proprietary geologic data acquired in the sub-surface near an existing power plant. The evaluation includes the projected cost, in 2014 dollars, to fully characterize, construct, operate, monitor and ultimately close the site consistent with EPA guidelines and current best practices. The sequestration facility will utilize a saline aquifer injection formation at a depth of approximately 8,000 FT (2,438 M). The

host site is a 280 MW power plant in the western United States and has an output of 1million metric tons of CO<sub>2</sub> per year, and an expected operating life of thirty years. The evaluation includes the impact on cost and operations of doubling the CO<sub>2</sub> plant output by adding a second generator of similar size.

#### Project Assessment and Evaluation of the Area of Review (AOR) at the Citronelle SECARB Phase III Site, Alabama USA

Hunter Jonsson, George Koperna, Jr., Steven M. Carpenter, Robin Petrusak, Advanced Resources International, Inc.; Rob Trautz, Dick Rhudy, EPRI; Richard Esposito, Southern Company, USA

The Southeast Regional Carbon Sequestration Partnership (SECARB) Anthropogenic Test is a demonstration of the deployment of CO<sub>2</sub> capture, transport, geologic storage, and monitoring technologies. This project is the first and the largest fully integrated commercial prototype coal-fired carbon capture and storage projects in the USA. The demonstration has reached the milestone 100,000 metric ton (tonnes) injection and is in the second year of injection operations. Two Class V Experimental Injection Well underground injection control (UIC) permits were issued in November 2011 and the project's injection wells were installed shortly thereafter.

This paper provides an assessment of the CO<sub>2</sub> injection program at the SECARB site after the first full year of injection and prior to reaching the milestone of 100,000 tonnes of CO<sub>2</sub> injected. The purpose of the project assessment is to re-evaluate the Area of Review (AoR) for the injection well, as compared to US EPA 40 CFR146.84 Class VI standards. The AoR is defined as the region surrounding the geological sequestration project that may be impacted by the injection activity. The AoR is further defined as the farthest reach of the tangible CO<sub>2</sub> plume and/or the region of 'significant' reservoir pressure increase.

An updated geologic model of the injection zones and storage reservoir sandstones incorporates geologic data obtained from the injection well and characterization wells drilled at the Phase III Anthropogenic Test site. The numerical modeling of the injection was conducted using the updated geologic model, plus the monitoring results obtained to August 31, 2013. The simulation demonstrates effective containment of CO<sub>2</sub> by the reservoir architecture of the upper Paluxy Formation, consisting of multiple, stacked, highly porous and permeable sandstones, separated by low permeability flow barriers.

This CO<sub>2</sub> containment, demonstrated in this paper, requires an AoR with a radius of 440 feet from the injection well. This is a downward revision that reduces the radius of the AoR from the pre-injection determination of 1,700 feet, which was based on a full three year injection program operating at peak rate. With the revised AoR, the only well within the AoR is the injection well itself, the D 9-7 #2. The nearest well to the injector is the D 9-8 #2. The surface location for this well is 870 feet away from the D 9-7 #2, placing the D 9-8 #2 outside the revised AoR.

Other key observations from the reservoir simulation of CO<sub>2</sub> injection for the period August 23, 2012 to August 31, 2013 include the following. The dip of the Paluxy Formation influences the migration of mobile CO<sub>2</sub> to a small degree after injection operations cease. The shallow angle of dip of approximately 1.25 degrees to the northwest limits the post-injection up dip migration. The maximum movement of CO<sub>2</sub> is less than 440 ft. (134.1 m) in any direction. The high transmissivity of the Paluxy results in a maximum CO<sub>2</sub> extent that is greater than the extent of significant pressure build up. Consequently, the AoR determination is based on the extent of the CO<sub>2</sub> movement.

#### 3 # Coal Seam Injection and Buried CO<sub>2</sub> Improve Coal-Bed Methane Recovery Test and Evaluate in Qinshui Basin Shizhuang North Block, Shanxi

Zhang Bing, Ye Jianping, China United Coalbed Methane Corporation Ltd., CHINA

At present, carbon dioxide is injected into the coal bed and enhanced coalbed methane production selection evaluation technology has been developed to the group well test stage. Test results around the world have shown that the technique can improve the CBM production and coal bed methane recovery, carbon dioxide can be sequestration. In this paper, base on the southern Qinshui Basin single well test results, laboratory test results and numerical simulation method, the results of carbon dioxide injecting into the southern Qinshui Basin CBM were evaluated. Analysts believe that the 3 # coal seam after injection of carbon dioxide, coal bed methane recovery degree increase above 10%.

#### SESSION 44

##### Shale and Coal Bed Gas: General - 2

#### Assessing Environmental Impacts of Unconventional Gas Development on Water Resources

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The Department of Energy (DOE) National Energy Technology Laboratory (NETL) has been pursuing multiple lines of investigation to assess and understand the potential impacts of unconventional gas development on water resources. Concurrent efforts in the field and laboratory are seeking to define links, collect data, model effects and reduce uncertainties. Field work includes developing or adapting groundwater and surface water monitoring instrumentation for the detection of drilling fluids and hydraulic fracture chemicals sourced from unconventional gas well sites. In collaboration with West Virginia University and URS Corporation, NETL is seeking to define surrogate monitoring parameters that can serve as environmental indicators of contamination events. Laboratory research includes sand column experiments to determine the degradation pathways and rates for the natural attenuation of organic compounds from drilling fluids and hydraulic fracturing chemicals. NETL laboratory data and microcosm experiments from collaborative research with Ohio State University are being used as inputs for reactive transport computer models to assess the fate and transport of these chemicals in groundwater and surface water environments. These and other simulations will help to determine if monitored natural attenuation is a viable remediation strategy for drilling-related organic contaminants in the environment.

An expected outcome of this research is to develop a more rigorous definition of indicators for detecting fluids associated with drilling and hydraulic fracturing chemicals in streams and groundwater. The goal is to ensure that monitoring equipment in boreholes and surface water bodies in the vicinity of unconventional gas development sites can reliably detect the presence of these chemicals, and distinguish them from background signals. Improved indicator assessment would provide a cheap and simple method for regulatory agencies to track potential impacts of unconventional gas production on water resources, and for industry to mitigate damage by detecting leaks or spills early and responding quickly. In the event contamination does occur, understanding the effectiveness of natural attenuation as a possible remediation strategy can help with site cleanup and restoration.

#### **Health and Environmental Impacts of Naturally Occurring Radioactive Materials Produced by Unconventional Gas Extraction from Marcellus Shale**

Tieyuan Zhang, Radisav Vidic, University of Pittsburgh, USA

Radium is a common naturally occurring radioactive material (NORM) with high mobility that is found in high salinity shale gas wastewater (flowback and produced water). Ra-226 is the dominant radionuclide encountered in shale gas water at activities exceeding ten thousand picocuries per liter (pCi/L). In comparison, the EPA maximum contaminant level (MCL) for drinking water is 5 pCi/L and the maximum radioactivity for disposal in RCRA-D non-hazardous landfill is 25 pCi/g. Traditional methods for Ra-226 determination either require long sample holding time to allow radon emanation to reach equilibrium (e.g. EPA method 903.0 and 903.1) or long detection time (e.g. EPA method 901.1). A novel detection method with reduced sample holding and detection time that utilizes Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) in combination with solid-phase extraction to separate radium isotopes from the background matrix in high salinity solution was first developed and validated in this study. This method requires a series of sample preparation steps and several minutes of detection time for each sample, which allows analysis of dozens of samples per day.

After hydrofracturing of horizontal Marcellus Shale wells is completed, large quantities of flowback water are generated from each gas well. The operators currently store flowback and produced water in centralized storage impoundments or tanks prior to reuse in subsequent hydrofracturing operations. The fate of Ra-226 in centralized storage impoundments in over a period for several years was investigated in this study using the analytical technique developed for rapid Ra-226 detection. Initial results of this study indicate that Ra-226 keeps accumulating in the impoundment sludge and increases from less than 10 pCi/g for fresh sludge to several hundred pCi/g for aged sludge. Toxicity characteristic leaching procedure (TCLP) (EPA Method 1311) was applied to study the leaching behavior of Ra-226 in sludge samples. Finally, a combination of sequential extraction procedure (SEP) and chemical composition analysis of impoundment sludge was utilized to determine the main carrier of Ra-226 in these surface impoundments.

The health risks associated with the NORM generated from shale gas extraction to the on-site worker and off-site residents during flowback/produced water and solid waste management is also investigated in this study. Health and environmental impacts of NORM based on the radiation exposure dose for different scenarios during shale gas exploration (e.g. well drilling, flowback and produced water management, solid waste disposal) are compared with EPA or NRC regulations.

Pradeep K. Agrawal, Gautami M. Newalkar, Carsten Sievers, Georgia Institute of Technology; Kristiina Iisa, National Renewable Energy Laboratory, USA

Pyrolysis and gasification of biomass-coal blends is of significant interest because of the potential of synergies offered through such blends. Pyrolysis occurs at low temperatures (300-600 °C), and char gasification appears to be the slow or rate-limiting step. Inorganic species present in the char catalyze char gasification in the presence of CO<sub>2</sub> or steam. The nature of these inorganics varies widely between coal and biomass. For example, coal has very low alkali content, whereas biomass tends to be high in alkali content. This work was undertaken to investigate the gasification of biomass-coal blends. Switchgrass was chosen as a biomass feedstock since it is an energy crop consisting of a considerable amount of inorganic ash.

Switchgrass (sieved to 180-250 µm) was pyrolyzed in an entrained-flow reactor at different temperatures (600-1000 °C), pressures (5-20 bar) and residence times (3-30s). The heating rate during pyrolysis is known to have a dramatic effect on the char morphology and other physical characteristics which are likely to affect gasification behavior. The entrained flow reactor used here can achieve heating rates which are close to large scale gasifiers (~10<sup>3</sup>-10<sup>4</sup> K/s), and thus the chars generated in this work represent those likely to be formed in industrial gasifiers. Chars were characterized using several techniques: SEM, N<sub>2</sub> and CO<sub>2</sub> adsorption, ultimate analysis, ICP, XRD, and Raman spectroscopy. Pyrolysis gases were analyzed using micro-GC and tars were analyzed using GCxGC-TOFMS. The char formed at high heating rates has surface area two orders of magnitude higher than the feedstock. The pyrolysis temperature and residence time appeared to have a more dramatic influence on the properties of the char than pressure during the pyrolysis. Especially, the graphite-like nature of char significantly increased with an increase in temperature, which could potentially have a negative impact on char gasification reactivity. Char gasification was studied in TGA/PTGA.

The effect of heating rate and pressure of the morphology of lignite chars is not as dramatic as that for the switchgrass. Lignite char has very low gasification reactivity as compared to that observed for the switchgrass chars. However, this low activity is attributed to the low alkali content. Lignite char, when blended with switchgrass char or biomass ash yields much higher activity, almost by an order of magnitude. The results will explore the conditions under which such synergies might be observed. Also, an attempt is made to find the most meaningful descriptor of char reactivity amongst the physical and chemical properties of char studied in this work.

#### **Catalytic Fixed Bed Gasification for Remote Sites Power Generation and Industrial/Municipal Waste Utilisation**

N. Kinaev, Strategic Energy Consulting, AUSTRALIA; V. Panfilov, MES Corporation; I. Grebenyuk, A. Babaev, Alexey Belov, Far Eastern Federal University, RUSSIA

The novel catalytic fixed bed gasifier has been developed for small-scale (<5 MW<sub>e</sub>) heat and power supply at remote sites with no access to the grid. The gasification unit is designed for utilization of wide variety of low quality carbonaceous fuel: biomass, municipal solid waste, lignites, coal and coal rejects, petroleum coke etc. Such fuel flexibility allows efficient utilization of industrial and/or municipal waste.

The unit consists of three main blocks. Fuel preparation unit forms briquettes from the carbonaceous fuel and catalytic bed material. The briquettes are then fed into the gasification block. The gasification block has a fixed bed gasifier and a syngas treatment unit, which ensures compliance with environmental regulations and emission control. The liquid carbohydrates produced during gasification could be fed into the gasifier to avoid complex waste treatment and increase carbon utilization. The processed syngas is used as a boiler fuel in heat and power block. The power generation performed by ORC turbine, which ensures low maintenance and high reliability of the system.

Depending on the site requirements, syngas could also be used to produce chemicals or synthetic oil (e.g. diesel, naphtha) products.

Effect of various feedstocks, such as coal rejects, wood biomass etc. and various regimes of gasification syngas composition and quality has been examined and discussed.

#### **Thiophene Hydrodesulfurization by Composites of Carbon and Magnesium**

Xiaoli Zhang, Naifei Wang, Qianqian Zhang, Zongying Han, Shixue Zhou, Shandong University of Science and Technology, CHINA

Sulfocompounds in raw gas and chemicals for synthesis are poisonous to metal catalysts, and those in fuels are corrosive to metal equipment and result in environmental pollution. Hydrodesulfurization (HDS) is effective to convert aromatic sulfur, e.g. thiophene and dibenzothiophene, into H<sub>2</sub>S which is easy to be removed by MnO<sub>2</sub> and ZnO etc. Mg-C composites were prepared by ball milling under hydrogen atmosphere with crystallitic carbon, which was prepared from anthracite coal by demineralization and carbonization, as milling aid. Carbon additives for milling can lead to smaller crystal size and even create dangling bonds at carbon particle surface, introducing new hydrogen adsorption sites and thus influencing the properties of the materials. The TEM observation shows that the particle size of MgH<sub>2</sub> is around 20-60

**SESSION 45**  
**Gasification: Novel Technologies - 2**

#### **Pressurized Pyrolysis and Gasification of Switchgrass-Lignite Char Blends**

nm in the presence of 30 wt.% of crystallitic carbon after 3 h of milling under 1 MPa H<sub>2</sub>, and the XRD analysis shows that the crystal grain size is approximately 29.7 nm. In the process of ball milling, the crystallitic carbon from anthracite coal reduced the Mg particle size, prevented Mg particles from cold welding and prevented fine Mg particle from being milled excessively. The DSC analysis shows that the onset, peak and end dehydrogenation temperatures of the magnesium-based materials are 293, 345 and 403 oC, respectively. The Mg-C composite material was then used for thiophene hydrogenation corresponding to hydrodesulfurization. The XRD analysis shows that the sulfur from thiophene combines with magnesium into MgS during hydrogenation with the hydrogen-storage material at 300 oC, and more MgS results with the increase of temperature up to which the hydrogen releasing matched with thiophene hydrogenating at about 350 oC. The gas chromatography analysis shows that the thiophene hydrogenation yields butadiene primitively, and then the butadiene converts into butene, butane, and even C1-3hydrocarbons by further hydrogenation. The C-S bond in thiophene molecule precedes C=C bond to carry out hydrogenation, and the thiophene reaction follows direct desulfurization pathway rather than hydrogenation pathway.

#### **Municipal Solid Waste Gasification for Coal Retrofit Applications**

Nicholas Siefert, DOE/NETL/ Carnegie Mellon University; Marius Paul Balla, Carnegie Mellon University, USA

This project analyzes using Municipal Solid Waste (MSW) as a clean alternative for retrofitting recently closed power plants. An economic analysis of a proposed system was completed to analyze the feasibility of using MSW to generate electricity without generating air emission. MSW can be used to create syngas using gasification techniques, which in turn can be cleaned and used as a fuel source in power plants that have shut down due to the cost of complying with environmental regulations. Here, we present a techno-economic analysis of gasifying all of the combustible MSW in Allegheny County, PA in a moving-bed, pressurized gasifier, and then sending the syngas to a hydrogen-permeable PBI membrane. Gases such as CO<sub>2</sub>, H<sub>2</sub>S and heavy metals remain on the retentate side of the membrane, and are subsequently separated from the combustible gases. We estimated the cost of all of the equipment, and will present the levelized cost of the electricity (LCOE) of this system.

#### **SESSION 46 Sustainability and Environment: General - 1**

#### **Greenhouse Gas Mitigation from Underground Coal Gasification (UCG)-based Hydrogen with Carbon Capture and Sequestration (CCS) in Bitumen Upgrading from the Oil Sands**

Aman Verma, Babatunde Olateju, Amit Kumar, Rajender Gupta, University of Alberta, CANADA

Synthetic crude oil (SCO) production from the Canadian oil sands is projected to increase from 1.9 million barrels per day (bpd) in 2013 to 4.8 million bpd in 2030. Hydrogen (H<sub>2</sub>) serves as an essential feedstock for bitumen upgrading to produce SCO; around 1.9 and 4.9 kg of H<sub>2</sub> are required to upgrade one barrel of in situ bitumen and surface-mined bitumen, respectively, to produce SCO. With that said, H<sub>2</sub> demand will exceed 0.02 million tonnes per day to meet the projected SCO production rate of 4.8 million bpd in 2030. While the principal H<sub>2</sub> production pathway – steam methane reforming (SMR) – involves significant amounts of greenhouse gas (GHG) emissions, there is a growing need to explore and examine environmentally sustainable H<sub>2</sub> production pathways. The Western Canadian Sedimentary Basin is not only endowed with enormous un-mineable coal reserves but also has favorable CO<sub>2</sub> sequestration characteristics. Considering the zero coal feedstock cost, underground coal gasification (UCG) along with carbon, capture, and sequestration (CCS) technology can be applied for sustainable development of the bitumen upgrading industry.

This study evaluates the environmental competitiveness of UCG-based H<sub>2</sub> against SMR-based H<sub>2</sub> for various scenarios in western Canada by implementing a life-cycle analysis (LCA). The LCA methodology was adopted to quantify the GHG emissions, and then calculate the CO<sub>2</sub> abatement cost in eight different H<sub>2</sub> production scenarios. These scenarios were developed to encompass four H<sub>2</sub> production pathways – SMR, SMR-CCS, UCG, and UCG-CCS – and two methods of CO<sub>2</sub> sequestration – enhanced oil recovery (EOR) and geological sequestration. The locations of the CO<sub>2</sub> sequestration sites were so chosen as to estimate the effect of CO<sub>2</sub> transportation distance on the GHG emissions and the costs and to put into perspective the current CCS projects in Alberta, i.e., Shell Canada's Quest and the Alberta Carbon Trunk Line. H<sub>2</sub> production from SMR without CCS was considered as the base case scenario for the comparative analysis. Furthermore, the impact of H<sub>2</sub> production scale on the overall results was studied.

#### **Common Sense Solutions for Management of Global Carbon Emissions**

Kimery C. Vories, E-Ternion: Energy, Environment, & Economy; J. D. Vories, UA-Grafix, USA

On April 13, 2012 and January 8, 2014, the U.S. Environmental Protection Agency (USEPA) proposed new regulations that amounted to a prohibition on the Best Technologies Currently Available for constructing new coal fired power plants. Instead USEPA would mandate that unless a coal fired power plant met the same carbon dioxide (CO<sub>2</sub>) emission levels as achievable with power plants utilizing Integrated Gas Combined Cycle (IGCC) combustion technology that in addition provided permanent sequestration of at least 25% of the CO<sub>2</sub> produced, it could not be built. This prohibition, like the historic prohibition of alcohol, is more likely to have negative rather than positive consequences.

