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ABSTRACTS BOOKLET

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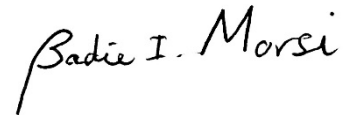
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On behalf of the Thirty-Fourth Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation to Mrs. Fabiana Arias for her meticulous leadership and control of the entire operation of the conference and to Dr. Omar Basha for his invaluable assistance in preparing this Abstracts Booklet.

Thank you,



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

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SESSION 1
Clean Coal Demonstration and Commercial Projects - 1

The Petra Nova Carbon Capture Project

Greg Kennedy, Petra Nova/NRG Energy, USA.

The Petra Nova Project is a commercial scale post-combustion carbon capture project developed by a joint venture between NRG Energy, Inc., one of the largest electricity providers in the U.S., and JX Nippon Oil & Gas Exploration Corporation, the leading integrated energy group in Japan. The Project was designed to separate and capture carbon dioxide (CO₂) from an existing coal-fired unit's flue gas slipstream at NRG's W.A. Parish Electric Generating Station located southwest of Houston, Texas. The captured CO₂ is then transported via an 81-mile long pipeline to the West Ranch Oil Field, where it is used in enhanced oil recovery operations and ultimately sequestered. The Project, which is partially funded by a grant from the U.S. Department of Energy under the Clean Coal Power Initiative, uses an advanced amine-based CO₂ absorption technology, jointly developed by Mitsubishi Heavy Industries, Ltd. and the Kansai Electric Power Co. Inc., to treat and capture at least 90% of the CO₂ from a 240-megawatt equivalent flue gas slipstream. The Bureau of Economic Geology, an arm of the University of Texas at Austin has been contracted to design and implement a 3-year monitoring plan to document what happens to the CO₂ during EOR operations. After a two and half year construction period, the Project was commissioned on December 29, 2016. Now, fully operational, the Petra Nova CCS Facility represents an advanced technology that ensures reliability of an affordable electric supply while simultaneously protecting the environment. When operating at full load, the Project captures approximately 5,000 tons of CO₂ per day, or 1.6 million tons of CO₂ per year, which would otherwise be emitted into the atmosphere, representing the largest commercial scale deployment of post-combustion CO₂ capture technology at a coal power plant in the world to date. This project update will discuss the final stages of construction and testing and the start of operations during the initial months of our 3-year demonstration phase with the DOE.

Update on the Kemper County IGCC Project

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

Mississippi Power Company has constructed a 2 x 1 Integrated Gasification Combined Cycle (IGCC) facility in Kemper County, Mississippi. The plant—based on the Transport Integrated Gasification (TRIG™) technology developed by Southern Company, KBR, and the U. S. Department of Energy (DOE)—can generate up to 582 MW of electricity at peak power production, with 524 MW from syngas produced from locally mined Mississippi lignite. The acid gas removal system at the plant captures carbon dioxide from the syngas and diverts it for use in 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. In addition to producing carbon dioxide, the plant also generates ammonia and sulfuric acid byproducts. The Kemper facility has achieved the integrated operation of both gasifiers, including the production of electricity from syngas by both combustion turbines. The project has also captured carbon dioxide and placed it in the pipeline for use in enhanced oil recovery. This paper describes the Kemper Plant design, reviews the project timeline, discusses the plant operational performance, reviews project highlights, and provides an update on the status of the project.

Low Cost 4500 TPD CO₂ Capture Plant from Coal-Fired Flue Gases

Ahmed Aboudheir, Pinnacle Industrial Services, CANADA. Zechuan Huang, Daoyong Yang, AEET Purenergy, CHINA

The post-combustion carbon dioxide (CO₂) capture from gaseous mixtures by means of liquid absorbents has been and will continue to be one of the leading industrial techniques for many years to come. By using conventional configurations and amine-based solvents, several commercial CO₂ capture plants from coal-fired flue gases have been producing CO₂ with a capacity ranging from 130 to 3,000 tonne per day (TPD), which is subsequently used for food processing, industrial applications, and enhanced oil recovery.

To improve the efficiency and the productivity of this existing and proven technology, it is important to implement enhanced process configurations together with formulated solvents in order to generate a larger production capacity while minimizing utility consumptions and meeting the environmental requirements and constraints. In this paper, a comprehensive design for a 4,500 TPD CO₂ capture plant is conducted based on coal-fired flue gas streams at three recovery rates ranging from 80% to 90% in a cost-effective and sustainable manner. More specifically, the DeltaSolv™ formulated solvent

and enhanced configurations are utilized to achieve the production capacity at minimum emissions to atmosphere, minimum utility requirements, and minimum capital/operating costs. In addition to integrating with an on-line solvent reclaiming system, this plant is designed and optimized by using the rate-based modelling technique which not only involves the use of actual chemical kinetics, thermodynamic properties, heat transfer, and mass transfer of multi-component systems, but also employs the real column configuration and internals. All the design parameters are based on the existing pilot/commercial plants scaled-up methodology. Performance comparison in terms of tables/figures between different solvents and CO₂ recovery rates is presented in terms of flue gas rate, solvent circulation rate, solvent makeup, cooling duty, steam consumption, power consumption, main equipment size, and emissions to atmosphere. The main findings from this design exercise show that it is technically feasible to capture 4,500 TPD CO₂ from a coal-fired flue gas power plant and that the CO₂ production capacities and the clean-up targets can be easily achieved at minimum operational costs using the formulated solvents, advanced but simplified process configuration, and optimum operating conditions.