This paper focuses on facts concerning fossil fuel utilization and its impacts upon global climate, the global economy, and the world population. It contrasts the impacts of current popular notions in the media and the regulations that govern our nation, that fossil fuels are an evil that must be stopped, versus the utilization of common sense to assess how to best use and advance currently available science and technology. It highlights best available control technology that could reduce the man made contribution of carbon dioxide in the atmosphere in a way that does not bankrupt the global economy and jeopardize the global population. It will assess the growth of renewable energy and project the number of generations that would be required to have them replace fossil fuel as an energy source.

The paper will compare the historical relevance of the impacts of the prohibition of alcohol in the United States from 1920-1933 that contributed to the rise of organized crime funded by the illegal trade in alcoholic beverages. It will examine this historic precedent on alcohol prohibition and contrast it with the probable result of government actions that seek to prohibit the production and use of fossil fuels. It will conclude that if existing proven technologies, such as those that are currently available for improving the efficiency and environmental performance of coal fired power plants were utilized worldwide, then coal power plant fuel efficiency would increase by 40% and the production of carbon dioxide would be reduced by another 40% for the remaining coal that is burned.

Any solution related to CO<sub>2</sub> reduction must evaluate its impact on the total supply of global energy which will directly impact the global economy. Solutions that are in effect a prohibition on any given energy commodity are not likely to find acceptance in the global economy without the introduction of affordable and available replacements. Given: (1) the world's current dependence upon fossil fuels (83% of the total) to run the world economy; and (2) the best projections for the reduction of this use by non-fossil fuels into any foreseeable future (a reduction of 6% in a 30 year generation); it would be extremely short sighted for the USA to not be in the forefront of nations with advanced technological knowhow to be: (a) systematically advancing currently available supercritical coal

fired boiler technology and (b) working on the development of promising new technologies such as the Integrated Gas Combined Cycle (IGCC) coal fired technology and carbon capture and sequestration technologies with the potential to increase the efficiency and environmental performance of coal fired electrical power plants so they could be made available to the rest of the world.

Since technological progress is evolutionary rather than revolutionary, prohibitions on resource specific technological progress as advocated by the USEPA will ultimately be interpreted by the public as the worst sort of policy proving grossly inadequate in limiting global CO<sub>2</sub> levels and promoting social injustice. Common sense would dictate that the USA place all of its efforts into promoting the systematic advancement of the best technologies currently available for improving the efficiencies and environmental performance of all energy resources, including fossil fuels, if we are to help the rest of the globe reduce CO<sub>2</sub> emission rates in a positive and significant manner.

#### **SESSION 47 Coal Science: General - 10**

#### **Upgrading Indian Thermal Coals Using Air-Table Dry Deshaling**

Nikhil Gupta, Robert Bratton, Gerald Luttrell, Virginia Tech; Thagata Ghosh, University of Alaska Fairbanks; Rick Honaker, University of Kentucky, USA

Coal preparation is relatively new to the Indian mining industry. Out of 555.32 million tonnes of total thermal coal production in fiscal year 2012-13, only 18.5% was beneficiated. Lack of beneficiation causes unwanted freight cost of ash-forming minerals, poorer thermal power plant efficiencies, and higher greenhouse gas emissions. Due to these reasons and the country's burgeoning energy gap, the Government of India has planned to build 15 new preparation plants providing an additional capacity of 93.6 million tonnes of upgraded thermal coal (Ministry of Coal, 2014). One potentially attractive technique for beneficiation is the air-table dry coal deshaling method. Dry coal deshalers have significant advantages over traditional wet

cleaning methods, such as elimination of processing water and waste slurries, reduction in transportation of mineral matters, and enhanced heating value. To evaluate the technique, a 5 tph pilot-scale air-table deshaler was tested at three different coal preparation sites in India for the specific purpose of upgrading thermal coals. The field test data indicate more than 90% combustible recovery can be achieved with a significant rejection of greater than 80% ash material from the run-of-mine (ROM) feed. A feasibility study based on the evaluation of the three test programs in India indicates that the technology can curb CO<sub>2</sub> emissions up to 5% with an improvement in power plant utilization efficiency by 1-3%.

#### **Site Selection for Coal Preparation Plant Using Analytic Hierarchy Process Method in Bursa, Turkey**

Seçil Çolpan, Turkish Coal Enterprises; Mahmut Yavuz, Eskisehir Osmangazi University, TURKEY

One of the common encountered problems in engineering applications is to determine the most convenient plant location. Selection of plant location is crucial for companies to minimize the cost and maximize the use of resources. The new plant site should be evaluated carefully for the competitiveness of companies. For this purpose, every potential criteria must be considered in selecting a particular plant location, including investment cost, human resources, availability of acquirement material, climate, etc. Therefore, choosing of plant location can be described as Multiple Criteria Decision Making (MCDM) problem. MCDM is one of the most considerable branches of Operation Research. MCDM refers to making decisions in the presence of multiple, usually conflicting, criteria. The problems in MCDM are classified into two categories: Multiple Attribute Decision Making (MADM) and Multiple Objective Decision Making (MODM). Analytic Hierarchy Process (AHP) is one of the well-known Multiple Attribute Decision Making (MADM) methods. The AHP method developed by Saaty gives an opportunity to represent the interaction of multiple factors in complex unstructured situations. This method is based on the pair-wise comparison of components with respect to attributes and alternatives.

In this study Analytic Hierarchy Process (AHP) model was presented to choose the plant location for coal preparation plant in coal mining industry. All criterias affecting the decision making process in coal industry was determined to solve plant location problem in the AHP model. To choose plant location for a new coal preparation plant is planned to install by Turkish Coal Enterprises located in the Orhaneli-BURSA region in Turkey, an analysis was performed using the AHP method according to expert opinion. Then solving the problem, sensitivity analysis was carried out on the results. AHP model outputs were evaluated and the most suitable location was proposed for coal preparation plant. The results show that AHP method can be used successfully for the selection of plant location as well as any decision making process in coal mining industry.

#### **Distribution of Sulphur Functional Groups in High Sulphur Bapung Coals of Assam**

Amritanshu Kumar, Theem College of Engineering; S.K. Srivastava, Central Institute of Mining and Fuel Research, INDIA

Studies for determination of sulphur functional groups present in Bapung coal of Assam State of North Eastern Region of India were carried out using Temperature Programmed Reduction (TPR) method. TPR studies were carried out in presence of Resorcinol and hydrogen gas to arrive at the final result. TPR studies on model sulphur compounds viz. L-Cysteine, synthetic rubber, Thiokol, having hydroxyl terminal groups, thioplast, pyrite with sand, and Garlic were carried out in order to assign various sulphur functional groups present in Bapung coal. Six numbers of hydrogen sulphide evolutions from Bapung coal were observed in the temperature range of 190 – 220°C, 260 – 290°C, 360 – 390°C, 460 – 490°C, 510 – 540°C and 590 – 620°C corresponding to mercaptan/ disulphide (0.20), Thiol (1.20), AromaticThioether (0.50), Thiophene (0.40), pyrite + part of complex thiophene (1.10), part of complex thiophene (0.30). The thioketonic sulphur in Bapung coal is estimated to be 0.30 using controlled nitric acid oxidation experiments.

#### **Producing Urea Fertilizer from Thar Coal Deposits in Pakistan**

Farid A Malik, FC College; Abid Aziz, Pak Motors Ltd, PAKISTAN

Thar coalfield is the biggest in Pakistan and is recognized as one of the largest in the world. The size as estimated by joint exploration of the geological survey of Pakistan and United States is around 175 billion tons at comparatively shallow depths (150 meters) but covered by aquifers.

Due to difficult hydrogeology, mining of the lignite has been a big challenge, no bulk samples are available. An ambitious plan has been formulated to build a semi-production mine to obtain bulk samples for gasification followed by Urea Fertilizer production either at mouth of mine or at the existing plant on the national gas pipe line grid. It will be the first fully integrated coal project of Pakistan where other clean energy applications like IGCC and FTD will also be evaluated.

#### **Development of Internal Surface Area During Pyrolysis and Combustion of Lignite**

Evan Granite, Elliot Roth, Sittichai Natesakhawat, Dennis Stanko, DOE/NETL, USA

The development of internal surface area during the pyrolysis and combustion of a powdered lignite coal was studied by using a small flow reactor. The BET surface areas, total pore volume, and average pore diameters of the chars formed were determined. The results have significant implications with respect to gasification and combustion of coals. The simple procedures employed in this study may also suggest means for forming inexpensive activated carbon sorbents.

#### **Kinetic Model of Coking Coal Fluidity Development**

Bartosz Mertas, Marek Sciazko, Aleksander Sobolewski, Institute for Chemical Processing of Coal, POLAND

When heated, coal undergoes chemical and physical structural transformations. These changes are of great interest, especially for coking coals, which exhibit a plasticizing phenomenon upon heating. This paper presents a fluidity model for coking coals to model this key phenomenon that occurs during the coking process.

The ability of coal to soften and cake is critical for coke production. Coke is currently the main raw material for blast-furnace crude steel production and will remain so for the near future. Coke quality is determined mainly by coal quality parameters; fluidity is one of these parameters.

This paper presents results of coal fluidity modeling from Gieseler plasticity measurements.

The following assumptions were made:

- Coal consists of melting (metaplast) and non-melting (inert) components.
- Fluidity depends on the amount of plasticized metaplast present.
- The amount of plasticized metaplast present is a result of parallel reactions melting and solidifying reactions.
- Melting and solidifying reactions are first-order.
- Fluidity is linearly dependent on volatile matter content.

Analysis was carried out on coals with a wide range of ranks (volatile matter content, V<sup>d</sup>, ranged from 16% to 32%) and fluidities (Gieseler maximum fluidity, F<sub>max</sub>, from 2 to 24042 ddpm).

The results of modeling were compared to experimental Gieseler fluidity measurements, and the correlation coefficients (R<sup>2</sup>) for almost all coals averaged 0,9, with a mean squared error (MSE) less than 0,5. These results indicate that the model predicts fluidity well. Additionally, kinetic results showed that, for fluidity modeling, first-order reactions can be described with an activation energy or a pre-exponential factor. Furthermore, the pre-exponential factor is linearly dependent.

With the additional assumption that the total metaplast amount can be approximated by the amount of volatile matter content in coal at the temperature that yields the maximum fluidity, it is possible to estimate the amount of plasticized metaplast in coal. These results all contribute to the understanding of coal fluidity.

#### **Binder Briquetting of Hard Coal Fines for Use in Smelting Reduction Processes**

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The availability of high quality coking coals is shrinking as a consequence of the rising production of steel, which in our days is based to 90 % on liquid hot metal produced by the traditional blast furnace process. The need for using good qualities of coke requiring huge amounts of these scarce coals in coke making thus has been and will be the motor of increasing prices. This fact is the origin for the development of alternative smelting reduction processes which has reached the state of reliable industrial plants like COREX® and FINEX®. The advantage of these processes is the usage of thermal hard coal which is available in a wide range of rank and at lower costs in comparison to coking coals.

For stable operation the COREX®/FINEX® process needs to be fed with coal lumps. But thermal hard coals usually contain 30 to 50 % fines which are not feasible for direct feeding into COREX®/FINEX® melter-gasifier. To make the substantial amounts of these fines suitable for the smelting reduction processes they have to be agglomerated using binder briquetting technology in an optimal manner.

This target has to be addressed by hard coal briquettes showing the mechanical strength required for handling as well as optimal process behaviour in COREX®/FINEX® melter-gasifier. To fit in these requirements the type and the optimal amount of binder is really important because both influence the briquettes properties. Besides this, binder type and amount are important economically factors, too. The work will give an insight in the major topics of current research and will

address the special problems with regard to methods for briquetting (e. g. optimal briquetting pressure and temperature as well as feasible grain size distributions of the feed), determination of briquettes quality (strength and process behavior). Data revealed from own investigations will be discussed with this regard.

For the experiments typical COREX®/FINEX® hard coals from deposits in Australia and South Africa are used. As binder various amounts of bitumen, molasses and polyvinyl acetate are applied and tested. Besides the pure mechanical properties of the briquettes like crushing strength, abrasion strength and shatter strength their behaviour under different heating conditions and atmospheres is investigated, too. In addition to these macroscopic quality determinations the changes of the microscopic briquettes structure after briquetting and different thermo-chemical exposure is investigated by spectroscopic methods.

For briquettes containing the binder molasses in combination with calcium hydroxide and water the best strength and also response to heating-up is observed. The binder bitumen produces also high strength but more problems while heating-up has been found. One reason for this effect is the different mode of action of film-type and matrix-type binders. Another reason is the different chemical composition and structure which leads to a good coking behavior of molasses which means the formation of a stable coke structure.

Acknowledgement:

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## SESSION 49

### Carbon Management: Storage of Carbon Dioxide - 2

#### Influence of Monitoring Intensity on the Cost of CO<sub>2</sub> Storage

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The United States (U.S.) Department of Energy (DOE) provides a worldwide leadership role in the development of advanced fossil fuel-based energy conversion technologies, with a focus on electric power generation with carbon capture and storage (CCS). As part of DOE's Office of Fossil Energy (FE), the National Energy Technology Laboratory (NETL) implements research, development and demonstration (RD&D) programs that address the challenges of reducing greenhouse gas emissions. To meet this challenge, FE/NETL is interested in better understanding the cost of storing carbon dioxide (CO<sub>2</sub>) in deep, saline geologic formations using currently available technologies. The cost of CO<sub>2</sub> storage will depend on: 1) the capabilities of technologies to track the evolving CO<sub>2</sub> plume and ensure retention of CO<sub>2</sub> in the storage complex; and 2) the requirements of regulatory agencies with regard to the application of these technologies. CO<sub>2</sub> storage in the U.S. is regulated by the U.S. Environmental Protection Agency (EPA) through the Class VI injection well regulations under the Underground Injection Control Program and Subpart RR of the Greenhouse Gas Reporting Rule. The intent of the regulations is to ensure the protection of underground sources of drinking water (USDWs) and monitor CO<sub>2</sub> to ensure its retention in the CO<sub>2</sub> storage complex. According to the Class VI regulations, CO<sub>2</sub> must be injected into saline formations that are overlain by a low permeability formation that will act as a seal (cap rock) and impede vertical movement of CO<sub>2</sub> and brine. These regulations require the operator of the CO<sub>2</sub> injection facility to monitor the evolution of the CO<sub>2</sub> plume in the storage formation and also monitor above the caprock to ensure retention of CO<sub>2</sub> in the storage complex (i.e., monitor deep formations above the caprock, monitor USDWs above the deep formations and monitor soil gas and the atmosphere above the USDWs).

This paper will summarize the capabilities of selected monitoring technologies to track the evolution of the CO<sub>2</sub> plume in the storage formation and monitor the presence of CO<sub>2</sub> and/or brine in deep formations above the caprock, monitor USDWs above the deep formations and monitor the soil gas and atmosphere above the USDWs. Example monitoring technologies include monitoring wells in the storage formation and above the cap rock, 2-D and 3-D seismic imaging, and vertical seismic profiling (VSP). These technologies will be combined in different ways to establish a variety of monitoring scenarios with each scenario providing a complete monitoring solution for the project. Because the capability of each monitoring technology is uncertain, each monitoring scenario will have a range of sub-scenarios that reflect different application intensities for each monitoring technology. For example, it may be the case that three monitoring wells in conjunction with 3-D seismic are sufficient to track the evolution of the CO<sub>2</sub> plume, so one sub-scenario would have three monitoring wells in the storage formation. However, it is also possible that more monitoring wells will be needed and the required number is a function of the anticipated areal extent of the CO<sub>2</sub> plume. Additional sub-scenarios will then be defined that have the number of monitoring wells specified as a function of the areal extent of the CO<sub>2</sub> plume. After the

monitoring scenarios and sub-scenarios have been established, the FE/NETL CO<sub>2</sub> Saline Storage Cost Model will be used to estimate the cost of storage for each scenario and sub-scenario.

To provide a point of reference, a zero-cost monitoring scenario will be defined where the cost of monitoring is assumed to be negligible and the cost of storage for this scenario will be determined. This zero-cost monitoring scenario is clearly implausible and unrealistic, but it will establish the lowest storage cost possible and allow the incremental cost of monitoring to be assessed for more realistic monitoring scenarios. The cost of storage for the various monitoring scenarios will be compared to each other and to the cost of storage for the zero-cost monitoring scenario. The influence of monitoring intensity for each monitoring scenario will also be presented. While FE and NETL are interested in the potential enhanced capabilities and cost reductions of advanced monitoring technologies, this analysis will be based on the capabilities and costs of existing monitoring technologies.

#### Utilization of Fluorinated Tracers to Monitor CO<sub>2</sub> Sequestration in Unconventional Reservoirs in Central Appalachia – Results from a Small-Scale Test in Morgan County, Tennessee

A. Kyle Louk, Nino S. Ripepi, Kray D. Luxbacher, Virginia Polytechnic Institute and State University; Ellen S. Gilliland, Michael E. Karmis, Virginia Polytechnic Institute and State University and Virginia Center for Coal and Energy Research, USA

Sequestering carbon dioxide (CO<sub>2</sub>) in unconventional underground reservoirs such as unmineable coal seams and organic shale formations can potentially mitigate greenhouse gas emissions while enhancing gas recovery within these formations. Enhanced gas recovery will not only add natural gas reserves throughout central Appalachia, but also extend the life of mature fields in this area. This paper discusses an overview of a small-scale ‘huff and puff’ injection of CO<sub>2</sub> into an organic shale formation in Morgan County, Tennessee, including the injection parameters, site descriptions, and utilization of fluorinated tracers to track CO<sub>2</sub> plume movement within the shale reservoir.

Approximately 500 tons of CO<sub>2</sub> was injected into a horizontal well located within the Chattanooga shale formation in Morgan County, Tennessee. Fluorinated tracers were also injected with the CO<sub>2</sub> to model plume movement within the underground reservoir by monitoring the arrival times and concentrations at offset wells. Sulfur hexafluoride (SF<sub>6</sub>), along with two perfluorocarbon tracers (PFTs), perfluoromethylcyclopentane (PMCP) and perfluoromethylcyclohexane (PMCH), were used as tracers for this project. Approximately 5,500 mL (0.574 kg) of SF<sub>6</sub> and 500 mL (0.85 kg) of PMCP were introduced within the first 50 tons of CO<sub>2</sub> injection to effectively simulate the initial plume movement through the reservoir, as well as compare the arrival times of the much smaller SF<sub>6</sub> versus PMCP. Later during the injection phase, 500 mL (0.89 kg) of PMCH were introduced once the total tons of injected CO<sub>2</sub> reached 300 tons. This allowed for a comparison between the arrival times of the similar PFTs at the offset wells at different phases of the injection. Injection of the CO<sub>2</sub>, along with the tracers, ended in mid-March 2014. The well will remain shut-in for a period between one to three months to allow the CO<sub>2</sub> to effectively adsorb to the shale. After this soaking period commences, the well will be flowed back into normal production.

A baseline study of the injection well, along with 13 offset wells, was conducted to analyze the gas quality as well as the concentration of naturally occurring CO<sub>2</sub> within the formation. Monitoring for increased tracer and CO<sub>2</sub> concentrations at the offset wells during the injection and soaking phase will determine communication from the injection well to the offset wells. During the flowback phase, gas quality and tracer concentrations will be monitored to account for enhanced gas recovery and desorption rates. Preliminary results from all three phases will be discussed including recent flowback results.