Optimizing Power Plant Performance through Coal Beneficiation

Mark Ness, Great River Energy; Nenad Sarunac, University of North Carolina. USA.

Pulverized coal combustion (PCC) power plants dominate the power industry and will continue to do so for the foreseeable future. In North America PCC plants are under constant pressure to reduce costs due to cheap gas and increasing renewables, while having to meet tighter emission standards. This can mean moving away from high-rank, high-sulfur fuel to cheaper low-rank, low-sulfur fuels.

The effects of reducing coal heating value and increasing moisture by blending or burning 100% low-rank coal in units designed for high-rank coals are as follows: total coal flow will increase, air flow and flue gas flow increase, and main steam and reheat spray flows increase along with flue gas temperatures. As a result of these increases the plant may become fan, mill or emission-limited, resulting in plant derates and or worsening plant heat rates and increased carbon intensity.

In order to decrease the effects of the burning low grade coal it can be beneficiated by drying and removing some sulfur and mercury using DryFining™ (a coal drying and cleaning process developed by Great River Energy with help from the DOE CCPI Program project # DE-FC26-04NT41763). For example; an 8,800 BTU/lb PRB (Powder River basin) coal with 23.9% total moisture dried to 15% results in 9,725 BTU/lb coal being sent to the mills. Burning this dried coal will also result in lower net sulfur, mercury, and heavy metal emissions.

Coal beneficiation processes such as this provide significant performance, reliability, and operations and maintenance benefits to the plant, as well as improving the potential fuel flexibility of the plant. Increased fuel flexibility directly benefits the busbar generation cost and dispatch importance of the power plant, which results in potential life extension of the valuable asset. The DryFining™ process can also have a significant performance impact by drying bituminous coals that have been water washed to remove sulfur.

Conceptual case studies have been conducted using EPRI's Vista fuel quality impact model on a CAPP/NAPP 665 MWe PRB coal conversion. An example of the potential derate recovery from coal beneficiation will be presented, showing in detail that by drying PRB coal from 23.9 to 15.9 percent moisture by weight can reduce is derate recovery of more than 120 MW while burning 100 percent PRB coal.

Since the low-rank, low-sulfur, high-moisture coals constitute a majority of the low cost coal in North America and new coal plants are not being built, it is important to develop processes that allow existing coal fired power plants designed for bituminous coal to burn lower grade coals efficiently and cleanly to maintain a competitive place in the market.

SESSION 2
Combustion Technologies - Environment

Ni@SiO₂ Core@Shell Nanocatalysts for Selective Combustion Reactions

Yahui Yang, Götz Vesper, University of Pittsburgh, USA.

The engineering of materials on the nanoscale enables precise tailoring of materials' functionality. Core-shell materials are a widely studied class of engineered nanomaterials with application in various technologies. In catalysis, core-shell nanostructures have drawn much attention due to their ability to isolate the nanoparticle cores inside the support and hence alleviate sintering issues. On the other hand, by tailoring the porosity of the shell material, these nanocatalysts can also be considered 'nano-reactors' with porous membrane walls for preferential diffusion of molecules, and hence enable tuning of selectivity.

Here, we designed nickel-silica based core-shell nanostructured catalysts (Ni@SiO₂), synthesized in a reverse micro-emulsion mediated sol-gel process. The silica shell is

microporous with pore diameters of ~0.8-1.2 nm. Diffusion of gases through these porous shells falls into the transition regime from Knudsen diffusion to configurational diffusion, suggesting the possibility of a membrane "sieving effect" in these core-shell structures. Fine control of SiO₂ shell thickness with near nanometer precision for Ni@SiO₂ can be achieved by adjusting several synthesis parameters, including hydrolysis time and SiO₂ precursor concentration, which allows us to control the degree of preferential diffusion and evaluate this effect in a systematic way.

Catalytic performance of Ni@SiO₂ with different shell thickness is evaluated in fixed-bed experiments using oxidation of hydrogen and methane as model reactions. We first studied the preferential oxidation of H₂ and CH₄ gas mixtures over pre-oxidized Ni@SiO₂. We observe that H₂ conversion indeed precedes methane conversion by 0.3 minutes, confirming the existence of significant preferential diffusion of the lighter molecule (H₂). As to CH₄/O₂ mixtures, we find that at oxygen-rich conditions (CH₄:O₂ feed ratio=1:5), decreasing shell thickness results in increasingly rapid loss of reactivity of the catalyst. This can be traced back to oxidation of the active Ni phase, i.e. formation of NiO which is known to show low combustion activity. Thicker shells result in delayed diffusion of O₂ and hence a less oxygen-rich gas mixture in the central cavity, slowing down the deactivation of the catalyst. Increasing the CH₄:O₂ feed ratio to the stoichiometric ratio for partial oxidation of CH₄ (CH₄:O₂=2:1), a strong ignition-extinction hysteresis is observed. Again, we find a strong dependence of this hysteresis on shell thickness, with both ignition and extinction occurring at increasingly high temperature with increasing shell thickness. This study opens the possibility to utilize preferential diffusion to selectively combust H₂ or lighter hydrocarbons in hydrocarbon mixtures through engineering of the core-shell structure. We are currently extending these studies onto higher hydrocarbon oxidation reactions.