#### Pressure Data and Interference Testing at the Citronelle SECARB Phase III Site, Alabama USA

Hunter Jonsson, George Koperma, Jr., Advanced Resources International, Inc.; Rob Trautz, EPRI; Barry Friefeld, Lawrence Berkeley National Laboratory, USA

The Southeast Regional Carbon Sequestration Partnership (SECARB) Anthropogenic Test is a demonstration of the deployment of CO<sub>2</sub> capture, transport, geologic storage, and monitoring technologies. This project is the first and the largest fully integrated commercial prototype coal-fired carbon capture and storage project in the United States. This demonstration, which is primarily funded by the United States Department of Energy, Southern Company and Mitsubishi Heavy Industries and the Electric Power Research Institute, has reached a milestone of 100,000 metric tons (tonnes) of CO<sub>2</sub> injection and is in the second year of injection operations. Two Class V Experimental Injection Well underground injection control (UIC) permits were issued in November 2011 and the project's injection wells were installed shortly thereafter. A pressure data monitoring and interference testing regime has been developed and applied at the site as part of the project's robust Monitoring, Verification, and Accounting (MVA) plan to help in understanding the subsurface movement of CO<sub>2</sub> and the associated pressure field generated by the injection.

To monitor the CO<sub>2</sub> movement in the subsurface at various distances from the injection well, a new observation well was drilled and two existing oil field wells were converted to observation wells. Downhole memory readout gauges were placed in the converted observation wells and surface readout gauges were placed in the newly drilled observation well, respectively. Two gauges are installed in each well (primary and backup) and are used to collect formation pressure and temperatures. The new observation well and one of the converted wells is perforated in the CO<sub>2</sub> storage formation, allowing for in-zone pressure interference testing. The second converted observation well collects bottom hole pressure and temperature data from a porous zone lying directly above the storage interval's primary confining unit. Spatially, these data are collected in close proximity (870 feet to east) to the injection well and at some further distance (3,100 feet to the northwest) from the injection point. These downhole pressure data have proven to be a useful monitoring tool to observe the impact of the CO<sub>2</sub> injection as well as for refining the modeling efforts through injection history matching.

When the pressure and temperature data is paired with injection rate data, the observation wells also provide the opportunity to conduct interference testing. Interference testing is a well-testing analysis method used to interpret the pressure variations at an observation well based upon injection rate data from the injection well. Standard pressure transient testing techniques allow the analysis of this pressure behavior in order to determine estimates of the formation's intrinsic permeability, how this permeability changes over time and also to determine the degree of communication across parts of the reservoir. This can, in turn, be used to validate or make improvements to the injection program as well as to improve the numerical history matching. The operational impact of intermittent injection and shut-in periods at the SECARB Test Site, due primarily to maintenance and dispatch demands, provided for multiple injection and pressure falloff periods for well test interpretation. These opportunities provided enhanced interference testing data points to observe changes over time that may be a result of the injected CO<sub>2</sub> volume. This paper will discuss the operational implications of the methodology as well as share data and interpretation results to date.

#### **Nondestructively Determining the Microstructure Evolution of Central Appalachian Basin Coals Through Carbon Sequestration**

Joseph Amante, Nino Ripepi, Virginia Polytechnic and State University, USA

This research demonstrates capabilities of microfocus X-ray computed tomography ( $\mu$ CT) in characterizing the development of coal porosity, fractures, and permeability of Central Appalachian Basin coals. The main focus is to quantify the dissolution of calcite in the cleat structures through the introduction of carbonic acid, which can occur from the addition of carbon dioxide for advances in gas recovery and sequestration. The aperture, spacing, spatial distribution of fractures, and mineral morphology are semi-quantitatively evaluated by  $\mu$ CT using a computer-aided design. The slicing analyses of coals demonstrated that distributions of cleat porosity in individual coals are highly anisotropic in terms of cleat aperture, cleat fillings, and general structure that are not correlated to the depth or location of the seam. The spatial disposition of cleats, pores, fractures, and minerals is the most important factor that influences coal porosity and permeability with various samples showing advanced stages of mineralization of both calcite and silica. In spite of the limitation in size of the scanning area, the high spatial resolution of  $\mu$ CT scanning has major advantages in nondestructive detection and 3D visualized characterization of pore space, fractures, and minerals compared to traditional methods. Scanning electron microscope is used in conjunction with  $\mu$ CT scanning to verify the results before and after the impregnation of the carbonic acid in select coal samples. This data is rendered in *Avizo Fire*® to calculate cleat porosity (open and closed), permeability, and possible calcium transfers in the coals. This software is used to visualize the material microstructure evolution of the coal at various pressures with various concentrations of carbonic acid.

#### **SESSION 50 Shale and Coal Bed Gas: General - 3**

#### **Development of the First Internationally Accepted Standard for Geologic Storage of Carbon Dioxide Utilizing Enhanced Oil Recovery (EOR) Under the International Standards Organization (ISO) Technical Committee TC-265**

Steven M. Carpenter, George Koperna, Jr., Advanced Resources International, Inc., USA

The Carbon Capture Utilization & Sequestration (CCUS) marketplace is lacking standardization and therefore the ability to allow CCUS projects to be advance as Clean Development Mechanism (CDM) projects as well as to advance to full scale commercialization. An international effort between the United States and Canada, funded by and the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide (IPAC-CO<sub>2</sub> 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 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.

International Organization for Standardization (ISO) Technical Committee (TC) 265, Carbon dioxide capture, transportation, and geological storage, recently announced the creation of a new working group (WG 6, CO<sub>2</sub> EOR) focused on standardization in connection with enhanced oil recovery (EOR)-related carbon dioxide (CO<sub>2</sub>) storage.

The new working group will focus on standardization efforts associated with low-pressure subsurface oil field operating environments and related CO<sub>2</sub> recovery operations, as well as the harmonization of CO<sub>2</sub> supplies with EOR operations both on a daily basis and over multi-year operational horizons, among other topics. Additionally, the working group must address buffer storage and plans to continue the international call for expert participation in its development of standards and other documents related to CO<sub>2</sub> EOR.

ISO TC 265 was first established in 2011 with a focus on advancing standardization in connection with CCS worldwide, including the development of related standards, technical specifications, and technical reports. Since its creation, the following WGs have been established to support the development of these documents:

WG 1, Capture – Carries out standardization work in connection with pre-combustion, post-combustion, and oxyfuel combustion capture, as well as the separation, purification, compression, pumping, and liquefaction of CO<sub>2</sub> streams, among other related topics.

WG 2, Transportation – Develops documents related to the transportation of captured CO<sub>2</sub> by rail, truck, or ship, as well as relevant health, safety, and environmental issues related to its transportation.

WG 3, Storage – Focuses on standardization work associated with the storage of captured CO<sub>2</sub> in saline aquifers and depleted hydrocarbon reservoirs, including site selection, construction, risk assessment, storage monitoring and storage leaking avoidance.

WG 4, Quantification & verification – Develops standards and other related documents associated with the monitoring and verification of CO<sub>2</sub> capture and storage, including subjects such as CO<sub>2</sub> quantification procedure, third-party verification, and relevant detection limits.

WG 5, Crosscutting issues – Focuses on standardization in connection with CCS-related risk management, reporting, terminology, and public engagement, along with other related topics.

This paper will address key issues experienced in the standard development process, which is a technical, consensus-based facilitated process. Membership of the Committee is drawn 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.

#### **Developing Porosity with a Neural Network Application for Geologic Modeling in an Active Oil Field (EOR)**

Hunter Jonsson, George Koperna, Jr., Advanced Resources International, Inc., USA

Permanent geologic storage of CO<sub>2</sub> requires its sequestration into the available pore space of subsurface reservoirs. Numerous research and development projects, both small and large scale, have been undertaken as part of the Department of Energy's (DOE) Carbon Storage Program, a comprehensive push to develop CO<sub>2</sub> sequestration into a commercially viable effort to reduce greenhouse gas emissions. As research moves forward, strategies to optimize these efforts have become increasingly important to take full advantage of the sequestration technology by improving its effectiveness and reducing the cost of implementation. The selection of a storage site with appropriate subsurface characteristics is vital to ensure the success of any geologic storage undertaking and maximize the volume of CO<sub>2</sub> sequestered. Site selection is based on a variety of criteria, but includes modeling efforts used to estimate reservoir storage potential. This project utilizes an artificial neural network to develop field wide reservoir porosity estimates to aid in the development of a highly detailed geologic model of the Citronelle Dome in southern Alabama, USA.

To build this model, this project relies on field data collected as part of the SECARB partnership's Anthropogenic Test, currently underway in the area. This demonstration, a fully integrated, large-scale storage project, has acquired large amounts of geologic data both prior to and through the monitoring of injection operations. This data includes historical electric log data, limited modern geophysical well log suites, core data, seismic surveys, and downhole pressure and temperature measurements. Detailed porosity of the field, a critical element of geologic modeling, is not widely available due to the age of the formation evaluation tools available at the time of initial field development. Electric log data throughout the field is limited to spontaneous potential (SP), induction (ILD), and short normal (SN) measurements. There are limited modern porosity measurements in a small section of the field, where the three SECARB wells were drilled. In order to obtain the field-wide porosity data needed to construct the model, this project takes advantage of an artificial neural network technology approach.

An artificial neural network is a computational model that uses machine learning to develop pattern recognition. The learning algorithm can be trained using a representative sample set of paired inputs and outputs that establish the interconnected weighting factors, or nodes, used to make predictions. When training is complete, a predicated, synthetic dataset can be developed based on other related input data. In this case, the modern porosity measurements from two of the three SECARB wells were paired with the localized vintage SP, ILD, and SN electric log data to develop a training set. The network was trained and porosity data was generated at the third SECARB well and compared against the modern porosity data collected at that location as validation of the training (e.g. history matching). When the training results were satisfactory, predicated porosity was generated at multiple points throughout the field. Utilizing this process and data, porosity isopach maps were generated to further develop the porosity behavior to feed into the geologic model.

Accurate and useful geologic models rely on the quality of the data used to characterize the reservoir. Obtaining this data is an expensive proposition during the preliminary site selection stage of a geologic storage project. However, utilizing an artificial neural network to leverage existing and available historical data with only limited amounts of modern and expensive logging operations has proved to be a useful when developing a detailed geologic model of a potential storage site.

#### **Variation in Mudrock (Shale) Geologic Parameters Across the Northern Appalachian Basin, USA**

Timothy R. Carr, Shuvajit Bhattacharya, Liaosh Song, West Virginia University, USA; Guochang Wang, University of Chinese Academy of Sciences, CHINA

In the last ten years, tremendous progress has been made in the exploration and development of unconventional gas worldwide, especially in North America. The application of horizontal drilling and hydrological fracture stimulation technologies provide economic gas flow in extremely low porosity and permeability reservoirs. In the northern Appalachia basin in the eastern United States of America, the organic-rich shale units the Ordovician Point Pleasant-Utica and Middle Devonian Marcellus Shale are some of the most active shale gas/oil plays in the world.

To date, successful mudrock plays have been primarily a function of drilling intensity and cost reductions and application of new technology (e.g., steerable rotary bits). Understanding of key reservoir engineering and geoscience parameters has lagged and represents an important area that can contribute to improved well architecture and optimal lateral placement. Changes in mudrock reservoir properties have been mapped across the Appalachian basin and can strongly influence productivity. Important mudrock reservoir properties include; the distribution of organic content, the "fracability" of the unit (mineralogy and containment), structural discontinuities (faults), the present and past stress regimes, and the thermal maturity. In addition to dictating type of hydrocarbon fluid or gas present, thermal maturity has a critical influence on the development of the reservoir porosity and permeability system.

Recently, established classification systems of pore size and structure for the Point Pleasant-Utica and Marcellus are compared considering types of gas storage, flow and production of reservoirs. The goal is to understand pore structure in mudrock reservoirs in order to evaluate the reservoir and predict the storage capacity and productivity. Migration of hydrocarbons from the matrix to the well bore is investigated from a geologic perspective and can have significant impact on productivity in numerous mudrock reservoirs.

#### **Sensitivity Analysis of Stimulated Reservoir Volume Parameters for Modeling CO<sub>2</sub> Injection into a Horizontal Shale Gas Well in Tennessee**

Cigdem Keles, Nino Ripepi, Virginia Tech, USA

When carbon dioxide is injected into organic rich shale formations, similar to coal, they desorb methane while adsorbing carbon dioxide. Injecting and storing carbon dioxide in shale formations decreases greenhouse gas emissions while at the same time can enhance the recovery of methane. Shale formations are normally low permeable reservoirs and methane production or carbon dioxide injection can be increased by the creation of fracture networks in the formations through hydraulic fracturing. This stimulated reservoir volume (SRV) is generally estimated based on microseismic data. A small scale injection test has been recently completed in order to examine the injectivity and the adsorption of CO<sub>2</sub> in to an unconventional shale reservoir in Morgan County, Tennessee. Approximately 509 tons of carbon dioxide was injected successfully in a thirteen-day period in March 2014 into a hydraulically fractured horizontal well. Due to the lack of microseismic data for this well, the volume of the stimulated reservoir was unknown. When microseismic data is not available, numerical modeling can help determine the size of the SRV.

In this paper, reservoir and production data of the horizontal well was used to perform a sensitivity analysis on SRV parameters. For this purpose, the grid refinement of the SRV, the permeability of the fracture network and dimensions of the stimulated volume were changed in reservoir models. This included changing the half-length of the fracture network, the number of layer formations in the SRV and the width of each stimulated stage. This study will use a sensitivity analysis to identify the most important parameters for matching the gas and water production, and the bottom-hole pressure of the wellbore.

### **SESSION 51 Gasification: General - 4**

#### **Characterization of Fine Particulate Material from Syngas in a Pilot Scale Entrained Flow Oxygen Blown Coal Gasifier During Two Stage Gasification**

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In this study, a high sulfur, low ash petcoke/coal blend was gasified in a pilot scale, pressurized, oxygen blown, slurry fed entrained flow gasifier to generate fine particulate representative of material which deposits on the convective syngas coolers in industrial IGCC plants. As far as the authors are aware, the characteristics of fine particulate material depositing on the syngas coolers have not been investigated previously.

The pilot scale oxygen blown, slurry fed entrained flow coal gasifier has a maximum thermal load of 600 kW<sub>th</sub>. The gasifier consists of reaction section, pre-quench section and water quench section. The gasifier is approximately 24 feet in height. Reaction zone is 5.3 feet in length and 0.33 feet in diameter.

The experiments were carried out at a pressure of 200 psi and temperatures between 2400-2800 °F. The solids content of the slurry was 51% wt. The fine particulate generated during gasification reactions were captured by a filter located downstream of the gasifier. The deposits were submitted to computer controlled scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) analysis. The results showed that, deposits were very rich in metallic elements. Si, Al, Ca, Fe were the dominant elements. For petcoke/coal blend, V, and Ni were also present in significant amounts. The two metals are believed to play major role in deposit formation on syngas cooler surfaces where petcoke is used in appreciable amounts. The internal surface area of the deposits were determined using N<sub>2</sub> adsorption. The internal surface area of the deposits turned out to be fairly high. In order to get more accurate chemical elemental analysis of the particles generated and captured, ICP-OES analysis was conducted. ICP-OES is a well established method to analyze elemental composition of sediments, coal, coal fly ash since 1990s. An acid matrix consisting of concentrated HCl, HF, H<sub>2</sub>O<sub>2</sub>, and HNO<sub>3</sub> was used to dissolve the particles.

#### **The Analysis of Hybrid Scheme of Steam-Gas Technologies on IGCC Low-Calorie Gases**

Tatyana Bogatova, Alexandr Ryzhkov, Sergey Gordeev, Nikolay Abaimov, Nikolay Valtsev, Ural Federal University, RUSSIA

Combined-cycle power plants with IGCC are one of the most advanced and actively developed approaches of coal usage around the world. However, low thermal effectiveness and low availability factor in comparison with gas-fueled plants limit widespread deployment of steam-gas plants with IGCC. The hybrid principle of working substance preparation for steam-gas plant can become a working solution. The analysis of hybrid scheme of PGU-IGCC with receiving synthesis gas in a gas generator according to the two-level scheme, with high-temperature heating of compressed air (800-1000°C) for coal conversion in the gasifier and for burning syngas in GT with an opportunity for hot gas purification (at 550°C), shows that this technology helps solid-fuel steam-gas plant catch up with gas-fueled steam-gas plant in thermal efficiency and availability factor. When viewed from an environmental perspective, hybrid system is in-between gas- and coal-fired power, allowing the emission rate to be significantly reduced (by about two times) than conventional coal-fired systems.

The application of the hybrid scheme allows to cut by half approximately also a gap in energy efficiency between conventional IGCC and gas-fired plant. This is determined by the following major factors. The comparison of IGCC and hybrid coal-fired PGU indicates that possibility of optimum distribution of the brought in gas and steam cycles warmth, are limited in IGCC to need of branch of a large amount of the warmth, which is produced in the complete coal gasification process, to the steam-turbine cycle. The warmth, which is taken away in a gas cooler, in the hybrid scheme of PGU is much less because use of hot blasting allows to cut specific fuel consumption as a result of multiplicative effect of economy of fuel both in a gas generator, and in the gas turbine. Decrease in fuel consumption and, respectively, production of synthesis gas leads to reduction of loading by system of gas purification and thermodynamic losses in it. The other factor, increasing the net efficiency, is opportunity to increase inlet temperature. Nowadays the leading gas turbines producers are conducting research work on inlet temperature increase up to 1500-1700°C, including using syngas in IGCC. However, the turbine inlet temperature increase is followed by the increase in local combustion temperature and emission of NO<sub>x</sub>. The other serious problem of working at high temperatures is lack of air to cool a combustion liner and combustion products dilute as gas inlet temperature increases. According to Japanese scientists such limitation appears when the syngas temperature is over 1500°C.

To overcome the mentioned challenges a range of technologies is used. The most effective are steam and nitrogen injection, combustion products recirculation or fuel and air pre-mixing. Lack of air needed for cooling down the gas turbine elements may be compensated by steam cooling. The measures mentioned above have some well-

known economic and maintenance drawbacks. The possible way out is gas turbine running on low-calorie gas with a low coefficient of excessive air and low theoretical combustion temperature served to reduce thermal  $\text{NO}_x$ . Gases with  $Q_i^d=3-7\text{MJ/m}^3$  and less are obtained in air and vapour-air conversion of low-quality fuel. While such gases burning under standard technologies the problem of flame stabilization arises. Leading power engineering companies worldwide are carrying out R&D activities to overcome syngases combustion problem in gas turbine installation and steam-gas plant. Driven by leading companies (Siemens, GE, MHI) steam-gas plant running on syngases produce over 400MW at full capacity and its fuel gas lower range limit is about 3-4  $\text{MJ/m}^3$ . Proposed hybrid steam-gas plant with high-temperature air heating and established methods will create a sound basis for the use of different syngas types. Such concepts will lead to abandonment of flame stabilization equipment (i.e. pre-ignition chamber) as well as kinetic combustion schemes and will meet environmental regulations. Redistribution of thermal loading from syngas to pre-heated air will be highly efficient measure to reduce air intake limitations on flame tube cooling along with combustion products dilution. The carried-out analysis of the hybrid scheme of PGU shows that air will be enough for cooling of gases before GT up to the temperature of 1700°C. Implementation of high-temperature heating of cyclic air before giving in the combustion chamber will allow to solve problems of stabilization of burning in the GT combustion chamber and to lower requirements to the caloric content of fuel gas that allows to refuse admixture to poor gases of an additive of natural gas, simplifies system of gas-preparation and introduces into economic circulation extremely poor gases, not used earlier, with  $Q_i^d<3-7\text{MJ/m}^3$ .