NO formation in flames with high oxygen feed gas concentrations

Klas Andersson, Thomas Ekvall, Chalmers University of Technology, SWEDEN

In our previous work we have observed a substantial reduction of NO in oxy-propane flames at inlet oxygen feed gas concentrations above 35 vol. %. In recent experiments the same tendency was observed also for oxygen-enriched air combustion where the increased NO reduction occurs already at a concentration of about 30 vol. %. This effect is something that is not possible to explain with homogenous reburning reactions only. What has been found so far is a possible link between increased oxygen concentration, temperature and soot formation that can influence the NO formation. This will be discussed in the present paper, based on experimental observations in a 100 kW combustion as well as kinetic modelling. The kinetic modelling includes both homogenous gas phase nitrogen chemistry as well as soot formation. These two modelling items are kept separate. The increased amount of soot found at high oxygen concentrations together with higher reaction activity for gas phase species of importance, for both NO_x formation and soot production (e.g. hydrocarbon radicals and acetylene), supports the theory that the high NO_x reduction - at high oxygen concentrations - can be a result of NO_x-soot interactions.

Fate of Sulfur in Coal Direct Chemical Looping Systems

Yaswanth Pottimurthy, Cheng Chung, Mingyuan Xu, Tien-Lin Hsieh, Dikai Xu, Yitao Zhang, Yu-Yen Chen, Pengfei He, Marshall Pickarts, Andrew Tong, Liang-Shih Fan, The Ohio State University, USA.

The fate of sulfur in the coal-direct chemical looping system (CDCL) was investigated in the sub-pilot reactor with a heat-traced gas analysis system. The CDCL process achieves 96.5% carbon capture efficiency with a 26.8% increase in cost of electricity compared to a conventional pulverized coal power plant without CO₂ capture. The sulfur balance was successfully closed during the injection of high sulfur coal. More than 69% of sulfur from coal exit the reactor as SO₂ and H₂S in the reducer flue gas while less than 5% exit as SO₂ in the combustor-spent air. The remaining sulfur was retained in coal ash as inorganics. The finding suggests an acid gas removal system targeting both H₂S and SO₂ is required to meet the recommended quality of CO₂ stream for sequestration and transportation. Using the determined ratio of SO₂ and H₂S, a properly designed Claus plant can potentially enable the recovery of elemental sulfur. On the other hand, the combustor spent air was found to comply with the US EPA sulfur emission regulation and can be released to the atmosphere without a costly acid removal system. The relationship between the sulfur and carbon capture efficiencies was established experimentally and was found to be proportional to each other throughout the experiment at a ratio of 0.8 below 93% of carbon capture efficiency and near 1 above 93%. This was attributed to the delayed release of organic sulfur during incomplete char gasification in the reducer. The finding reaffirms the effectiveness of the counter-current moving bed design in minimizing the amount of carbon and sulfur emission in the combustor spent air with an average carbon and sulfur capture efficiency of 96.5 and 95%. Sulfur deposition on the iron based oxygen carriers did not affect the system performance and complete removal of deposited sulfur was observed during oxidation in a thermogravimetric analyzer. The findings demonstrate the robustness of the coal-direct chemical looping system to handle high sulfur coal without complicated acid gas cleaning scheme or severe performance penalties. A 250 kWth pilot scale coal-direct chemical looping reactor has been constructed by Babcock and Wilcox Power

Generation Group in Barberton, OH that is undergoing unit testing with both low and high sulfur coal in 2017.

SESSION 3 Coal Ash Management - 1

Harvesting of Coal Combustion Products Stored in a Dry Storage Area for Beneficial Use

Marty Leedy, Rafic Minkara, Headwaters Construction Materials, LLC, USA

According to the American Coal Ash Association, millions of tons of coal combustion products (CCPs) are sent to long term storage facilities (landfills or surface impoundments) every year; much of this material retains its ability to provide a functional benefit in concrete or other beneficial use applications. Even though stored for potentially, many years, these materials can still substitute for the use of virgin materials and can be lightly processed as necessary to meet relevant product specifications. Therefore, these CCPs can and should be harvested from these storage sites for beneficial uses elsewhere.

Headwaters Construction Materials, LLC is leading the way in the development of scientifically supported, economically feasible and environmentally protective projects as well as the development of BMPs and a framework to address critical aspects related to the recovery of CCPs situated in existing ash storage facilities (surface impoundments and dry storage) for beneficial use.

CCP Harvesting Protocol – Embracing ASTM E50.003 for Beneficial Use of CCP from Active and Inactive Storage Areas

William G. Petrucci, Headwaters Construction Materials, LLC, USA.

The demand for quality coal combustion products (CCP) for use as feedstock in construction products is expected to exceed the production of new CCP materials moving forward. As such, we are challenged with finding non-traditional sources of CCP to feed the market. Harvesting CCP from active and inactive storage areas units, formerly known as landfills and lagoons, is the logical and responsible approach to source materials for construction products that meet the required performance standards in a safe and economical manner. Harvesting CCP yields other benefits, including addressing airspace needs; achieving site closure; addressing corrective measures; promoting proactive risk and liability management; and embracing conservation, restoration and sustainability initiatives. In an effort to establish guidelines that benefit energy plants, regulatory agencies and other stakeholders, the international ASTM E50 Environmental Assessment, Risk Management, and Corrective Action Committee formed a subcommittee to address the need for direction on the matter of harvesting CCP. The ASTM E50.03 subcommittee is now developing a guideline on Beneficial Use of Coal Combustion Products from Active and Inactive Storage Areas. The draft guidance includes a pathway to address project phases that need to be considered as we embrace harvesting CCP. These phases are: 1) site background review of CCP storage areas; 2) detailed characterization of CCP storage areas; 3) reclamation and planning of CCP storage areas; 4) reclamation detailed design and approval of CCP storage areas; and 5) reclamation implementation of CCP storage areas. This group prepared a decision flow chart included in the guidance that takes the user through the process.

Engineering Cost-Effective Project Outcomes: Construction Quality Programs for CCR Projects

Dale W. Evans, Kathleen Whysner, Remedial Construction Services, L.P, USA

Construction quality assurance (CQA) processes are an important tool to ensure that CCR programs can be implemented to meet design prerogatives. However, while the activities associated with CQA efforts are essential, absent an engineering focus on what outcomes need to be attained, CQA programs may be both costly and relatively ineffective in demonstrating that the desired outcomes have been met. At the heart of this issue are the oftentimes highly variable site conditions and the uncertainties attributed to most CCR projects which places a focus on the consideration that while most anything can be measured, it is important to focus on measuring what matters most. In particular, because site variabilities often affect materials handling technologies as well as the associated contractor means and methods, the measures of quality employed must be appropriately adapted. Further, as the long-term field behaviors may represent a critical functional goal, time-rate performance factors may be necessary to incorporate as part of the CQA and field monitoring efforts regardless of the performance assessment processes used at the time of construction.

In effect, the solution to the issues associated with CCR projects is for engineers to assume a pivotal role in linking design programs with performance outcomes and the quality measures necessary to quantify success. In particular, focus is needed on the anticipated construction means and methods, the appropriate measures of quality, and

how they are to be considered in relation to the design. This paper addresses this critical issue for engineers to understand, particularly with respect to recognizing their role and importance in the design process and in project delivery. Therefore, this paper outlines appropriate considerations and defines a process for planning CQA programs that include up-front scoping, engineering design linkages, field monitoring, performance evaluations, and adaptation to contractor means and methods. Also, while not typically considered, an evaluation is provided of the methods available to link CQA programs for CCR impoundment closures with the method chosen for project delivery. Specifically, because many designs lack full front-end site characterization, they inherently become largely prescriptive with an emphasis on defining key features and overall lines and grades. These processes may lead to oftentimes more generic application of specifications that may measure but not support understanding of critical field performance parameters. Thus, procurements focused on contractor means and methods may not effectively consider key aspects of quality-based assessments.

What's Really in the Water? New Treatment Options for Coal Combustion Residuals (CCRs) and Mining-Influenced Water

Pamela Dugan, Carus Corporation, USA

Boron is an emerging contaminant at coal ash impoundments that readily leaches from coal combustion residuals (CCR) and commonly detected at high concentrations in groundwater. The USEPA promulgated the Federal CCR Rule in 2015 which identifies boron as an Appendix III indicator constituent for detection monitoring. Unlike other CCR regulated constituent's boron does not attenuate onto aquifer solids via sorption or precipitation of new minerals and thus can produce large plumes in groundwater downgradient of CCR units. A recent settlement between utilities, EPA, and NGOs indicates that boron should be added to the list of constituents in Appendix IV of the final CCR Rule. Under the proposed change, a statistical exceedance of background concentrations for boron will trigger cleanup to background. Constituents in the CCR Appendix IV such as As, Se and Hg are also of great concern due to their toxicity and regulated standards. There are a wide variety of stakeholders that are directly affected by the presence of emerging and newly regulated compounds that may include utility providers, municipal water treatment facilities, remediation practitioners. Navigating the rapidly changing regulatory environment and discerning what the effective treatment technologies are for emerging contaminants of concern can be daunting. To this end, a variety of batch and column experiments were conducted using coal ash and coal ash leachate to evaluate the removal efficiencies of boron, mercury, arsenic and selenium using novel oxidative and sorptive treatment approaches. The results of these laboratory efforts will be presented as well as two case studies highlighting Mn and Fe treatment options for mining-influenced water.

The Decommissioning Process and Consideration of Environmental Factors That Can Impact Cost, Schedule and Reuse Options

William Ahlert, HDR Engineering, Inc., USA

As more utilities move to close coal fired power plants and make decisions about the end use of these sites, plant owners are faced with unplanned and sometimes competing fiscal and regulatory challenges when planning and budgeting for plant decommissioning. Early consideration of end usage is critical to the overall decommissioning planning and budgeting. A solid decommissioning process and understanding when and what environmental factors, specifically soil and groundwater contamination, need to be considered is imperative. Understanding groundwater hydrology, potential sources of contamination and remediation alternatives should be considered in the end use decision making process as well as understanding the potential cost impacts and remediation timeline. Additionally, the Coal Combustion Residuals Rule will influence the method and timing of closure of some impoundments. This results in an increased need for strategic planning and coordination among multiple groups within the utility. Remediation of these impacts can take many forms, each of which operates on its own timeline. Depending on the unique geologic setting of a given site, there can be many complicating factors that must be considered and potential remediation alternatives.