**SESSION 52**  
**Sustainability and Environment: General - 2**

**A Field Evaluation of Alternate Coal Processing Waste Management Technology**

Liliana Lefticariu, Paul T. Behum, Yoginder P. Chugh, Southern Illinois University,  
USA

Previous investigations have identified coal processing and refuse disposal areas as a significant sources of elevated sulfate and chloride derived from the weathering of coal waste, which triggered greater restrictions on water quality standards for these facilities to protect aquatic life. Coal processing waste has increased with mining thinner seams under more difficult mining conditions. Slurry impoundments and coal processing waste disposal areas are costly, difficult to permit, and may be a long-term liability due to stability concerns and sulfate discharges.

The main objective of the proposed study has been to demonstrate that co-disposal of coarse coal processing waste (CCPW) and fine coal processing waste (FCPW) could provide both the geotechnical stability needed to lower refuse facility liabilities and the geochemical environment necessary to minimize sulfate discharges. Authors will present the results of a 15-month study of field-scale column leaching experiments and geochemical testing performed to determine the sulfate, chloride, and associated metal leach rates of a simulated combined coal refuse disposal area. In addition, a small amount of low-cost limestone sand added the mixture could further increase refuse fill stability by lowering moisture content. Furthermore, the added limestone has the potential to greatly improve refuse chemistry by alkalinity addition. The results of this research are used to develop and implement innovative concepts for engineered co-management of FCPW and CCPW. Our approach has the potential to greatly reduce the rates of coal and pyrite weathering and, thereby, minimize sulfate discharges into the environment.

**Design of Frustrated Lewis Pair Functionalized Metal Organic Frameworks for  $\text{CO}_2$  Capture and Conversion**

Jingyun Ye, Karl Johnson, University of Pittsburgh, USA

The combination of  $\text{CO}_2$  capture and conversion is an attractive strategy which is of great environmental and economical importance in treatment of greenhouse gases. Metal organic frameworks (MOFs) are a class of crystalline microporous hybrid materials with an extended 3D network which have been widely studied in near decade due to their large surface areas, tunable porous structures, desired functionality, and promising applications in  $\text{CO}_2$  capture. Because of their structural and functional tailorability, we use density functional theory (DFT) methods to design functionalized MOFs that are capable of chemically binding and hydrogenating  $\text{CO}_2$ . We employ UiO-66 as our starting base material because it is a MOF that has chemical and thermal stability, is highly selective toward  $\text{CO}_2$  and can be modified (functionalized) post-synthetically. We design functional moieties for  $\text{CO}_2$  hydrogenation based on frustrated Lewis pairs (FLPs) because these have been shown to be very active for chemisorption of  $\text{CO}_2$  and the heterolytic dissociation of  $\text{H}_2$ . One candidate FLP is 1-[bis(pentafluorophenyl)boryl]-3,5-di-*tert*-butyl-1H-pyrazole, denoted **1**. We have developed a family of functional groups based on a modified version of **1**, denoted **2** which is built by replacing two (pentafluorophenyl)boryl ( $-\text{C}_6\text{F}_5$ ) groups at site 1 with  $-\text{BF}_2$  and one *tert*-butyl ( $-\text{C}(\text{CH}_3)_3$ ) group at site 3 with H, another at site 5 with  $-\text{CH}_3$ .

Structure **2** has both Lewis acid and base sites embedded within the molecule but has much less steric hindrance than the FLP **1** because internal steric hindrance is not needed once the Lewis pair moiety is chemically bound within a MOF. We have examined the properties of UiO-66 functionalized with derivatives of **2**. We have replaced the  $\text{BF}_2$  group on **2** with the following moieties:  $-\text{BH}_2$ ,  $-\text{B}(\text{CN})_2$ ,  $-\text{B}(\text{CF}_3)_2$ ,  $-\text{B}(\text{NO}_2)_2$  and  $-\text{AlCl}_2$ . We computed the electronic structure, charge distribution, and  $\text{CO}_2/\text{H}_2$  binding energies and found that chemisorption of  $\text{CO}_2$  and dissociation of  $\text{H}_2$  are both energetically favorable with many of the functional groups. We have also investigated UiO-66 having two functional groups per cell in order to provide both  $\text{CO}_2$  binding sites and  $\text{H}_2$  dissociation sites in close proximity. We have identified possible scenarios for  $\text{CO}_2$  hydrogenation through an enzyme-like pathway where one of the functional groups in the pore binds and activates  $\text{CO}_2$ , while the second functional group heterolytically cleaves  $\text{H}_2$  and supplies the resulting hydride and proton to the activated  $\text{CO}_2$ .

**SESSION 53**  
**Coal Science: General - 11**

**Effect of Rapid Heating Extraction of Coal in Hyper-Coal Production Process**

Koji Sakai, Shigeru Kinoshita, Takuya Yoshida, Noriyuki Okuyama, Maki Hamaguchi, Naoki Kikuchi, KOBE STEEL, Ltd., JAPAN

Hyper-Coal (HPC) is produced by coal solvent-extraction using 2-ring aromatic solvent. HPC has excellent thermoplasticity and large potential as caking additive to make strong coke. The yield of HPC depends on the coal solubility to solvent because HPC is the soluble component of coal. Therefore, it is important for HPC production process to increase the rate of extraction. The coal dissolution takes place by thermal relaxation of molecular cohesion structure by heating whereas high temperature condition would enhance polymerization, causing decrease of coal extraction yield. However, rapid heating during solvent extraction is thought to prevent polymerization and increase solubility of coal.

In this study, we focused on the extraction heating rate condition. In conventional method, after coal and solvent are mixed, the slurry is heated. In this method, the heating rate is lower than 100 K/min. In order to increase the heating rate solvent is heated to higher temperature than the extraction temperature beforehand, and coal is thrown into high temperature solvent. The latter method enables to increase the heating rate at >1000 K/min, and the consequent coal extraction yield increased with increasing the heating rate. The property of HPC produced by rapid heating is difference from that with conventional method.

**Strength and Reactivity Control of Metallurgical Coke Using Coal Derived Caking Additive**

Takuya Yoshida, Koji Sakai, Noriyuki Okuyama, Maki Hamaguchi, Naoki Kikuchi,  
KOBE STEEL, Ltd., JAPAN

Kobe steel has developed a coal solvent extraction process, the product of which can be used as a caking additive (High Performance Caking additive: HPC) in metallurgical coke making processes, as well as clean ash-free fuel, carbon feedstock for electrode production, etc. It had been revealed that HPC can enhance coke strength by adding expansibility to coal blend during coal carbonization process and our recent achievements are coke strength improvement by grain refining together with HPC and development of coke reactivity control method. The key function can be explained by a concept of void filling ability.

The results of this study indicate that grain refining of coal feedstock can enhance resulting coke strength as high as  $\text{DI}^{150}_{15}=89.7$  when the coal feedstock contains strongly caking coal more than 55%. By contrast, grain refining can have negative effect on coke strength when the coal blends contain caking coal less than 41%. Moreover, by blending HPC to the coal blends that contain strongly caking coal less than 41%, coke strength can be improved as high as  $\text{DI}^{150}_{15}=90.4$ . These results suggest that coke strength has been improved because HPC increase caking component in coal blends with high content of slightly- and non-caking coal.

As for the reactivity of coke grain refining of feed coal results in high reactive coke, which could be explained by content of ash component and its distribution in the coke due to grain refining.

**Role of Water on Oxygen Consumption of Brown Coal at Low Temperature**

Toshinori Inoue, Kobelco Research Institute Inc.; Maki Hamaguchi, Toru Higuchi,  
Naoki Kikuchi, Takuo Shigehisa, KOBE STEEL Ltd.; Haruo Kumagai, Hokkaido  
University; Takayuki Takarada, Gunma University, JAPAN

Oxygen consumption of a brown coal at low temperature is accelerated by an addition of water. In order to gain a better understanding of the mechanism, oxygen consumption of an Indonesian brown coal was examined after treatments with several



kinds of chemicals. When the coal was treated with vapor of polar solvents such as acetone, the oxygen consumption at 30 °C remarkably increased compared to that of non-treated coal. Similar behavior was observed for the coal treated with calcium hydroxide (Ca(OH)<sub>2</sub>), which broke a part of hydrogen bonds in the coal. Acceleration of the oxygen consumption by these treatments is probably attributed to the relaxation of the macromolecular structure of the brown coal in addition to chemical mechanisms which have been conventionally proposed. These results suggest that oxygen consumption of a brown coal is accelerated by the exposure of latent active sites through the relaxation of the coal structure by watering.

#### **Production of Carbon Fiber from the Low-Molecular-Weight Compounds Prepared from Low Rank Coal and Biomass by the Degradative Solvent Extraction**

Kouichi Miura, Ryuichi Ashida, Kensiro Okuda, Hideaki Ohgaki, Kyoto University; Osamu Kato, Kyushu University, JAPAN; Janewit Wannapeera, King Monkut's University of Science and Technology, THAILAND

The authors have recently proposed a novel degradative solvent extraction method that dewater and upgrades low grade carbonaceous resources such as low rank coals and biomass wastes into clean products at around 350 °C in a nonpolar solvent. The raw materials are decomposed to be deoxygenated and extracted by the solvent to be separated into upgraded coal (UC), high molecular weight extract (Deposit), and low molecular weight extract (Soluble). The properties of Solubles produced from various raw materials are almost independent of raw materials: the average molecular weights are 350 to 370, the average contents of carbon, hydrogen, and oxygen are C = 80 to 83 %, H = 6.5 to 7.5 %, and O = 8 to 11 %, the ash contents are less than 1.1 %. In addition Solubles completely melted below 100 °C.

Carbon fiber was intended to be prepared by utilizing the unique properties of Soluble. Soluble obtained from a rice straw in the yield of 56 % on carbon basis was used as the raw material. First, the Soluble was film distilled at 180 to 220 °C to remove 10 to 15 % of small molecular weight compounds, which increased the softening temperature of the Soluble up to 250 °C. The treated Soluble was spun by a mono-hole continuous spinner. The spun fiber was stabilized in an air stream by heating it up to 300 °C at the heating rate of 1 °C/min, then the stabilized fiber was carbonized in a nitrogen stream at 800 °C to form carbon fiber. The carbon fibers produced were 9 to 13 μm in diameter and had tensile strength over 800 MPa. These preliminary examinations showed the possibility of utilizing Solubles as raw materials of carbon fiber for general purpose.

#### **SESSION 54 Coal Science: General - 9**

#### **The Transient Swelling Behaviour of Large South African Coal Particles during Low-Temperature Devolatilisation**

Sansha Coetzee, Hein W.J.P. Neomagus, John R. Bunt, Christien A. Strydom, North-West University, SOUTH AFRICA; Harold H. Schobert, Penn State University, USA

Coal particle swelling results in the formation of chars having different structures. These, consequently, influence char combustion and gasification, as well as ash formation. Therefore, the understanding of the plastic behaviour of coal can assist in predicting coal behaviour under specific operating conditions, and is also critical to improve and develop coal conversion technologies. Thus far, studies investigating the devolatilisation behaviour of coal, specifically the swelling behaviour, have mainly focused on pulverised coal samples, while millimetre-sized coal particles have occasionally been utilised in studies concerning fluidised bed combustion. Previous studies have included the comparison of coals and chars before and after devolatilisation, and only limited research has been conducted on the transient behaviour of large coal particles during devolatilisation.

The aim of this study is to investigate and quantify the swelling behaviour of large coal particles (-20+16 mm) during low-temperature devolatilisation (< 700 °C). Three South African coals, with varying swelling characteristics, were selected for this investigation. Coals TWD and GG are both medium rank-C bituminous coals with Free Swelling Index (FSI) values of 0 and 6.5, respectively. Coal TSH is a medium rank-B bituminous coal with an FSI of 9.

Various methods were used to describe the swelling behaviour of the large coal particles. Single coal particles were devolatilised (from ambient to 700 °C at 7 °C/min) in a Carbolite AFT furnace equipped with a video camera, and the transient swelling behaviour of the coal was continuously monitored. The images captured during devolatilisation were analysed using image analysis, in order to describe the swelling behaviour of single particles during devolatilisation, as a function of temperature. X-ray computed tomography (XCT) and mercury submersion were used to analyse particles before and after devolatilisation, to determine the degree of swelling (volumetric swelling ratio).

While the FSI, dilatometry and Gieseler results did not indicate any plastic behaviour for the TWD sample (-212 μm), the large particles did exhibit a significant degree of swelling during devolatilisation. It was also observed that the GG and TSH large coal particles started swelling at a slightly lower temperature than the initial softening temperature obtained with dilatometry for the -212 μm coal particles. It was found that image analysis can be used to qualitatively describe the swelling behaviour of large coal particles during devolatilisation, while both the XCT and mercury submersion methods can be used to accurately quantify the volumetric swelling ratio of large coal particles. From the observed variance in swelling behaviour between the TWD powder and large coal particles, it is hypothesised that the FSI, and other conventional techniques used to describe the swelling and fluidity of small particles of coal, can in general not be used for the prediction of large coal particle swelling.

#### **Discussion of the Cross-Braced Briquette Plug Applicability for the Lock-Free Pressurized Gasifier Feeding**

Alexander Rosin, Hans-Werner Schröder, Jens-Uwe Repke, Institute of Thermal, Environmental and natural Products Process Engineering, GERMANY

One challenge by the development of novel gasifiers operating at high pressures (up to 65 bar) is the construction of proper continuous working lock-free feeding systems for brown coal without obstacles of the currently used feeders. The currently used feeding systems are designed for a maximum pressure level of approx. 35 bar and operate discontinuously using locks. A new developed feeding system has to achieve a higher pressure level without using the locks. The required gas tightness of the lock-free transport channel between the feeding system and pressurized gasifier can be achieved using a briquetting press, which creates a plug with sufficient density and cross-bracing by compression of the brown coal. The analysis of different technical solutions taking into account a high transport pressure, continuous operating mode and high throughput reveals the briquetting press for brown coal as a potential alternative comparing to currently used feeding systems. Prior to the studies of the briquetting press a series of fundamental studies on a specially constructed experimental apparatus were performed. The aim of these studies were to understand how the sealing of a transport channel with briquettes works and in which areas of the plug the gas flow is expected. The results showed that the gas flow occurs directly through the porosity of the briquettes and also in the region between briquettes and the transport channel wall. For this reason, a successful sealing of a transport channel can be achieved if the briquettes have a dense structure with the lowest possible porosity and if a sufficient cross-bracing of the briquettes in the transport channel is guaranteed. Additionally the different brown coal sorts have a various briquetting behavior, the adaptation of the press channel geometry to the particular type of coal is essential. The press channel geometry is decisive also for the level of the briquette cross-bracing. From the extraordinary importance is the measurement of the gas diffusion rate through the briquette structure and determining the optimal briquetting parameter constellation to keep this diffusion rate as low as possible. The fundamental studies with the test rig are used for the modification of the classical briquetting press for the function as feeding system. The tests on the modified briquetting press applying the results from the basic studies on the test rig are serving for adjustment of the briquetting press operating parameters to ensure a stable operation briquetting pressure without large fluctuations over the time. At this point, the optimal setting of the operating parameters as briquetting velocity, speed of screw feeders and cooling water flow rate are of significance. After adaptation of material and operating parameters to the specific types of coal and press channel geometry, feeding tests into the pressurized vessel are carried out. In this presentation, the basic research on the test rig and the feeding experiments into a pressurized vessel by means of a briquetting press with variation of the operating parameters and raw materials are explained in more detail.

#### **Influence of the Rapid Heating Process on Coal Extraction Yield and Properties**

Noriyuki Okuyama, Koji Sakai, Shigeru Kinoshita, Takuya Yoshida, Maki Hamaguchi, Naoki Kikuchi, KOBE STEEL, Ltd., JAPAN

A coal extract, produced by thermal extraction and solvent de-ashing in coal derived methylnaphthalene-based solvent, has an excellent thermoplasticity even though the parent coal appears no thermoplasticity. We named it "HPC, Hyper-coal", and have been developing to utilize as a caking additive to make strong coke for blast furnace.

This study concerns with the effect of heating rate on the coal extraction yield and the property of the extraction products. The rapid heating, higher than 1000 °C/min. of heating rate, improved coal extraction yield compare to the conventional heating, lower than 100 °C/min. This effect appeared with the coal which had lower extraction yield by the conventional heating. The characteristics of the product obtained from the rapid heating were compared with the conventional heating. <sup>13</sup>C-NMR spectra showed a little difference, but suggested that the rapid heating product contained slightly larger amount of aliphatic carbons, such as naphene rings. Relatively higher H/C atomic ratio of the rapid heating product provided it. The Gieseler plastometry showed that the rapid heating product has higher fluidity and gave higher improvement of fluidity to a slightly caking coal by 10% of addition. On the other hand, the improvement of dilatation of a slightly caking coal was almost same by addition of each product. It expected that more efficient process will be constructed by applying the rapid heating

process, which product has equal or higher performance as the caking additive compare to the conventional heating process.

#### Steam Reforming of Dimethyl Ether Using Coal-Supported Nickel Catalyst

Jiho Yoo, Soohyun Kim, Sangdo Kim, Donghyuk Chun, Hokyung Choi, Youngjoon Rhim, Jeonghwan Lim, Sihyun Lee, Korea Institute of Energy Research, KOREA

Dimethyl ether (DME) is one of the promising reforming substrates for H<sub>2</sub> production due to its high energy density and easy handling/transportation. Steam reforming of DME may happen at relatively low temperature, compared to most popular coal, methane, and propane. In this work, H<sub>2</sub> is produced by the steam reforming of DME over Ni catalyst dispersed on low rank coal (LRC) support. LRC contains many oxygen functional groups, such as carboxyl, which provide the ion-exchange sites for incoming metal ions. TEM and ICP analysis show the existence of 5 – 20 wt% well-dispersed Ni particles (< 10 nm). More than 80% of 1% DME is reformed when catalyzed by 10 wt% Ni/LRC, producing mainly H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and CO at 400 °C. The conversion efficiency varied with temperature, steam to carbon (S/C) ratio, and space velocity. However, the efficiency was not much affected by the amount of Ni in the range of 10 – 17 wt%.

#### A Study of China's Supply-Demand Gap of Coking Coal Resources and the Corresponding Strategies

Shuguang Ouyang, Guanghua Wang, Xuanming He, Xiaoqin Wu, Wuhan University of Science and Technology, CHINA; Di Gao, University of Pittsburgh, USA

China now produces as well as consumes the biggest amount of coking coal. Along with the successive increase of coke production capacity is the ever sharpening supply-demand gap of coking coal resources, which is represented by the following three problems: the disequilibrium between the shortage of high-quality coking coal resources and high market demand, the conflict between the common practice of mixing other types of coal into a single coal in the market and coking plants' detestation of the mixed coal, and the contradiction between the great discrepancy in qualities of the same grade coal and coking plants' high expectation for stable quality of coal. Aiming at these problems, the author puts forward some corresponding strategies: developing and promoting new coking techniques and equipment to reduce the ratio of high quality coking coal, avoiding undue pursuit of large-scale blast furnace and coke oven to avert further increased demand for high-quality coking coal, improving and refining the classification criteria of coking coal to reduce occurrences of coal mixing and fluctuation of coal quality, enhancing theoretical research in coking mechanism and coal blending so as to lessen the reliance on the quality of a single type of high-quality coking coal and make quality evaluation of coal blend the central task of coal blending. The discussion of these strategies is intended to serve as a reference for interested researchers, standard setters and policy makers.

#### POSTER SESSION 1 Gasification

#### Perovskite Sorbents for Oxygen Separation from Air

Ashley LeDonne, Elliot Roth, Sheila Hedges, Dennis Stanko, Jonathan Lekse, Evan Granite, DOE/NETL, USA

A less expensive route for the production of oxygen would be of tremendous value in applications such as gasification, oxy-combustion, smelting, chemical production, welding, and in health care. A laboratory-scale packed bed reactor and thermogravimetric analyzer (TGA) were used to screen potential perovskite sorbents for the capture of oxygen from oxygen-nitrogen mixtures. An on-line electrochemical sensor, used in a continuous mode, monitors the oxygen concentration in the inlet and outlet streams of the packed bed reactor. The TGA was employed to determine temperatures of active oxygen capture and release to or from various gas streams. The capacities and breakthrough times of several novel sorbents were determined as a function of various parameters. The mechanisms of oxygen removal by the sorbents are suggested by combining the results of the packed-bed and TGA testing with various analytical results.

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authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

#### Steam Gasification of Tailored Ash-Free Coals at Mild Condition

Jiho Yoo, Yongjin Kong, Donghyuk Chun, Sangdo Kim, Hokyung Choi, Youngjoon Rhim, Junghwan Lim, Sihyun Lee, Korea Institute of Energy Research, KOREA

Coal has been considered one of the most important carbon sources in nature and is potentially applicable to all the cases related to carbon chemistry. However, its use is currently limited to mainly coal-fired power plant and smelting iron, partly because of a lack of appropriate technologies that can modify the coal. This work addresses if the property of the coal can be tailored, targeting the coal gasification at mild condition. Following the production of ash free coals (AFCs), steam gasification of AFCs is performed. As a means to achieve the enhanced reactivity, the thermal extraction is performed varying the raw coals of various ranks and the organic solvents with different polarity such as 1-methylnaphthalene, N-methylpyrrolidone, ethylenediamine, and tetralin. The reactivity is significantly changed depending on the kind of the coal and the extraction solvent. Combination of low rank coals and highly polar solvent results in highly reactive ash-free coal, concluding that the property of the raw coal is modifiable and steam gasification of the tailored coals can occur at relatively mild condition.

#### Numerical Analysis of an Entrained-Flow Coal-Slurry Gasifier with Separated Oxygen-Feeding Streams

Yin-Chu Chen, Tsung Leo Jiang, National Cheng Kung University; Yau-Pin Chyow, Po-Chuang Chen, Institute of Nuclear Energy Research Atomic Energy Council, TAIWAN

The characteristic design of a Texaco gasifier, with a coaxial coal-slurry oxygen-jet nozzle and an outer annular oxygen-jet, has a significant influence on the gasification process. For the fuel-oxidant coaxial jet nozzle, the central oxygen-jet flow impinges on the coal-slurry stream and assists in the atomization of the coal slurry. The outer oxygen-jet, which splits the oxygen intake stream into two, makes the flame position away from the nozzle and provides a better protection for the nozzle from being burned down. In the present study, numerical simulations of the coal slurry gasification process inside an entrained-flow gasifier with separated oxygen feeding streams are investigated by using the commercial computational fluid dynamic software, ANSYS/FLUENT. The Eulerian-Lagrangian approach is employed for the multi-phase flow. Coal slurry is supplied for the gasification process with a feeding rate of 47.32kg/s and the coal slurry concentration of 35% of water and 65% of coal. Gasification of coal slurry includes several physical sub-processes, such as moisture vaporization, devolatilization, volatile combustion, char oxidation and water-gas shift reaction. The transport exchanges of mass, momentum, and energy between different phases are taken into account in the present numerical model. The physical models for the gaseous flow include turbulence and radiation models. The coal combustion and gasification processes are considered in five homogeneous reactions and three heterogeneous reactions. The heterogeneous reactions are determined by a finite-rate reaction model and the homogeneous reactions are determined by the finite rate and eddy-dissipation combustion model. Three parameters, namely, positions of the outer annulus feeding tunnel, oxygen/carbon ratio, and oxygen feeding velocity of the outer annulus streams, have been examined to determine the effects of operating conditions on the gasification process. The numerical results show that the flame distribution is affected by the positions of the outer tunnel. As the outer tunnel is moved away from the central axis, the flame surface is extended and leads to a higher temperature in the downstream of the gasifier. In the investigations of the oxygen/carbon ratio, the lower the oxygen/carbon ratio is, the lower outlet temperature and the poorer the coal conversion rate. The distribution of the combustion region and the coal conversion rate is strongly affected by the feeding velocity of the outer annulus stream. The coal conversion rate and the cold gas efficiency are in a descending trend when the oxidant feeding is operated in high velocity. The compositions of the product gases are affected by the WGS. Moreover, the reaction rate of the WGS reaction is sensitive to the temperature of the gasification chamber.

#### Evaluation of Palladium-Based Sorbents for Trace Mercury Removal in Electricity Generation

Christopher L. Munson, Pradeep Indrakanti, Massood Ramezan, Leonardo Technologies, Inc./DOE/NETL; Evan Granite, Jenny Tennant, DOE/NETL, USA

The development of warm-gas cleanup (WGCU) systems for synthesis gas (syngas) cleanup in integrated gasification combined cycle (IGCC) power plants has the potential to lower the costs of generating power. WGCU includes the removal of mercury (Hg), present in coal, from the syngas. Carbon-based sorbents used for Hg removal are not suitable for high-temperature Hg removal in conjunction with the WGCU. The U.S. Department of Energy's National Energy Technology Laboratory's (DOE/NETL) Office of Research & Development (ORD) has been developing various sorbent alternatives to address the problem of high-temperature Hg removal. This

study presents analysis of the capture of Hg from syngas streams as a polishing step to attain U.S. Environmental Protection Agency (EPA) Mercury and Air Toxics Standards (MATS) requirements for Hg (0.003 lb/GWh<sub>gross</sub> for new IGCC plants) using palladium (Pd) adsorbent being tested by DOE/NETL in association with Johnson Matthey (JM).

For the present study, it was assumed that syngas is already cleaned to 5 parts per billion by weight (ppb<sub>w</sub>) Hg, and the Pd sorbent technology is used as a polishing step to achieve the EPA MATS requirements (0.003 lb/GWh<sub>gross</sub>, equivalent to 2 ppb<sub>w</sub> given representative process configuration and material flows). The incremental cost of Hg polishing and the additional capital cost needed were estimated for several scenarios/cases. These cases were differentiated by variance in the following parameters, which are important because they have direct impacts on additional capital costs (\$/kW), and in turn impacts on the leveled cost of electricity (LCOE):

- Pd cost (varied from \$4,000 to \$12,000/lb Pd).
- Gas hourly space velocity (SV) (varied from 500 to 13,500 h<sup>-1</sup>).
- Pd loading (varied between 2 w/w% Pd and 5 w/w% Pd).
- Sorbent make-up rate (varied between 3%, 1%).

The ranges were chosen in order to reasonably reflect, in the cases that are analyzed, the actual fluctuations that have been observed in past experience in these important parameters that affect cost (e.g., the Pd cost has kept to within the \$4 to 12k/lb range in recent years). In the case of SV, the high and low points of the range are extremes beyond which costs would either be unreasonable, or increase in cost benefit would be negligible. For a typical case (i.e., using mid-range values of the parameters, including SV of 8,000 h<sup>-1</sup>, 2% Pd loading, 3% make-up rate, \$9,500/lb Pd cost), the increase in LCOE due to the Pd-polishing system is approximately 0.4% and the additional capital cost is ~\$10/kW. As a comparison, the incremental capital cost of conventional Hg removal in an IGCC plant is ~\$4 to 8/kW, and the increase in the LCOE is less than 0.4%. Results indicate that in the range of SVs from 3,500 h<sup>-1</sup> to 10,000 h<sup>-1</sup>, the Hg-polishing step is expected to function adequately and with increase of LCOE limited to about 1-2%. The use of a Pd sorbent-based polishing system to reduce trace Hg levels to the EPA MATS requirements for new IGCC power generation appears to be feasible and reasonably cost-effective.

### The Laboratory Research of Syngas Composition and its Calorific Value in UCG

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The idea of the transformation of coal in underground into synthetic gas so called syngas has interesting in world more centuries. The principal advantage claimed for Underground Coal Gasification (UCG) over mining is that it will be able to use coal that is not economically available through shaft or strip mining from a variety of reasons. UCG is both a coal recovery and a coal conversion technology. The syngas is possible to use either in chemical or energy industry but it depends on its composition. If syngas will be used as raw for chemical industry, the syngas should contain a higher or maximal reached amount of carbon monoxide. In case if syngas is fuel for producing electrical power by its combustion, the UCG should produce the syngas with higher concentration of methane because the methane has the highest calorific value from individual compounds of syngas. Today, similarly to all other countries in the world also in Slovakia there is an interest in the revival and perfection of the UCG technology. Therefore the UCG laboratory was built in Technical University of Kosice by aim to study syngas composition and its calorific value. The goal of this study is to gain greater understanding of the evolution of syngas composition in gasification channels, and from it to extract knowledge useful for the practitioner of UCG in situ. In pursuit of this goal, the research has been based on two approaches: experiments in UCG laboratory and mathematical modeling, including of simulation studies. Both approaches have helped to discover complicated relationships during UCG and they will be subject of this lecture.

### Utilization of Bituminous Coal as Adhesive in Caking Nanocrystalline Magnesium for Hydrogen Storage

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

Magnesium has attracted considerable attention as a promising candidate for hydrogen storage due to the earth-abundant composition and high hydrogen capacity. Unfortunately, MgH<sub>2</sub> is quite stable, which significantly limits the application. In order to enhance the hydrogen absorption performance, tremendous efforts have been made to engineer Mg-based materials. Nanocrystalline magnesium has received tremendous attention due to its high hydrogen storage performance. However, at present, keeping nanocrystalline structure for Mg still remain a challenge. In this work, we proposed to prepare hydrogen storage materials by milling of magnesium and bituminous coal and heating them at 500 oC. Bituminous coal can produce plastic mass with a high thermal stability when heated, which is an excellent adhesive for caking nanocrystalline magnesium. The heat treatment temperature and the relative amount of bituminous coal in the material both influenced hydrogen storage performance. The optimal temperature for the heat treatment was about 500 oC and the optimal relative

amount of bituminous coal was around 20 wt.%. This work will pave a new pathway for improving the hydrogen storage performance of Mg by keeping the nanocrystalline structure.

### The Effect of Drying Temperature on Surface Structure of Lignite

Li-hua Liu, Mo Chu, Zhi-bing Chang, Yang Qu, China University of Mining and Technology (Beijing), CHINA

This study explored the effect of an internal-heating rotary-kiln drying process using nitrogen gas on the surface structure of upgraded lignite. Changes in oxygen-containing functional groups in the dried products were examined as a function of temperature using chemical analysis and Fourier transform infrared spectroscopy (FT-IR). The morphology of the dried lignite surface was observed using a scanning electron microscope (SEM). Specific surface areas were determined using the Brunauer-Emmett-Teller (BET) method, and pore volume was analyzed using the Barret-Joyner-Halender (BJH) method. The number of oxygen-containing functional groups decreased with increasing temperature, with carboxyl groups mostly being removed below 280 °C and phenolic hydroxyl groups being removed at higher temperatures. The pore volume and specific surface area gradually decreased as the temperature was increased to 330 °C and then sharply increased at 380 °C.

### Feasibility Study of Underground Coal Gasification in Western North Dakota

Peng Pei, Junior Nasah, Jarda Solc, Scott F. Korom, University of North Dakota, USA

The Harmon bed, Fort Union formation, in North Dakota has huge lignite reserves, most of which are too deep to be mined using conventional mining technologies. Underground coal gasification (UCG) provides a potential opportunity to economically recover this vast resource. An ongoing project conducted by the Institute for Energy Studies at the University of North Dakota is investigating the feasibility of UCG by studying the lignite properties, hydrogeological and geomechanical properties of the strata in western North Dakota. Four test wells have been drilled at a selected site. Coal and surrounding rocks are cored and used in the gasification and geomechanical tests. The hydrogeological test is in progress. Utilizing the results of the gasification tests, an initial feasibility analysis will be performed for the conversion of UCG-produced syngas to liquid fuels and chemicals. The knowledge provided by the geomechanical and hydrogeological tests will significantly enhance our understanding of the selected area, offer key parameters necessary to design a UCG pilot plant and optimize its operation strategy to produce liquid fuels in an environmentally-responsible manner.

## POSTER SESSION 2 Combustion

### Behavior of Recirculation Zone as Functions of Swirl-Modes in Pulverized Coal Swirling Flames

Yonmo Sung, Sangmin Lee, Xing Wang, Cheoreon Moon, Gyungmin Choi, Duckjool Kim, Pusan National University, SOUTH KOREA

As one of aerodynamics staging methods, the burner aerodynamics is the crucial factor for optimizing NO<sub>x</sub> reduction in wall fired type boilers. The present work focuses on the analysis of the combustion aerodynamics of the low-NO<sub>x</sub> swirl burner by the control of the internal recirculation zone (IRZ). For low-NO<sub>x</sub> coal particle trajectories, the longer residence time of coal particles in the oxygen lean IRZ which creates a reducing environment with fuel-rich conditions and lowering the temperature to reduced NO<sub>x</sub> emissions. For this reason, the detailed measurements of the flow field of coal particles are required to fully understand NO<sub>x</sub> reduction mechanism of the near burner regions. The detailed structure of pulverized coal swirling flames with swirl-mode was studied experimentally by particle image velocimetry and local flame colors based on OH<sup>\*</sup>, CH<sup>\*</sup>, and C<sub>2</sub><sup>\*</sup> radicals. A laboratory-scale dual swirl pulverized coal combustion burner is specially fabricated. The effects of swirl-modes such as the outer swirl intensity (OSI), co- and counter-swirl flows on local flame structures and characteristics were investigated regarding the burner aerodynamics for NO<sub>x</sub> reduction. For all co-swirling conditions, the internal recirculation zone (IRZ) was observed near the inner shear layer with respect to the precessing vortex core structure. Plus, a co-rotating vortex in the outer shear layer and the exhaust tube vortex (ETV) along the central axis were observed. However, the EVT was not observed in counter-swirling combinations. The IRZ was larger with increasing the OSI and then the stagnation point moved toward downstream region. In the counter-swirling flames, the merged stagnation point was observed without the EVT. This merged IRZ in counter-swirling flames could contribute to reduce NO<sub>x</sub> emissions because of enhancing the IRZ in comparison to the co-swirling flames. The intensity of CH<sup>\*</sup> signal was lower with increasing the OSI, conversely, the size of the distribution of the CH<sup>\*</sup> signal becomes larger. The CH<sup>\*</sup> signal intensity of counter-swirling conditions was higher than in co-swirling conditions, and thus increases the local rate of chemical reaction. The counter-

swirling condition reduces flame expansion due to the counter-rotating shear layer that promotes a strong mixing region between the inner and the outer shears. Thus, the CH<sup>\*</sup> signal intensity starts slightly earlier near the burner port. Therefore, the control of the burner aerodynamics with changing swirl intensities may play an important role in improving both environmental and combustion performances.

### Factors in Mercury Oxidation for the Co-Combustion of Coal and Dried Sludge

Sang-Sup Lee, Chungbuk National University, KOREA

The conversion of sewage sludge to energy is required to find an alternative way to ocean dumping. Because the sludge after drying has a comparable heat value to low rank coal, the dried sewage sludge can be used as a solid fuel. The co-injection of the dried sludge into the existing coal-fired boilers has been proposed. Due to the high mercury contents of dried sludge, increased mercury emission is expected from the co-combustion of dried sludge. In addition, the high metal contents of dried sludge may change the behavior of mercury in the flue gas. This study was designed to find the factors in the oxidation of mercury in the flue gas from the co-combustion of coal and dried sludge. A coal sample was pre-mixed with dried sludge samples at a different ratio and combusted in a lab-scale combustor. The combustion flue gas was sampled for gas analysis to check the status of combustion and for mercury analysis, respectively. The sampled mercury was also speciated by the Ontario Hydro Method. Effects of the factors in mercury oxidation were investigated based on the mercury speciation results.

### POSTER SESSION 3 Clean Coal and Gas to Fuels

### Effect of Carbon from Anthracite Coal on Decomposition Enthalpy Change and Heat Absorption of Magnesium Hydride

Xiaoli Zhang, Haipeng Chen, Bogu Liu, Dexi Wang, Shixue Zhou, Shandong University of Science and Technology, CHINA

Ball milling of magnesium under hydrogen atmosphere was applied to synthesize MgH<sub>2</sub> in the presence of carbon which was prepared from anthracite coal by demineralization and carbonization as milling aid. The carbon plays a role of dispersant for the Mg particles to prevent them from aggregating during milling according to SEM observation. Particle size distribution is approximately a logarithmic normal distribution processed by software SPM based on SEM image. The particle size range is 25-260 nm and most particles are mainly about 60 nm as well as TEM analysis shows, which is 50 nm. The carbon plays an important part in reducing the Mg particle size efficiently by its particles with hard edges and protrusions as milling media like milling balls. Also, the carbon significantly improves the MgH<sub>2</sub> decomposition enthalpy change and heat absorption. Carbon additives for milling can lead to smaller crystal size and even create dangling bonds at carbon particle surface, introducing new hydrogen adsorption sites and thus influencing the properties of the materials. The XRD analysis presents that hydriding takes place during milling and most Mg gets hydrided after 3 h. The onset and peak temperatures of the material are 258.2 °C and 300.2 °C by DSC analysis. TPD analysis shows that the onset and peak temperatures are 256.7 °C and 315.7 °C. The enthalpy change of the hydrogen desorption reaction is 42.7 kJ/mol calculated by van't Hoff equation according to the *p-c-T* data in 300-380 °C. The heat absorption of the hydrogen desorption reaction is 38.4 kJ/mol by integration of heat flow according to DSC data.

### Determination of Total Sulfur Content in Coal Pyrolysis Oil

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Oil is one of products of coal pyrolysis, and can be upgraded to more valuable transportation fuels. Catalysts used in oil upgrading process can be poisoned when trace amounts of sulfur bearing compounds are contained in the feed stocks. Therefore, development of a fast and reliable sulfur determination method is an important task of process optimization and quality control for coal pyrolysis oil upgrading. Feed stocks, process streams and final products need to be analyzed for sulfur content precisely.

The analytical techniques used for sulfur determination include classical wet chemistry, X-ray fluorescence, inductively coupled plasma atomic emission spectrometry, and various micro-elemental combustion methods using various detection techniques such as micro-coulometry, ultraviolet fluorescence, electrochemistry, etc. The existing international standard methods for the determination of total sulfur content in oil and products include ASTM D2622, D5453, DIN51-400T6, JIS K 2541, ISO 14596, etc. There are advantages and limitations for these test methods regarding sample requirements, sample size, operation procedures, test instruments and operation conditions. Appropriate selection of a reliable method

for the analysis of total sulfur would depend on the matrix, sulfur concentration, and the desired precision of the analysis.