This presentation will focus on understanding the steps in the decommissioning process and when soil and groundwater issues need to be considered. Additionally, lessons learned relative to groundwater hydrology associated with power plants will be discussed. End use alternatives of property and the potential remediation methods will be covered.

SESSION 4 Coal Science - 1

Involvement of Radicals as Intermediates in Coal Autocatalytic Heating During Storage

Haim Cohen, Ariel University and Ben-Gurion University of the Negev; Sharon Ruthstein, The Bar Ilan University; Zeela Taub, Ariel University, ISRAEL

When coal is exposed to atmospheric oxygen it undergoes a low temperature oxidation process which is exothermic. Thus, during storage it might result in formation of hot spots in the piles. In extreme cases, fire eruptions and explosions have been reported. The main reaction products are carbon dioxide and water but also carbon monoxide, low molecular weight hydrocarbons (C1-4) and molecular hydrogen are produced. The mechanism by which the molecular oxygen interacts with the coal macromolecule has been suggested to occur in several steps. These steps primarily involve diffusion to the surface where physical adsorption followed by chemical adsorption takes place. The chemical adsorption forms different types of surface oxides that can subsequently react to form several products, primarily CO₂. Some studies related to the oxidation process occurring at these low temperatures (30-120C) have suggested that the mechanism of the process involves radicals as intermediates.

Indeed, some studies in the past have demonstrated that at increasing temperatures (100, 200, 300 C) as the coal undergoes significant oxidation, there is a decrease in the measured radical concentration. However, as the previous studies were conducted under conditions where significant structural changes occur, it is possible that in the low temperature range (T < 100C) the oxidation mechanism is different.

The occurrence and nature of stable radicals in fresh and oxidized coals (bituminous and lignite) using EPR spectroscopy have been studied. Distinct differences between as the lower rank (lignite- German origin) and the higher rank coal (bituminous American mined Bailey coal) have been observed. Three types of stable radicals have been determined and the results also corroborate the suggestion that radicals are involved in the LTO process.

Coal Ash Fusion Temperature and Viscosity at High Temperature by Molecular Dynamics Simulation and Experiments: The Role of CaO/Fe₂O₃ Ratio

Xin Dai, Jin Bai, Du Shiyu, Xiaodong Wen, Lingxue Kong, Zongqing Bai, Wen Li, Chinese Academy of Sciences, CHINA

The role of CaO/Fe₂O₃ ratio on ash fusibilities and flow properties was investigated in this work by combining the molecular dynamics simulation and Raman spectrum as well as X-ray Photoelectron Spectroscopy (XPS). The ash fusion temperatures (AFTs) varied largely as the ratio of CaO/Fe₂O₃ was lower than two. The viscosity-temperature curves of ash slags were change from the crystalline slag to glassy slag when the CaO/Fe₂O₃ increased above two. Insight from molecular dynamics simulation revealed the effect of CaO/Fe₂O₃ ratio on the structural variation. The radial distribution and oxygen species variation from the simulation results were employed to demonstrate the depolymerization effect of the calcium oxide and ferric oxide. The Raman spectrum and XPS analysis were adopted to reveal the oxygen species variation gotten from the simulation results. The combination of the molecular dynamics simulation and experiments can provide new insight into the mechanism of coal ash fusion behavior and viscosity-temperature influenced by CaO/Fe₂O₃ ratio.

SESSION 5 Gasification Technologies: General 1

An Overview of DOE's Gasification Systems Program

K. David Lyons, NETL; Christopher Munson, Massood Ramezan, KeyLogic Systems, USA

The U.S. Department of Energy's (DOE) Gasification Systems Program focuses on advanced technology developments to reduce the cost of coal gasification—by lowering technology capital costs, reducing energy penalties, and increasing plant efficiency and availability—to enable more economical conversion of coal into affordable and reliable electricity, and a market-flexible slate of byproducts with greatly reduced greenhouse gas emissions. Research activities include developing lower-cost technologies to separate oxygen from air for efficient coal conversion; improving high-pressure solid feed systems to enable use of low-rank coals in high-pressure gasifiers; facilitating co-feeding of coal with biomass or waste; and further developing hydrogen production technologies to lower the capital requirements and increase the efficiency of gasification technologies and polygeneration applications.

One effort underway focuses on coal conversion research and development (R&D). Specifically, the program is investigating the feasibility of small-scale, modular systems with heavy reliance on advanced manufacturing, sophisticated modeling and simulation,

and reaction and process intensification. This initiative aims to reduce the cost and environmental impact of coal conversion while turning low-value feedstocks, such as coal and biomass, into a multitude of higher-value products. In addition, the initiative creates the possibility of accessing new markets, such as remote villages that use high cost fuel for electricity and other rural communities near coal mines that are subjected to high electricity costs. Modular systems are expected to increase deployment opportunities by breaking dependence on “economies of scale” and affording the following advantages:

- Lower capital investment, reducing investment risk.
- Can be strategically located close to resources and/or the markets for their products, lowering transportation costs.
- May be tailored in size and characteristics to locally available stocks of biomass and refuse-derived fuel, opening the potential to leverage these “opportunity fuels” in conjunction with coal, with the accompanying lowering of carbon emissions of these systems.