Comparing with crude oil, coal pyrolysis oils contain higher content of oxygen, and have higher viscosities. Conventional standard test methods for petroleum products are not applicable, and poor precision becomes the barrier for the analysis of total sulfur in coal pyrolysis oils. In this study, a modified test method based on the D 5453 combustion ultraviolet-fluorescence technique for the determination of total sulfur content in coal pyrolysis oil has been developed. Solvent for sample dilution, mixing time, furnace temperature, the flow-rate of carrier gas and oxygen in elemental analyzer were optimized to obtain good precision and accuracy. The scope of application, data accuracy and precision of the modified test method were investigated. The developed method was successfully applied to the determination of total sulfur contents in different types of coal pyrolysis oils.

### Calcination Temperature Influence on the Catalytic Performance of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> for Low Temperature Steam Reforming of Methane

Kui Wu, Jieying Jing, Wenyong Li, Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), CHINA

Steam reforming of methane (SRM) is the primary method to produce hydrogen. Commercial Ni-based catalysts have been optimized for SRM with excess steam (H<sub>2</sub>O/CH<sub>4</sub> > 3) at high temperatures (> 700°C). However, commercial catalysts are not suitable under severe reaction conditions such as less steam (H<sub>2</sub>O/CH<sub>4</sub> ≤ 3) and low temperature (500°C). In this study, a co-precipitation method was employed to prepare 15% Ni-Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalysts under different calcination temperature (450°C, 550°C, 650°C, 750°C) for SRM. Structures of the catalysts were systematically examined by N<sub>2</sub> adsorption/desorption, X-ray diffraction (XRD) and hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) techniques. The activities of these catalysts were evaluated at the reaction condition of 500°C, 1atm, GHSV of 30000 mL/g<sub>cat</sub>·h, the molar ratio of methane to steam is 1:3. Results showed the 15% Ni-Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst calcined at 650°C exhibited superior catalytic activity with 47% CH<sub>4</sub> conversion and 63% for H<sub>2</sub> yield and the activity was maintained without significant loss after 100 h running. The remarkable catalytic performance might be due to the balance between the relatively large surface area and the suitable interaction between Ni and CeO<sub>2</sub>-ZrO<sub>2</sub>.

### The Study of CO<sub>2</sub>/CH<sub>4</sub> Reforming on Ni(111) and NiCo(111) Surfaces by Using DFT Method

Hongxia Fan, Xiaohong Li, Yunpeng Guo, Jie Feng, Wenyong Li, Taiyuan University of Technology, CHINA

The density functional theory (DFT) were employed to investigate the reaction pathways of CO<sub>2</sub> reforming of CH<sub>4</sub> on Ni(111) and NiCo(111) surfaces. The dissociation of CH<sub>x</sub> (x = 1~4), the activation of CO<sub>2</sub> to produce reactive O, and the oxygenation of CH by O as well as CHO detached were systematically examined. The calculation results showed that all these reaction were favor to take place on NiCo(111) surface with the lower activation energies than that on Ni(111) surface.

### Thermodynamic Analysis of the Magnesium-Carbon Composite Hydrogen Storage Materials

Qianqian Zhang, Haipeng Chen, Shixue Zhou, Xiaoli Zhang, Bogu Liu, Shandong University of Science and Technology, CHINA

Magnesium-carbon composites with different ratio of raw materials were prepared by mechanical ball milling method in 1MPa H<sub>2</sub> for different milling time. Results show that β-MgH<sub>2</sub> phase appears at first and γ-MgH<sub>2</sub> phase grows with β phase at the same time with ball milling time increases, which can be observed in TEM images and XRD pattern of the materials 70Mg30C. Compared with β phase, γ phase presents the lower stability during the hydrogen desorption heat treatment. DSC curves indicate that there are double endothermic peaks when ball milling time over 10 h, and the corresponding peak temperature is 365.5 °C and 419.9 °C, respectively. In addition, the raw materials and the ratio can also influence the thermodynamic performance. 80Mg20C and 60Mg30C5Ni materials in which the numbers represents the weight percentage were measured by DSC, and the results show that double peaks appear in the curves of both materials which may be result from the slight hydrogen absorption of carbon from the carbonized anthracite coal and the spill-over catalysis of metal nickel.

### Influencing Mechanism of ZnO Morphology on the Performances of Co/ZnO Catalysts for Fischer-Tropsch Synthesis

Wensheng Ning, Wanmin Di, Qianqian Liu, Yangfu Jin, Shoubin Yang, Xiaozhen Yang, Zhejiang University of Technology, CHINA

Reliable and enough supply of liquid fuels is a key factor to support quick and stable development of national economy. Cobalt-based catalysts are efficient to convert syngas (mixture of CO and H<sub>2</sub>) into C<sub>5+</sub> hydrocarbons. Therefore, Fischer-Tropsch

synthesis relied on cobalt-based catalysts is a technology fit for the sustainable production of liquid fuels from coal, natural gas or biomass via syngas instead of exhausted crude oil.

The activity of cobalt-based catalysts is proportional to the number of exposed metallic cobalt atoms, which is decided by two conflicting parameters, i.e., reducibility of cobalt oxide and dispersion of metallic cobalt atom. We have found that Co/ZnO catalysts prepared by ZnO impregnated with cobalt nitrate solution are able to be reduced at low temperature, which is beneficial to apply Co/ZnO catalysts in slurry reactor. Recently, ZnO possessing different morphologies is synthesized by hydrothermal, homo-precipitation methods. Co/ZnO catalysts supported on these ZnO materials are tested for Fischer-Tropsch synthesis. Two kinds of plate-like ZnO were hydrothermally synthesized from zinc acetate and hexamethylene tetramine by tuning the reaction temperature. The ZnO synthesized at 100 °C (Z100) is rich of polar facet on the surface, while the ZnO synthesized at 140 °C (Z140) is mainly composed by nonpolar facet. Catalyst CZ100 is more active than CZ140 in Fischer-Tropsch synthesis measured by fixed-bed reactor. The reason is attributed to small size of Co<sub>3</sub>O<sub>4</sub> particles deposited on the polar facet.

### Process of M-/P-Cresol Adsorption Separation by Zeolite X

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An experimental and modeling study of the liquid phase adsorption on zeolite X was addressed for separating the close boiling point mixtures of m-/p-cresol. The measured adsorption equilibrium data were compiled with the Extended-Langmuir isotherm model. Then, the software Aspen Adsorption was used to simulate the adsorption dynamic behavior, and the effects of process variables such as bed height, bed porosity and mass transfer coefficient on the breakthrough profile were investigated. Results revealed that the bed height and bed porosity effect the breakthrough time, while the MTC has an impact on the breakthrough curve shape. The optimum values of bed height, bed porosity and MTC are 0.5m, 0.4m<sup>3</sup>void/m<sup>3</sup>bed and 1s<sup>-1</sup>, respectively. These optimal simulation data will be useful for further applications in the adsorption separation of m-/p-cresol.

### Hydrodesulfurization of Carbon Disulfide by Solid Hydrogen in Magnesium-Carbon Composite

Haipeng Chen, Naifei Wang, Qianqian Zhang, Zongying Han, Shixue Zhou, Shandong University of Science and Technology, CHINA

The preparation of magnesium-carbon composite and its utilization in removing carbon disulfide were investigated. The crystalline structure and hydrogen desorption property of the magnesium-carbon composite were determined by XRD, DSC and *p-C-T* analysis. Results indicated that Mg crystallized into two kinds of hydrides during hydrogenation, tetragonal β-MgH<sub>2</sub> and rhombohedral γ-MgH<sub>2</sub>, with hydrogen desorption temperature of 286 and 338 °C respectively. From XRD analysis, carbon disulfide hydrodesulfurization at 250 °C by the solid hydrogen of the composite are obvious, with obvious magnesium sulfide, hydrogen sulfide and methyl mercaptan generated. With the increasing of reaction temperature, the reaction rate increased and more magnesium sulfide generated. Hydrogen molecules have a blocking effect on generation of magnesium sulfide in the reaction. This work provide a potential method for carbon disulfide hydrodesulfurization in application.

### Hydrocarbon Production of Middle Distillates Range from Syngas on the Extruded Cobalt-Based Hybrid Catalysts; Effect of Cobalt/ZSM-5 Ratio

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Fischer-Tropsch synthesis (FTS), using syngas derived from coal, natural gas, biomass or other carbon-containing materials, has recently received considerable attention as an alternative method for synthesizing clean fuels and chemicals due to the fast depletion of crude oil. Thus, FTS has emerged as one of the most promising routes to solve the energy crisis. However, the polymerization mechanism (known as Anderson-Schulz-Flory (ASF) distribution) of FTS reaction is inherently found to show a wide-range of hydrocarbon distribution from methane to heavy waxy products and its distribution is explained by the chain growth probability. In general, the selectivity towards gasoline range products is known to be limited to a maximum value of 48 mol%. To obtain branched hydrocarbons selectively through FTS reaction directly without any upgradation, especially for high-octane gasoline production, many intensive efforts have been made by modifying cobalt-based catalysts with the addition of acidic components. Some researchers have investigated the hybrid or composite systems consisting of cobalt-based FTS catalysts and acidic zeolites as a cracking catalyst by using the following preparation methods; i) cobalt-based FTS catalyst physically mixed with zeolites, ii) zeolite supported cobalt-based hybrid catalyst prepared by wet-impregnation method, iii) zeolite membrane-coated Co/SiO<sub>2</sub> catalyst. In this work, FTS reaction for the direct production of middle distillates range hydrocarbons (C<sub>5</sub>-C<sub>22</sub>) from syngas was investigated on cobalt-based catalysts with

promoter as Pt. The hybrid catalysts were synthesized by co-precipitation method in an aqueous solution containing Co and Al metal precursors (cobalt nitrate and aluminum nitrate with the weight ratio of Co/Al<sub>2</sub>O<sub>3</sub> = 20/100) and Na<sub>2</sub>CO<sub>3</sub> solution as a precipitating agent at 70°C in a slurry of ZSM-5 (Si/Al=25). The precipitate was further aged for 3 h at 70°C and then the wet hybrid catalysts were molded by extruder. The calcination of hybrid catalysts was carried out at 500°C for 5 h. The same procedure was followed for the different ratio of Co/ZSM-5. Finally, the ratios of cobalt and promoter metal components to that of ZSM-5 in the hybrid catalysts were fixed at 20-30-0.1/5 (or 15, 30, 45) by weight. The hybrid catalysts are noted as a Co-Al<sub>2</sub>O<sub>3</sub>-Pt/xZSM-5 (x is 5, 15, 30 and 45). Catalytic activity test was carried out in a tubular fixed bed reactor. Prior to the reaction, the catalyst was reduced at 450°C for 12 h in a flow of 8% H<sub>2</sub> balanced with nitrogen. After reduction, the synthesis gas (H<sub>2</sub>/CO = 2) was fed into the reactor. The FTS reaction was carried out subsequently under the following reaction conditions; T = 240°C, P = 2.0 MPa and SV = 3,000 ml/g<sub>cat</sub>/h. The hybrid catalysts are characterized using BET, XRD, H<sub>2</sub>-TPR, NH<sub>3</sub>-TPD, SEM, TEM and XPS. As results, the impregnated Co/ZSM-5 hybrid catalyst as a reference catalyst is taken as a reference show higher values for conversion and C<sub>1</sub> selectivity at 240 °C than that of Co-Al<sub>2</sub>O<sub>3</sub>-Pt/xZSM-5 hybrid catalysts. All hybrid catalysts show the C<sub>5</sub>-C<sub>22</sub> yield (%) higher than that of Co/ZSM-5 catalyst. Co-Al<sub>2</sub>O<sub>3</sub>-Pt/xZSM-5 hybrid catalysts show low C<sub>1</sub> and olefin selectivity and high C<sub>5</sub>-C<sub>22</sub> yield. The molded hybrid catalysts are found to be more promising towards direct production of the hydrocarbons of middle distillate range.

### Syngas Production from CO<sub>2</sub> Reforming on Plasma Enhanced Catalyst System

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Currently, most of syngas (or hydrogen) is produced from fossil fuels in the world. The significance of syngas production is increasing because fossil fuels are being depleted. For this reason, new methods of syngas production need to be developed. CO<sub>2</sub> reforming (or dry reforming) of methane has been introduced as a method for syngas production. The utilization of CO<sub>2</sub> for the reforming of CH<sub>4</sub> gas attracted significant attention in recent decades due to its advantages over steam reforming of CH<sub>4</sub>. Traditionally, CO<sub>2</sub> reforming of CH<sub>4</sub> has been achieved by catalytic means. However, the industrial application of this means is still limited. Carbon deposition on catalyst surface which leads to the deactivation of the catalysts became the great barrier to enlarge this process from laboratory to the industrial scale. The attractive benefit for CO<sub>2</sub> reforming of CH<sub>4</sub> with plasma is that reactions are induced by the energetic electrons and/or its high temperature state. Compared with catalytic reaction, there are a few advantages in CO<sub>2</sub> reforming of CH<sub>4</sub> by plasma, such as the high conversions and no necessary to worry about the carbon deposition. Therefore, reforming by plasma has drawn increasing attentions. Microwave discharge plasma can be operated at a frequency range of GHz and a wide pressure range. CH<sub>4</sub>-CO<sub>2</sub> reforming by microwave discharge shows higher conversions and selectivity, larger treatment capacity, as well as higher energy efficiency, which benefit from its larger discharge space and better discharge uniformity. The chemical reaction in microwave plasma is induced by energetic electrons and high gas temperature.

In this work, syngas (mainly, CO and H<sub>2</sub>) production via CH<sub>4</sub> reforming in CO<sub>2</sub> microwave plasma enhanced catalyst at atmospheric pressure. The plasma reforming system is mainly composed of a 2.45 GHz microwave plasma and the CO/CH<sub>4</sub> ratio 1 of Ar balance is introduced into the microwave plasma stabilized by a swirl flow. The plasma converts both CO<sub>2</sub> and CH<sub>4</sub> to intermediate hydrocarbon species as well as syngas and then the reforming gas conversion showed about 40% CH<sub>4</sub> and 16% CO<sub>2</sub> at 1000 ~ 1200°C. Hereafter, the converted reforming gas is cooled and is introduced into the catalyst system with addition steam. The catalytic steam reforming was tested in a tubular stainless steel reactor (inside diameter of 2.22 cm) that was operated at 850°C for 8hr of atmospheric pressure with Ni-based catalyst. The GHSV, which was calculated based on the introducing reforming gas flow rate from plasma and the volume of the catalyst, was 5,000 h<sup>-1</sup>. The CH<sub>4</sub> and CO<sub>2</sub> conversion at 5,000 h<sup>-1</sup> was approximately 98.54 % and 50.62%, respectively. In addition, H<sub>2</sub>/CO ratio was 2.27 and CO<sub>2</sub>/(CO+CO<sub>2</sub>) ratio was 0.14. From these plasma enhanced catalyst system result, we are found to be higher reforming conversion without coking of catalyst and the H<sub>2</sub>/CO ratio 2 of syngas will be estimated adequately to apply for production of the chemical or the fuel.

### Computational Fluid Dynamics Modeling of Slurry Bubble Columns for Fischer Tropsch Synthesis

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In this work, a multi Eulerian three-phase three-dimensional computational fluid dynamics (CFD) model was developed with the aim of investigating local hydrodynamics and overall reactor performance for a Fischer Tropsch (F-T) Slurry

Bubble Column Reactor (SBCR). Drag and turbulence models were optimized and the model was validated against experimental results from the literature at conditions relevant to F-T industrial operations. The effect of internals on the local hydrodynamics was investigated and various internals configurations with both varying pipe diameters and number of pipes were modelled. Moreover, the effect of the gas sparger design was also investigated. Four different sparger designs were modelled, single nozzle, perforated plate, spider-type and concentric rings. The effect of the sparger type on the SBCR hydrodynamics at various gas holdups and temperatures was investigated. Also, the effect of the orifice diameter and the number of holes on the overall gas holdup was modelled. Additionally, the CFD simulation results were used to optimize gas holdup correlations for F-T operations.

#### Hydrodynamic and Mass-Transfer Parameters of Gases in NICE F-T Wax Using a Pilot-Scale Slurry Bubble Column Reactor

Laurent Sehabiague, Omar Basha, Yemin Hong, Badie I. Morsi, University of Pittsburgh, USA; Haolin Jia, Li Weng, Zhuowu Men, Ke Liu, National Institute of Clean and Low-carbon Energy; Yi Cheng, Tsinghua University; Zhansheng Shi, National Institute of Clean and Low-carbon Energy and Tsinghua University, CHINA

The hydrodynamic and mass transfer parameters (gas holdup,  $\epsilon_G$ , Sauter-mean diameter of gas bubbles,  $d_s$ , and volumetric liquid-side mass transfer coefficient,  $k_{L,a}$ ) were measured for  $N_2$  and  $N_2/He$  gaseous mixtures in a molten Fisher-Tropsch (F-T) wax produced by the National Institute of Clean and Low-Carbon Energy (NICE), China (NICE wax). The data were obtained in a pilot-scale (0.29 m) slurry bubble column reactor (SBCR) operating under different pressures (4-31 bar), temperatures (380-500 K), and superficial gas velocities (0.1-0.3 m/s) in the absence and presence of solid (iron-based catalyst) concentrations (0-15 vol.%). The effects of different operating variables on the hydrodynamic and mass transfer parameters were investigated and the results were essentially compared with those previously published in a light F-T cut and in other F-T liquids.

The data obtained in NICE wax showed that increasing reactor pressure increased  $\epsilon_G$  and decreased  $d_s$  which led to high values of  $k_{L,a}$ ; while increasing temperature increased  $\epsilon_G$  and  $k_{L,a}$  and decreased  $d_s$  due to the decrease of the liquid-phase viscosity and surface tension. Increasing the superficial gas velocity increased  $\epsilon_G$  and  $k_{L,a}$ , while  $d_s$  values either remained the same or decreased due to the high rate of gas bubbles breakup. Increasing catalyst concentration, however, decreased  $\epsilon_G$  and  $k_{L,a}$ , increased  $d_s$  and appeared to reduce the effect of the superficial gas velocity on  $\epsilon_G$ . Also, under similar operating conditions,  $\epsilon_G$ , gas-liquid interfacial area ( $a$ ) and  $k_{L,a}$  of  $N_2$  or  $N_2$ -rich gaseous mixtures were greater than those of He or He-rich mixtures due to the former's greater density and momentum, which led to the formation of smaller  $d_s$  and greater  $\epsilon_G$ . Under high temperatures, the gas-liquid interfacial areas were greater, whereas the  $k_{L,a}$  values were smaller in NICE wax when compared with those reported in the light F-T cut. This behavior was attributed to the smaller mass transfer coefficients ( $k_L$ ) of NICE wax due its higher viscosity when compared with that of the light F-T cut.