This paper will provide an overview of DOE’s Gasification Program, including a review of the modular energy systems initiative and detailed discussion of advances in technologies to date that will serve as the foundation for future low-cost, low-carbon emissions, coal-based energy systems.

Experimental Study on Tar Formation during Pressurized Brown Coal Pyrolysis as Part of the British Gas/Lurgi (BGL) Gasification Process

David Scheithauer, Marco Küttner, Steffen Krzack, Denise Reichel, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

The mechanisms of pyrolysis product formation under pressure, especially the formation of condensable hydrocarbons (tar), are still not well understood, which obstructs the performance prediction of counter-current moving-bed gasification processes. Furthermore, the tar fraction that is withdrawn with the rawgas recently gains importance as marketable by-product.

Therefore, the present work studies tar formation of a Czech brown coal in a lab-scale fixed-bed reactor, which imitates the conditions in the upper part of BGL gasifiers under different process conditions. The study comprises a variation of temperatures between 500–800 °C and pressures up to 30 bar as well as different atmospheres (inert and steam) and gas residence times.

The investigation is accompanied by a broad characterization of the different tars, which enables an assessment of gasification tars as feedstock for specialty chemicals production or for an energetic use. Here, standardized chemical analysis to determine the water content, elemental composition and heating value are complemented by a range of physical property analyses to measure viscosity, density, boiling curve, carbon distribution, relative molecular mass etc. Organic compounds of the tar are identified by gas chromatography with flame-ionisation and mass spectroscopic detection (GC-FID/MS). These results are compared with analytical pyrolysis using pyrolysis GC-FID/MS.

Gasification of PRB Coal Solvent Extraction Residue

William C. Schaffers, Ying Wang, , David Bell, University of Wyoming, USA

The coal industry is facing increasing pressure in traditional markets due to increased regulatory pressure resulting from climate change fears and due to low natural gas costs. Older coal fired electrical plants are being phased out rather than upgraded and new electrical generation capacity needs are increasingly being filled by natural gas fired plants and renewable sources. In addition, the use of coal to produce liquid fuels is also not economically feasible in the current oil and gas market with increased supplies and decreased demand for oil and gas. As a result, the University of Wyoming, with help from the state of Wyoming, is looking for new and novel ways to utilize its huge coal resources. One of the processes under study is the solvent extraction of coal to produce chemicals and other products. A byproduct of this liquid extraction process is the residue left behind after removal of the solvent soluble material.

A potential method for utilization of the remaining solvent extraction residue is gasification. Syngas produced from gasification could be used as a source of energy as well as a source of hydrogen, via the water-gas shift reaction, for coal upgrading processes. Limited data is available regarding the ease of gasification of this residue, especially for low rank coals such as Wyoming PRB coal. There has also been little investigation into the kinetics of the residue gasification and how they compare with those of the unprocessed coal.

In this study, soluble compounds were extracted from PRB coal using an organic solvent at temperatures and pressures representative of those used in a coal solvent extraction process. Extraction of the coal sample continued until the solvent passing through the sample lightened, indicating that most of the soluble material had been removed. The remaining residue was dried and then gasified in a modified drop-tube reactor at various temperatures and pressures. Carbon dioxide or steam were used as gasification agents. Results were then used to fit kinetic models to the gasification process. The results were compared with those obtained from gasification of untreated PRB coal to see the relative ease of gasification of the extraction residues. In addition, surface area analyses of the residue and char formed from the residue were performed and compared to those for PRB coal. SEM images were also taken.

Results of these studies should provide important information about the possible use of residues remaining after coal solvent extraction processes, especially for sub-bituminous coals such as Wyoming PRB. The data will aid in the determination of gasification conditions required to effectively convert the residue into syngas and thus aid in determining the type of gasifier which would be most effective for this purpose. Overall, these results could help make solvent extraction processes more feasible since the remaining residue could be used effectively and possibly provide needed energy and hydrogen for coal conversion processes.

Steam Gasification of Weihua Subbituminous Coal with Ca(OH)₂ as a Catalyst

Dianmiao Cui, Longpeng Cui, Research Institute of Petroleum Processing, China Petrochemical Corporation, CHINA

The effect of Ca(OH)₂ catalyst on the steam gasification of Weihua sub-bituminous coal was investigated by a fixed-bed reactor at atmospheric pressure and 800 °C. The results show that Ca(OH)₂ as a catalyst raw material can significantly enhance the gasification reactivity of coal, and the carbon conversion increased greatly from 59.3% (without the Ca catalyst) to 79.9% (with 17 wt.% Ca(OH)₂ catalyst). The influence of different factors including pyrolysis temperature, Ca(OH)₂ loading, gasification temperature and reaction pressure on the coal char gasification were evaluated as well. The char obtained by pyrolyzing the low-rank coal at low temperature had higher activity than that obtained at high temperature. The gasification rate increased with increasing the Ca(OH)₂ loading, but Ca(OH)₂ loading possesses a saturation point. With increasing the gasification temperature from 670 °C to 800 °C, the carbon conversion and H₂ production increased significantly from 30.8% and 0.85 Nm³/kg-C to 77.7% and 2.33 Nm³/kg-C, respectively. The carbonation reaction can be enhanced by raising reaction pressure, and the carbon conversion and H₂ production increased correspondingly. The catalytic activity of Ca(OH)₂ decreased slowly with the amount of calcination/carbonation cycles. Analyzing the coal via FT-IR reveals the dispersion mechanism of Ca(OH)₂ into the matrix of coal through ion exchange and diffusion, which is a key factor to improve the coal gasification reactivity.