#### POSTER SESSION 4 Sustainability and Environment

#### Catalytic Pyrolysis of Sunflower Stalk with Ca-Fe-Ni-La Oxides and Coal Semi-Coke

Shaoli Zhang, Fuxin Chen, Huikuan Zhang, Shihua He, Yanyan Lei, Anning Zhou, Xi'an University of Science and Technology, CHINA

The catalytic pyrolysis property of sunflower stalk with Ca-Fe-Ni-La oxides composite and coal semi-coke were researched. Firstly, the Ca-Fe-Ni-La oxide composite catalyst was prepared by co-precipitation, and the Shenfu semi-coke catalyst by fixed bed. And then, The catalytic pyrolysis of sunflower stalks with the obtained catalysts were studied employing thermal gravimetric analyzer at the heating rates of 5, 10, and 20 °C/min, respectively, and with nitrogen as the carrier gas. The results show that the pyrolysis average activation energy of sunflower stalk with none, Ca-Fe-Ni-La oxide (10%w/w), and the Shenfu semi-coke catalyst (10%w/w) is 225.38 kJ/mol, 164.97 kJ/mol, 201.87 kJ/mol, respectively. Both the Ca-Fe-Ni-La oxide catalyst and the Shenfu semi-coke catalyst can promote the pyrolysis of sunflower stalk, and the catalytic pyrolysis property of Ca-Fe-Ni-La oxide composite catalyst is better than that of semi-coke catalyst.

#### Effect of Ammonium Ions on Structure of Bentonite and Hg<sup>0</sup> Removal Performance of Modified Bentonite

Min Li, Li Wang, Jiangyan Chen, Xiuli Liu, Jun Gao, Shandong University of Science and Technology, CHINA

The Hg<sup>0</sup> removal performance of bentonite that was modified by ammonium bromide and potassium bromide has been investigated in a laboratory-scale fixed-bed reactor. The sorbents have been characterized by the methods such as X-ray diffraction (XRD) and Thermo gravimetric Analysis(TG). The experimental results show that Hg<sup>0</sup> removal performance of NH<sub>4</sub>Br-Ben/Na sorbent is remarkable, compared with that of KBr-Ben/Na sorbent. Moreover, the highest Hg<sup>0</sup> removal efficiency of the NH<sub>4</sub>Br-Ben/Na sorbent reached 94.3%; furthermore, it maintained at a higher level for a long time, which indicates that the ammonium ions play a role during the process of the oxidation between Br<sup>-</sup> and Hg<sup>0</sup>. Calcinations and solution impregnation are beneficial to the improvement of the mercury removal performance of the sorbents. In the course of calcinations, the ammonium ions formed a relatively stable material combining with bentonite within the layers which would contribute to the mercury removal.

#### Study on Surface Properties and Adsorption Performance of Acid Modified Semi-Coke for Gas-Phase Hg<sup>0</sup>

Xiuli Liu, Jiangyan Chen, Min Li, Huawei Zhang, Li Wang, Shandong University of Science and Technology, CHINA

The adsorption performance of modified lignite semi-coke with HCl or HNO<sub>3</sub> solution for gaseous Hg<sup>0</sup> was investigated to develop more effective and lower price adsorbents for reducing emission of elemental mercury. The adsorption experiments of new adsorbents for gas-phase Hg<sup>0</sup> were carried out with a laboratory-scale fixed-bed reactor, and the elemental mercury analyzer was used to determine the on-line concentrations of inlet and outlet gas-phase Hg<sup>0</sup>. The surface properties of these adsorbents were characterized with methods of acid-base titration, Boehm titration, Brunauer-Emmett-Teller (BET) measurements, scanning electron microscope (SEM) and Fourier Transform infrared spectroscopy (FTIR). Characterization results show that modified lignite semi-coke with oxidation of nitric acid or hydrochloric acid resulted in the decrease in ash content of semi-coke sample, and the values of specific surface area, surface oxygen and phenolic hydroxyl group increasing of modified semi-cokes. The gas-phase Hg<sup>0</sup> was primarily absorbed into the micro pores and surface of modified lignite semi-coke in the form of physical adsorption at low temperature and chemical adsorption at high temperature zone, respectively. So, the specific surface area and pore structure of semi-coke are principal influencing factors for its Hg<sup>0</sup> adsorption performance. Compared to raw lignite semi-coke (NM-SC), the modified lignite semi-coke with HCl or HNO<sub>3</sub> solution (Cl-SC or N-SC sample) could improve adsorption performance for gas-phase Hg<sup>0</sup>. Especially, the adsorption performance of Cl-SC sample was obviously improved from flue gas when adsorption temperature increased to 140°C. These results are related to the surface properties of modified semi-coke and its contents of carboxyl group, phenolic hydroxyl and C-Cl functional groups, which can provide active sites for gaseous Hg<sup>0</sup> chemical adsorption. Finally, adsorption mechanism of modified lignite semi-coke was also discussed.

#### Preparation of Activated Carbons for Mercury Removal

Hyo-Ki Min, Sang-Sup Lee, Chungbuk National University, KOREA

Activated carbon has been used for removing liquid and gaseous pollutants as a porous material having high surface area. With carbon-containing materials such as wood, coal and coconut shell, activated carbons can be produced through carbonization and activation process. Through the carbonization char is produced by removing volatile matters from raw materials, and through the activation the pores in the char are expanded. Because each material has different components and properties, the produced activated carbon has different properties depending on the kind of raw material. In addition, the conditions during the carbonization and activation largely influence the physical and chemical properties of activated carbon. Different micropore and mesopore distributions are obtained with different materials and conditions. In this study, activated carbons were prepared using various raw materials with several carbonization and activation conditions. The prepared activated carbons were analyzed to determine their surface area and micropore and mesopore distributions.

#### POSTER SESSION 5 Carbon Management

#### Development of a New High Temperature Rechargeable Li/Mg Battery System

Huang Guo, Bruce Kang, West Virginia University; Sin Chien Siw, Minking Chyu, University of Pittsburgh, USA

In addition to carbon capture and sequestration (CCS) techniques, a possible approach to mitigate the greenhouse gas (GHG) emission is to decompose it into useful products. Described in this paper is a study concerning a Solid Oxide Electrolyzer Cell (SOEC) with ODF/YSZ or nickelate/YSZ electrodes and YSZ electrolyte that is utilized to decompose oxygen-containing gases, i.e carbon dioxide (CO<sub>2</sub>) into solid carbon (C) or

carbon monoxide (CO) and generate oxygen (O<sub>2</sub>) in a continuous process. A Mechano-Chemical Bonding (MCB) process is adopted to prepare Oxygen-Deficient Ferrite (ODF) or nickelate-based materials mixed with YSZ powder. The cells are tested in a NexTech Probostate™ apparatus combined with EIS/potentiostat and gas chromatography (GC). The preliminary tests indicate that CO and O<sub>2</sub> are generated at cathode and anode side respectively, when CO<sub>2</sub> is fed to the cathode side and a small potential bias is applied across the electrode. As the applied potential increases, the system is capable of decomposing CO<sub>2</sub> into solid carbon. Through in-situ EIS and exhaust gas analyses as well as post mortem microstructural analyses using SEM, XRD, and XPS, the capability and efficiency of CO<sub>2</sub> decomposition are evaluated. An energy assessment shows that the net energy input in this process is smaller compared to CCS. Based on this ODF/YSZ SOEC method, a high temperature (HT) rechargeable battery system is further developed. Preliminary results are presented for assessment of energy density of this HT rechargeable battery system and the potential for energy storage application.

## POSTER SESSION 6 Coal Science

### Investigation of Arsenic Poisoning on Novel SCR Catalysts

Benjamin Galloway, Bihter Padak, University of South Carolina, USA

The reduction of nitrogen oxides (NO<sub>x</sub>) using selective catalytic reduction (SCR) through the injection of ammonia is a common practice in coal-fired power plants today. However to meet increasing emission standards, numerous novel SCR catalysts have been developed to make the catalysts more reactive over a wider range of operating conditions, such as temperature. Modern mixed-oxide catalysts used to carry out this reaction are susceptible to poisoning and deactivation over time due to the numerous species present in the flue gas such as arsenic. Sorbents, such as CaO, can be injected into the flue gas to protect the catalysts and increase its operating lifetime. Due to these limitations of current SCR catalysts, novel SCR catalysts are currently being investigated. While the deactivation mechanism has been studied on traditional V-Mo-Ti oxide catalysts to an extent, it is unknown what effect the arsenic species might have on novel SCR catalysts.

In this study, small pore zeolites, SSZ-13 and SAPO-34 with and without impregnated Fe or Cu, are evaluated for their resistance to arsenic as they have shown promise as SCR catalysts in other deNO<sub>x</sub> applications. They are compared to a commercially available (V-W-Ti oxide) catalyst, as well several large pore zeolites such as ZSM-5 and zeolite-Y. The catalysts are exposed to a simulated flue gas stream that is created by combusting methane, creating an environment representative of the one present in a coal-fired boiler. Prior to combustion, the stream is premixed with arsine (AsH<sub>3</sub>), which is converted to arsenic oxide (As<sub>2</sub>O<sub>3</sub>) as it passes through the oxygen-rich flame. The catalysts are characterized before and after exposure to arsenic using XPS, XRD, SEM/EDX and NH<sub>3</sub>-TPD, to determine the specific mechanism of arsenic adsorption on the surface of the catalysts. Finally, the gas stream composition is varied to include SO<sub>2</sub>, NO, NO<sub>2</sub>, and HCl to study the effect that other flue gas components play in arsenic adsorption.

### Evaluation of Direct Carbon Fuel Cell Using Various Carbon Fuels

Jiho Yoo, Jongbae Lee, Muhammad Khan, Donghyuk Chun, Hokyung Choi,  
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KOREA

This work describes the performance of both the electrolyte- and anode-supported direct carbon fuel cell (DCFC) using various carbon fuels such as ash-free coal (AFC), lignite raw coal (PC), active carbon (AC), carbon black (CB), and graphite (GP). As expected, the anode-supported cell that is less inherently resistant shows better performance than the electrolyte-supported cell at 800 °C, when AFC is used as fuel. Ash in solid fuels would inhibit the cell operation and hence ash-less carbon is recommended for the long-term operations. In common, the electrochemical reactivity of carbon fuels seems to be determined by a degree of carbonization. Less graphitized carbons (AFC and PC) likely provide more reaction sites through the structural defects and thus perform better, compared with better-crystallized carbons such as GP and CB. The increase of the power density is consistent with the enhanced production of the fuel gases (H<sub>2</sub> and CO) via coal-water and Boudouard reaction, compared to N<sub>2</sub> pyrolysis environment. Simultaneous occurrence of direct carbon and conventional gas reaction is most likely present in the DCFC operation.

### Characteristics of Ash-Free Coal Produced by Dilution Crystallization from Solvent-Extracted Solution

Youngjoon Rhim, Hokyung Choi, Sangdo Kim, Jiho Yoo, Donghyuk Chun,  
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We produced the solvent-extracted solution in which the organic substances of coal were dissolved, separated out the solid ash-free coal (AFC) from the liquid solvent in the solution by dilution crystallization (DC), and analyzed the basic properties of the AFC.

In the conventional AFC production process based on the solvent extraction, an evaporator or a spray dryer, which evaporates the solvent by heating the extracted solution above the boiling point of the solvent is usually used to obtain a solid form of AFC. In the process, dried AFC particles are exposed to a hot environment, such as the wall and gas in the dryer, and some parts of the dried AFC can be volatilized. To prevent the loss of the AFC during the drying process, we applied the DC method, by which the AFC is crystallized by reducing the solubility of the solute in the solvent through adding a diluent to the extracted solution.

We mixed Kideco coal, a sub-bituminous coal from Indonesia, with n-methyl-2-pyrrolidone (NMP) to make a slurry. We then stirred the slurry for one hour at 350°C in an extraction reactor and filtered the slurry to obtain a solution containing the solvent and the dissolved organic substances of coal. We let the hot solution cool down with flowing nitrogen until it reached room temperature and no further evaporation of the solvent took place. Then, we poured the solution into a water container. The organic substances of coal dissolved in the solvent agglomerated in the form of lump as soon as we poured the solution into water. This occurred because the solubility of the organic substances of coal in the NMP reduces rapidly as the water acts as a dilute. The lumped organic matter was filtered, washed in water twice, and dried in nitrogen in an oven at 107°C. The properties of the AFC produced by DC (DC-AFC) were compared with those of the AFC produced by evaporating the whole solvent in a hot inert chamber (EV-AFC).

The biggest weakness of the EV-AFC is the reduced surface area compared to that of the parent coal. This reduced surface area causes reduced reactivity when it is applied to processes such as combustion and gasification. On the other hand, according to a BET surface area analysis, the surface area of the DC-AFC is not only larger than that of EV-AFC but also over twice as large as the surface area of the parent coal.

According to a thermogravimetric analysis, the DC-AFC begins to burn at a lower temperature and burns entirely in a shorter period compared to the EV-AFC. The DC-AFC begins to burn at a higher temperature compared to the parent coal because it has fewer functional groups on its surface. However, the DC-AFC burns faster than the parent coal because the surface area of the DC-AFC is larger.

According to the results, we can expect that the AFC produced by the dilution crystallization method can be effectively applied to the field of combustion and gasification due to its enlarged surface area relative to the AFC produced by the conventional method.

### A Theoretical Study on Bond Dissociation Enthalpies of Coal-Based Model Compounds

Lu Li, Lijun Jin, Yang Li, Hongjun Fan, Haoquan Hu, Dalian University of  
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The understanding of the thermochemistry and reactivity of specific bonds within the coal structure may lead to advances in coal processing. In this work, the performances of various contemporary theoretical procedures in predicting the homolytic bond dissociation enthalpies (BDEs) for various type compounds were assessed. The procedures considered include density functional theory (DFT), such as B3LYP and M062X, double-hybrid DFT (MPW2PLYP and B2PLYP), and the high-level method G4MP2. The results indicated that G4MP2 achieves the smallest mean absolute deviation (MAD) for small molecules with less than 10 heavy atoms. Nevertheless, G4MP2 is generally overestimates the larger molecules, and performs poorer than the double-hybrid DFT methods. Double-hybrid DFT methods generally give smaller deviations for BDEs than those obtained from typical DFT procedures. MPW2PLYP performs comparable to B2PLYP for the test sets under our study. Consideration of achieving high precision, we chose MPW2PLYP to calculate 107 BDEs of typical bonds (C-H, C-C, C-O, O-H) in aromatic molecules that are representative of the functionalities in coal, due to most of those molecules containing more than 10 heavy atoms.

### In Situ Analysis of Volatile Products from Brown Coal Pyrolysis Using Electron Impact and Vacuum Ultraviolet Photoionization Mass Spectrometry

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Volatile species from pyrolysis of two kinds of lignite (sample A and sample B) were investigated in-situ with electron impact and vacuum ultraviolet photoionization mass spectrometry (EI/VUV-PIMS). Mass spectra of products at different temperatures were measured during pyrolysis process of two coal samples. The results show that H<sub>2</sub>, H<sub>2</sub>O, CO, and CO<sub>2</sub> are dominant inorganic products and their formation temperatures accord with the temperatures of different chemical bond cleavage. 1-ring aromatic compounds are dominant organic pyrolysis products, while a number of aliphatic products were also identified. The comparisons of two coal samples reveal that the condensation reactions in pyrolysis process of sample A occurred more intensively than that of sample B at high temperatures (above 600°C). The differences on pyrolytic products

were probably due to the different structures of the macromolecular network between sample A and B. Besides, the concentration of sulfur in sample B is more than sample A and the peak of H<sub>2</sub>S (m/z=34) is clearly observed in pyrolysis process of sample B. This work also illustrates the good performance of EI/VUV-PIMS in-situ analysis of complex coal pyrolysis.

### **An Investigation on the Fluidization Behaviour of Biomass-Coal Granular System**

Zhiguo Guo, Xueli Chen, Yang Xu, Haifeng Liu, East China University of Science and Technology, CHINA

For the co-gasification of biomass-coal blends in entrained flow gasifier, proper fluidization of blends is critical to obtain the better flow performance and effective conversion, i.e., mass and heat transfer, in reactor. The paper aimed to obtain the biomass-coal minimum fluidization velocity ( $U_{mf}$ ) and separation characteristics in fluidization, further to propose an improved model to predict the related  $U_{mf}$ . With an increase of biomass mass fraction, the declined pressure drop and the enlarged  $U_{mf}$  are obtained. Improper fluidization (segregation and channeling) occurs at near 5% and 10% for rough and fine biomass particles, respectively. The larger diameter ratio of biomass to coal, the more ineffective fluidization. The results also demonstrate that the mixtures with sawdust possess the better fluidization behavior than that of rice straw due to its less difference of density with coal and less aspect ratio. Fluidized binary mixtures appear sequentially solid-like, fluid-like and bubbling with the increase of gas superficial velocity, and the mechanisms of fluidized state transition are analyzed and verified through the bed expansion and inter-particle attractive forces. In addition, mixing and segregation behaviors of blends after the complete fluidization has been discussed which is evaluated by separation index and relative concentration profile.

### **Integrated Process of Coal Pyrolysis with Methane Steam Reforming: The Influence of Pyrolysis Conditions**

Chan Dong, Lijun Jin, Yang Li, Zheng Fu, Haoquan Hu, Dalian University of Technology, CHINA

In this work, a novel method to integrate coal pyrolysis with steam reforming of methane (SRM) (CP-SRM) was put forward for improving tar yield and quality. The experiments were carried out with a Chinese lignite, Xilinguole lignite (XL), and commercial catalyst (Ni/Al<sub>2</sub>O<sub>3</sub>) on an atmospheric fixed-bed reactor containing upper catalyst layer and lower coal layer. The effect of pyrolysis conditions as pyrolysis temperature, CH<sub>4</sub> flow rate and ratio of coal to catalyst on coal pyrolysis was investigated. Results show that higher tar yield can be obtained in CP-SRM process than that in XL pyrolysis under N<sub>2</sub>(CP-N<sub>2</sub>) or H<sub>2</sub>(CP-H<sub>2</sub>) at the investigated temperature (550-750 °C). The increase of methane concentration in the feed gas can increase tar yield obviously even with lower methane conversion. Tar yield can also be improved by higher catalyst to coal ratio with the increase of methane conversion. The highest tar yield is 17.2 wt % (daf) from CP-SRM at 650 °C with methane flow as 220 ml/min, steam to methane ratio as 1 and catalyst to coal ratio as 1.5:5, which is 1.94 times and 1.78 times as the yield in CP-N<sub>2</sub> and CP-H<sub>2</sub>, respectively. Char yields also increase with the increase of tar yield. From the simulated distillation of tar, CP-SRM achieves higher contents of phenol oil (boiling temperature  $T_b < 170$  °C), wash oil (230-300°C) and anthracene oil (300-360°C) and lower asphaltene content ( $T_b > 360$  °C) at the investigated temperature than CP-N<sub>2</sub>. Light tar (boiling temperature below 360 °C) yield increases with higher methane concentration. To prove the positive effect of SRM on coal pyrolysis, experiments of increasing the distance between coal layer and catalyst layer were carried out. The lower tar yield with increase the distance indicates that radicals produced during SRM contribute to the stabilization of coal radicals from condensation into char, thus increasing tar yield and tar quality.