Kinetic Benefits of Small Particle Size for Fluid Bed for Transport Coal Gasification

Irish Srinivas, Staci Van Norman, Steven C. Gebhard, Steven Schwab, Drew Galloway, Nathan Weinstein, Jeff Martin, TDA Research Inc., USA

There are many processes that can be used convert coal into fuels, chemicals and electrical power including direct combustion (power generation), gasification (chemicals, fuels and power) and direct liquefaction (fuels). Of all of these processes, only coal gasification has the potential to make all of these products. Unfortunately, coal gasification is expensive and to make the process economically viable generally requires very large, capital intensive plants to achieve economies of scale. As a result, small scale gasification for local/on-site uses (such as local power generation) thus far has not been economical. What is needed is a new gasification technology that is more economical at smaller scales, and can be part of a modular power production facility. TDA Research is developing a unique gasification reactor that takes advantage of the fact that small coal particles are more reactive than larger particles. In our technology, the gasifier can be small enough that it can be economically constructed without using a refractory lining, thus reducing its cost and making the gasifier faster to start and stop as needed.

In Phase I, TDA quantified the reactivity of several types of coal as a function of particle size using statistically designed experiments and developed an empirical model of coal reactivity. We then correlated the results with detailed analysis of the coal. We then designed, built and tested a cold flow model of our novel gasification reactor and used the test results to design a high-temperature, high-pressure, bench-scale metal gasifier to be built and tested in Phase II.

Our gasifier design is ideally suited for smaller-scale gasification units for use at mine-mouth and coal preparation locations.

SESSION 6 Rare Earth Elements- 1

Feasibility of Recovering Rare Earth Elements from Coal and Coal By-Products

Mary Anne Alvin, NETL, USA

The Feasibility of Recovering Rare Earth Elements (REE) Program which was initiated by DOE-NETL in 2014 includes conduct of both intermural as, well as extramural projects, ranging from concept definition and development, through laboratory and bench-scale testing, and additionally pilot-scale testing, in order to validate the technical and economic feasibility for design, construction, and operation of functional prototype, salable, high purity, REE separation and extraction systems. Efforts associated with current projects that are being conducted, as well as recent technical accomplishments will be discussed.

Recovery of Rare Earth Elements from North Dakota Lignite-Related Feedstocks

Daniel A. Laudal, Steven A. Benson, University of North Dakota, USA

According to the U.S. Department of Energy National Energy Technology Laboratory, rare earth elements (REE) provide significant value to our national security, energy independence, environmental future, and economic growth. REEs are utilized in a suite of high importance end-uses, such as cell phones, hybrid vehicles, magnets, computer components, catalysts and many others. The unique magnetic properties of REEs, in particular, make them crucial materials for the growing renewable energy and electric automotive markets. REEs are used in the strongest permanent magnets currently known, and are used in generators for wind turbines and in motors for hybrid/electric vehicles. These same types of magnets, as well as other critical REE-based products are used in a host of military defense applications, as well.

China, in part due to its deposits of a unique REE resource (ion-adsorbed clays) that combines high quantities of heavy and critical REE, as well as simple and low cost extraction, dominates the global supply market. In 2010, China established new quotas on exports of REEs, which resulted in huge increases in REE prices peaking in 2011 due to an expected supply shortage for critical applications. As a result, production at the California-based Mountain Pass Mine was re-started after several years of dormancy. However, after peaking in price in 2011, prices have dropped substantially to slightly above 2010 levels, challenging the profitability of non-China based production which consists mainly of hard rock carbonatite deposits, that are deficient in critical REE and heavy REE. Some researchers have noted that mining of the Mountain Pass and similar resources will neither mitigate the crisis in REE resources nor eliminate the shortage of the most critical REE, but will only result in overproduction of excessive Ce.

According to the USGS 2017 Mineral Commodity Summary report, China accounted for about 83% of the total global REE supply in 2016, down from about 95% prior to 2010. Meanwhile, the US production was zero, with the Mountain Pass mine having declared bankruptcy and closing operations in the last quarter of 2015. The U.S. is currently 100% import reliant for REEs. Although still dominating global supply of the heavy REE, some researchers have estimated that the Chinese ion-adsorbed clays resource will only last another 15-20 years. The Chinese clays represent essentially the entire global supply of heavy REE and most of the critical REE. Further, the bulk of Chinese reserves and production is from a carbonatite-type deposit (Bayan Obo) that contains only trace amounts of heavy REE (98.7% light REE), and supplies roughly 80% of the global light REE demand. Due to its limited supply, and because the Chinese clay resource is rich in heavy and critical REE, while most other traditional resources are deficient in these less common and more valuable elements, it is imperative that new domestic sources of REEs, especially the heavy and critical REE, be identified and processes be developed to produce them. Coal and coal byproducts have recently been identified as one of these potential new resources for REEs.