### **Pyrolysis Reactivity and Kinetics of Coal and Coal Extract as well as Residue by Tetrahydrofuran**

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It is thought that the organic matters in coal include mobile phase with smaller molecular weight and fixed phase. To understand the kinetics and mechanism of coal pyrolysis, it is necessary to study the effect of different phases on coal pyrolysis. In this work, a Chinese Baiyinhuo lignite was extracted with tetrahydrofuran to obtain extract and extraction residue, and then the pyrolysis of extract, residue together with raw coal were carried out. The FT-IR result shows that extract has a similar structure with coal and residue except more aliphatic compounds and almost no minerals. The pyrolysis reactivity and kinetics of raw coal, extraction residue and extract were investigated by TG-MS analysis. TGA results show that coal and residue have similar weight loss but significant different from extract. Extract has two obvious weight loss peaks due to volatile and pyrolysis of extract, respectively. The evolutions of H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CO, CH<sub>4</sub> and some low carbon organics were investigated. The results show that all the products from pyrolysis of coal extraction residue are similar to those from coal but different from coal extract. Extract pyrolysis has lower H<sub>2</sub> ion count at 500°C but higher at 700°C than coal pyrolysis. The H<sub>2</sub>O maximum evolution peak temperature of

extract is lower than that of coal and residue significantly. However the H<sub>2</sub>O evolution peak appears at above 600°C is obvious higher than that of coal due to rich H· during extract pyrolysis. Although CO<sub>2</sub> ion count from extract is lower than that of coal and residue, it has obvious multiple peaks compared with a big single peak during coal and residue pyrolysis. Gaseous alkanes have wide evolution temperature region from 300°C to 700°C. The evolution temperature region of olefins is similar to that of alkynes from 350°C to 550°C. What is interesting is that only C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> have significant two peaks compared with other alkanes and olefins due to the cracking reaction of long chain hydrocarbon at higher temperature. Extract has the same aromatics evolution region and two peaks as coal and residue which illustrate the stability of aromatic structure and coal pyrolysis mainly occurs in bridged bonds and side chains. Phenol has the highest evolution temperature from 500°C to 800°C and extract has the maximum evolution but coal has the minimum one which illustrate that extract has more phenolic hydroxyl group than coal, and the oxygen functional groups in extract and residue may have high activity. All the other detected organic ion counts have same law: extract > coal > residue. Coats-Redfern method was used to calculate the pyrolysis kinetic parameters of samples from 300°C to 700°C. The best fitting curve was obtained when the reaction order is 1.5. The average activation energy of coal pyrolysis is higher than that of coal extract and residue pyrolysis which illustrate that the pyrolysis of coal residue and extract are easier than that of coal although the product yields of residue are little lower than that of coal.

### **Preparation of Briquette Binder from Sunflower Stalk Hydrolysis Residues**

An-ning Zhou, Jian-guo Wei, Xin-fu He, Hui-kuan Zhang, Xi'an University of Science & Technology, CHINA

A novel method to make briquette binder from sunflower stalk hydrolysis residues (SHR) was put forward. The effect of hydrolysis process parameters such as concentration of NaOH solution, temperature, reaction time and addition amount of SHR on properties of briquette binder was investigated by the drop shatter index of briquette prepared from Shenfu pulverized coal and the binders. Mechanism of the hydrolysis was proposed by comparing the characterization of sunflower stalk and its residues by using SEM and FT-IR. A new type of composite binder was prepared by adding sodium humate into SHR to increase the thermal properties of the binders. SHR with higher performance were prepared by controlling hydrolysis conditions at NaOH solution concentration 1.0% (wt.), hydrolysis time 3 h, hydrolysis temperature 90 °C, and the composite binder was prepared with 6% sodium humate and 10% SHR (Both accounting for pulverized coal quality), which has low prices and do not increase the ash of the briquette, it is a practical promising briquette binder.

### **The Transformation of Mineral Matter During Coal Ash Heating in O<sub>2</sub>/CO<sub>2</sub> Atmosphere**

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

Two Chinese coals (Coal SF and Coal XYC) were crushed in a jaw crusher and ground to micrometer size in a planetary ball mill. Five laboratory standard sieves, with a sieve size of 15, 45, 75, 100 and 150 μm, respectively, were used to obtain four coal fractions, then to gain ashes from these coal fractions at 815±10°C in O<sub>2</sub>/N<sub>2</sub> atmosphere and O<sub>2</sub>/CO<sub>2</sub> atmosphere. The effect of particle size and environment conditions on the chemical composition and ash high temperature thermal behavior were investigated by X-ray-Fluorescence (XRF), X-ray-Diffraction (XRD) analysis and Simultaneous thermal analysis (STA). For Coal SF, when particle size increased, the fluxing chemical compositions such as Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O decreased, but the refractory chemical composition Ti<sub>2</sub>O increased. XRD analysis showed that calcium carbonate is one of the major products in ashes in O<sub>2</sub>/CO<sub>2</sub> atmosphere due to partial pressure of carbon dioxide. The STA technique was applied to the ash of all coal fractions in O<sub>2</sub>/N<sub>2</sub> atmosphere and O<sub>2</sub>/CO<sub>2</sub> atmosphere, respectively, the melting reactions were more active in finer particle than that in coarser particle and the melting onset were around 70°C higher temperature in O<sub>2</sub>/CO<sub>2</sub> atmosphere compared to that in O<sub>2</sub>/N<sub>2</sub> atmosphere. The low temperature eutectic such as calcium-aluminium silicates was produced at higher temperature in coarser coal particles and O<sub>2</sub>/CO<sub>2</sub> atmosphere. For Coal XYC, the chemical compositions of ashes were not different in all coal fractions. XRD analysis showed that calcium carbonate is also one of the major products in ashes in O<sub>2</sub>/CO<sub>2</sub> atmosphere. The melting behaviors were not different in all coal fractions and O<sub>2</sub>/CO<sub>2</sub> atmosphere. It implied that the ashes of coarser coal particles exhibited less fusibility and the melting behavior was restrained at high temperature in O<sub>2</sub>/CO<sub>2</sub> atmosphere to a certain degree for some coal. The results also indicated that the applied techniques proved to offer valuable information for the ash behavior during heating process.

### **Role of Anthracite Coal in Reduction of Copper Oxide During Reactive Milling with Magnesium**

Haipeng Chen, Bogu Liu, Qianqian Zhang, Naifei Wang, Shixue Zhou, Shandong University of Science and Technology, CHINA



The reduction of Cu<sub>2</sub>O from CuO by reactive milling method of Mg and crystallitic carbon was investigated. Crystallitic carbon was prepared from anthracite coal by demineralization with alkaline melting and acid rinsing, and carbonization at 1500 °C without oxygen for 1.0 h. The morphology and crystalline structure of Cu<sub>2</sub>O after reduction were determined by SEM, EDS, TEM and XRD analysis. The results showed that the particles size from 1.5 h of milling was at the range of 50-100 nm. The crystallite size for Cu<sub>2</sub>O was 15.4 nm from XRD analysis. The relative amount of Cu<sub>2</sub>O was 24.79 wt.% from XRD data refinement. The crystallitic carbon and Mg were all in amorphous state after milling. In reduction, the Mg played a role of reducing agent, whilst crystallitic carbon acted as a dispersant.

#### **Different Coal-Based Carbon for Preparation of Magnesium-Carbon Nanocomposites with High Hydrogen Storage Performance**

Naifei Wang, Qianqian Zhang, Xiaoli Zhang, Tao Li, Haipeng Chen, Shandong University of Science and Technology, CHINA

The Mg-C nanocomposites from reactive milling of Mg and different carbon allotropes, e.g. anthracite coal, carbon deposit, coal-tar pitch coke, and activated carbon, were prepared and characterized in this work. Results showed that the carbon materials greatly prevented the Mg powders from agglomeration in milling, so most of the powders were milled into nanoscale for 3.0 h of milling from SEM analysis. The hydrogen absorption property of the Mg-C nanocomposites was influenced by the amount of carbon additive. The carbon could also store a small amount of hydrogen. Introduction of such carbon materials also significantly changed the hydrogen desorption behavior, which was strongly dependent on the nature and amount of carbon additives. The hydrogen desorption temperature was decreased with the increase of carbon additive, whilst the activation energy of hydrogen desorption also showed a decrease trend.

#### **Effectiveness of Crystallitic Carbon and Bituminous Coal in Milling Process to Prepare Magnesium-Based Material with Low Activation Energy for Hydrogen Desorption**

Tao Li, Xiaoli Zhang, Bogu Liu, Naifei Wang, Shixue Zhou, Shandong University of Science and Technology, CHINA

Crystallitic carbon from anthracite coal was used as milling aid to synthesize MgH<sub>2</sub> under hydrogen atmosphere during ball milling of magnesium. The anthracite coal was demineralized by alkaline melting and acid rinsing treatment to remove most of the mineral matter inherent to the coal, and the ash content was reduced to 0.05 wt.% before carbonization to prepare crystalline. The XRD analysis showed that the particle sizes increased from 17.9 nm to 19 nm after 3 h milling process, and the TEM, DSC and SAED analysis researched the influence of crystallitic carbon further. The crystal structure, morphology and isothermal/non-isothermal hydrogen desorption of the materials are investigated. Carbon demineralized coats the Mg particle dispersing the Mg particles to prevent them from aggregating during milling and improved the decomposition kinetics of MgH<sub>2</sub>. SADE images showed that Mg crystal defects became obvious and particle size was smaller and smaller with the content of crystallitic carbon increasing. The apparent activation energy of the pure MgH<sub>2</sub> desorption reaction was 158.8 kJ/mol and the energy decreased to 116.8 kJ/mol when the crystallitic carbon was added.

#### **Effect of Coking Coal Addition on Hydrogen Desorption Kinetics and Morphology of Magnesium-Based Materials**

Bogu Liu, Tao Li, Haipeng Chen, Qianqian Zhang, Shixue Zhou, Shandong University of Science and Technology, CHINA

The magnesium was milled for 20 minutes with anthracite as milling aid and coking coal as additive to make Mg-based composites for hydrogen storage. The kinetics parameter and hydriding and dehydriding properties of this materials has been analyzed after heat treatment. The crystal structure, isothermal/non-isothermal hydrogen desorption and morphology of the materials were investigated. The SEM image showed that magnesium was coated by crystallite carbon and formed bigger particles that had larger size and irregularly shaped surface. The heat treatment not only provided a good environment for chemical reactions, but also was a great deal of benefit to the granulation of Mg-based composites materials. hydrogen absorption and desorption performance were characterized through the calculation of kinetic parameters of hydrogen absorption. Size effect and surface effect were improved because magnesium was coated by crystallite carbon. The best temperature of dehydriding reduced from > 400 °C to < 380 °C by analyzing TPD. Enthalpy change reduced though the calculation of *p-c-T* curves.

#### **Distribution of Sulphur Functional Groups in High Sulphur Jeypore Coals of Assam**

Amritanshu Kumar, Theem College of Engineering; S.K. Srivastava, Central Institute of Mining and Fuel Research, INDIA

Temperature Programmed Reduction (TPR) studies on Jeypore coal of Assam State of North Eastern Region of India have been carried out in presence of Resorcinol and Hydrogen gas from room temperature to 620 °C with 10 °C/minute heating rate. Six numbers of hydrogen sulphide evolutions from Jeypore coal were observed in the temperature range of 190 °C – 220 °C, 260 °C – 290 °C, 360 °C – 390 °C, 460 °C – 490 °C, 510 °C – 540 °C and 590 °C – 620 °C corresponding to disulphide (1.10), Thiol (1.57), Thioether (0.50), Thiophene (0.43), pyrite + part of complex thiophene (0.70), and part of complex thiophene (0.14). These assignments were made based on the experimental results obtained using model sulphur compounds viz. synthetic rubber, Thiokol, thianthrene, dibenzothiophene, L cystein, Resin containing thiol terminal group, thioplast, pyrite with sand, and Garlic. The thioketonic sulphur in Jeypore coal was estimated to be 0.28, using controlled nitric acid oxidation experiments.

#### **Effect of Different Coal-Carbon on the Structure and Properties of the Magnesium-Carbon Nano-Composite Materials**

Qianqian Zhang, Tao Li, Haipeng Chen, Naifei Wang, Shixue Zhou, Shandong University of Science and Technology, CHINA

As the minor additive phase in the magnesium-carbon composite materials prepared by ball-milling method, the role of different coal-based carbons which can affect structure and performance of the materials has been investigated in the paper. The structure and morphology of the materials by forming processing were characterized by SEM and TEM, and the hydrogen absorption/desorption performance were tested by its heat treatment at 500 °C. In order to compare with the materials without coking, 15 wt.% of coking coal was added to the magnesium-anthracite crystalline carbon composite materials before the heat treatment. The result shows that particle clearance of materials with coking decreases after heat treatment, and metaplast fills the particle gaps and wraps around the particles. The phases mainly consist of Mg and MgH<sub>2</sub>, and have not changed much. Hydrogen absorption & desorption performance test results show that the hydrogen capacity of materials with coking coal decreased to 300 mL/g, reducing 250 mL/g than the materials without coking coal.

#### **Optimization of Parameters During the Milling Preparation and Properties Analysis of Magnesium-Carbon Composite Hydrogen Storage Materials**

Qianqian Zhang, Bogu Liu, Dexi Wang, Xiaoli Zhang, Haipeng Chen, Shandong University of Science and Technology, CHINA

With microcrystalline carbon as the grinding aid after anthracite coal carbonization, magnesium goes through the ball milling process in hydrogen atmosphere during the preparation of magnesium-carbon composite hydrogen storage materials. In the materials preparation and analysis, various test parameters have a huge impact on the morphology and properties of composite materials. Experimental results show that with ball milling time increased, the hydrogen storage density of materials increased at first, then tended towards the saturation state about 3 wt.%, and so do the composites density with metal nickel. At the same time, the number of desorption endothermic peaks increased with milling time, the non-crystallization occurs, and the hydrogen desorption temperature increased from about 275 °C to about 330 °C from DSC curves. In addition, with the number of cycle hydrogen absorption/desorption increases, hydrogen storage density attenuate approximately from 5 wt.% to 3 wt.%, and initial desorption temperature of hydrogen composites is 267.8 °C after second ball milling in hydrogen which is similar to the first initial temperature.

#### **The Influence of Carbon Content on the Performance of Mg-Based Hydrogen Storage Material**

Naifei Wang, Xiaoli Zhang, Qianqian Zhang, Tao Li, Haipeng Chen, Shandong University of Science and Technology, CHINA

With crystallitic carbon from anthracite coal carbonization as dispersant of magnesium powder can effectively prevent the welding of magnesium by ball milling. Crystallitic carbon content in 40 wt.%, magnesium carbon powders have been showed good dispersibility, and crystallitic carbon content is too little (under 30 wt.%), different levels of adhesion and welding will take place in the jar bottom and the surface of the grinding balls with magnesium poor dispersion. TEM images show that the particle size of the material decreases with increasing carbon content. The hydrogen amount detection shows that Mg-based hydrogen storage materials hydrogen storage density have a trend of decrease after the first increases with the increase of adding amount of carbon. Crystallitic carbon will coat on surface of magnesium powder, holds back the reaction of hydrogen atoms and magnesium with too much content of carbon, in addition, magnesium content decrease is the cause of the hydrogen storage density decreased.

## Upgrading Illinois Bituminous Coal with Asphaltene by Agglomeration

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The University of North Dakota's Institute for Energy Studies is proposing to perform bench scale tests to determine the technical and economic feasibility of upgrading Illinois bituminous coal using asphaltene. The objective of the proposed project is to determine if the use of inexpensive asphaltene as a binder for fine coal agglomeration provides an effective and affordable beneficiation technique for Illinois bituminous coal. Illinois bituminous coal is characterized by an average heating value of approximately 12,000 Btu/lb, ash content of approximately 11% and a sulfur content usually ranging from 2.5% to 3.5%. Asphaltene are a class of hydrocarbons that exhibit high molecular weight, high viscosity, density of approximately 1.2 grams per cubic centimeter, and are soluble in toluene but insoluble in straight chain alkanes. The asphaltene dissolved in an oil solvent, would act as an oleophilic binder for the ground coal, favoring agglomeration of the organic content of the coal over the inorganic content which is the main contributor of ash and sulfur. Consequently, the method is expected to reduce the ash, sulfur and moisture content of the beneficiated coal, thus increasing its energy content. Past research using more expensive bridging oils such as crude oil and bitumen, saw significant decreases in sulfur content, ash content, moisture content and increases in energy content of the agglomerates. This project proposes to use asphaltene dissolved in a suitable oil solvent due to its low cost as compared to binders used previously. Preliminary feasibility studies will be performed at the end of the bench tests to evaluate the potential impact of the proposed process on Illinois coal beneficiation. Testing would consist primarily of bench scale agglomeration and separation tests to evaluate the upgrade potential of the process to Illinois bituminous coal. Parameters investigated would consist of types of oil solvent, viscosity of the bridging oil (oil solvent + asphaltene), size fraction of the coal, shearing speeds and duration of agglomeration process.

### POSTER SESSION 7 Coal Mining

#### Methodology for Managing Coal Dust for Underground Mining in Colombia

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The aim of this study is to propose a methodology for a proper handling of coal dust. An underground coal mine in North-East of Colombia was chosen. The procedure consists in detecting places where it, produces, transports and deposits, the coal dust; these places usually are: the working faces, transferences of coal and return of the ventilation. Having identified these spots, the next is to collect samples of the coal dust, which are collected with manual shovel and brush, leaving a proper mark on the spot. Getting new samples within followings 30 days.

The new sample of coal dust is collected to determine the rate of accumulation of coal dust. These samples were subject of granulometric analysis, inertization with rock dust, petrographic and proximate analysis.

Among the results obtained, it is high volatile A bituminous coal, with high content of free hydrocarbons (Exsudatinite); high calorific value ( $> 8200$  Cal / g); high amount of dust production during mining activities ( $> 50$  kg / day); high percentage of size particles smaller than  $150\mu\text{m}$  ( $> 50\%$ ); this means that most of those dusts require a high content of rock dust for inertization (generally greater than 85%). However, it can be seen that in all parts of the mine is not recommended carry out activities of inerting with rock dust, because the rates of deposition of coal dust are very high ( $> 50$  kg / day), therefore it is most convenient carry out alternative activities such as the implementation of water sprays, and establish cleaning seasons in places where the amount of dust is very high. It is also noted that the coal dust often retains many of its properties, although this had been transported by the ventilation system for miles of galleries. Finally, the places inside the mine where there is a high risk of coal dust explosion were identified, and they should be prepared for that situation.

#### Using the Geological, Tectonic, and Lithologic Structure Index to Predict Water Abundance in Sandstone Aquifers from Coal Deposits

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Water abundance in sandstone aquifers associated with coal deposits has been an important objective of hydrogeological research focused on preventing groundwater hazards in coal mines. However, it is common that hydrogeological studies cannot keep up with the geological exploration during mining activities and this happens especially in new coal mines. Therefore, it is important to accurately predict the water abundance in the aquifers using data from geological exploration. This way the hazards

posed by groundwater present in both the roof and floor sandstone that brackets the coal seam can be controlled.

We put forward a method of forecasting the water abundance in sandstone aquifers from Permian- age coal deposits using data collected from those mines facing groundwater hazards from sandstones. The main objective of the proposed study is to demonstrate that the geological, tectonic, and lithological structure index can predict the water abundance even without direct hydrogeological information. GTLSI combines geological, tectonic, and lithological features such as faults, fractures, folds, lithology, and thickness and it is based on a great number of drilling data. The normalization of all data, building of a prediction model to estimate the water abundance in the aquifers, and further corrections based on hydrogeological conditions developed during mining activities can tally with the actual hydrogeology.