As part of the US Department of Energy effort to identify alternative domestic sources of Rare Earth Elements (REE), the University of North Dakota was awarded a project to determine the feasibility of recovery of REE from North Dakota lignite coal and related feedstocks. The project team includes the University of North Dakota, Barr Engineering, and Pacific Northwest National Laboratory (PNNL) with the support of the cost share partners North American Coal Company, Great River Energy, and the North Dakota Industrial Commission/Lignite Energy Council as well as technical support from the North Dakota Geological Survey. The overall goal of this Phase I project was to develop an economically viable and environmentally benign process to concentrate REE to a goal of 2 weight percent to form a synthetic mixed REE ore. As part of the project, an extensive sampling and analysis campaign was completed to identify promising feedstocks, which was followed by laboratory-scale concentration testing and a technical and economic feasibility study. Finally, the design of a bench-scale test system was developed, which is to be constructed and tested in a subsequent Phase II project, if awarded by DOE. This paper will provide the results of the Phase I project and the plans for a subsequent Phase II project.

The originally proposed concept involved recovery of REE from the reject stream of the Great River Energy lignite drying system located at the Coal Creek Station power plant in North Dakota. However, upon further investigation in the project, it was discovered that on an ash-basis, the REE are more concentrated in certain locations within the coal seams than in the associated roof/floor sediments. Therefore, the focus for the remainder of the project was shifted towards development of methods to concentrate the REEs from these selected coal seams.

Laboratory testing of a novel concentrating method has shown very high recovery of about 80-90% of the REEs from two potential feedstocks, ranging from 580 to 2300 ppm REE content on an ash basis, with excellent selectivity/recovery of the critical and heavy REE. Details of a processing scheme to economically concentrate the REE to the goal of 2 weight percent using a simple and environmentally benign method have been established. The project team has also developed the concepts for integration of the REE recovery process within an existing coal conversion facility that will provide cost-saving synergies, multiple saleable product streams, and infrastructure to reduce costs. Based on the results of the Phase I work, the project team believes North Dakota lignite-related feedstocks to be a highly promising alternative domestic source of REE that will limit dependence on foreign supply.

An Environmentally Friendly Approach to Recovery of Rare Earth Elements from Coal Production and Utilization Byproducts

Maohong Fan, Zaixing Huang, Kai Li, Hanjing Tian, University of Wyoming; Yan Luo, West Virginia University; Eric Williams, Gabrielle Gaustad, Rochester Institute of Technology; Hertanto Adidharma, Maciej Radosz, University of Wyoming, USA

The markets for rare earth elements (REEs) based materials have been steadily increasing. However, how should we meet the increasing demands and where should be get the materials in a both cost-effective and environmentally friendly manner? Coal production and utilization byproducts (CPUB) have been considered to be one of the important REEs resources. However, there are a number of challenges people have to overcome before production of REEs from CPUB can be successfully realized. Wyoming is rich in coal, thus it has a lot of coal byproducts also, including fly ashes. Supported by U.S. DOE, the UW-WVU-RIT team led by Dr. Fan has been developing new pollution-avoidance or pollution-prevention, and cost-effective technologies with enhanced performance and great scalability for recovering high-value REEs from coal ashes with the goal of enriching the REEs from 300 ppm in coal ashes (eventually coal and other coal utilization byproducts) to 2 wt% targeted by DOE. The results achieved by the team to date show that the goal set by DOE has been successfully achieved. In addition, factorial tests are being conducted to minimize the cost and maximize the REEs recovery efficiency of the new REEs extraction processes. The overall progress shows that recovery of REEs from coal fly ashes with the new extraction technology is promising.

Bioleaching of Rare Earth Elements from Coal-based Products

Yanna Liang, Ji Zhang, Southern Illinois University Carbondale, USA

Rare earth elements (REEs) including the 15 lanthanides plus yttrium and scandium are valuable and extraordinarily useful elements for our society. Currently, however, the US does not produce REEs at commercial scales and the lack of a secure and stable supply of domestic REEs could result in potential risk to the U.S. economy and defense. During recent years, research and development on extracting REEs from coal-based products are on the rise. Typically, the REE recovery process involves physical enrichment followed by chemical leaching. While this approach certainly works effectively for separating REEs from the feedstocks, it does have several drawbacks, such as high energy and chemical expenses and issues related to disposal of spent harsh acids and/or bases.

Besides chemical leaching, REEs can be leached out of feedstock materials through biological processes, an approach termed bioleaching, biomining or biohydrometallurgy. Even though bioleaching is a natural process, use of it for leaching REEs out of domestic coal and coal by-products has not been investigated yet to the best of our knowledge. Thus, in this talk, I will describe how this process works and how it can be integrated into other existing technologies for REE recovery. In particular, I will discuss how REEs can be extracted efficiently from abundant coal resource generally with low REE concentrations.

SESSION 7 Clean Coal Demonstration and Commercial Projects - 2

Keeping Coal Competitive in Future Markets with Flameless Pressurized OxyCombustion

Peter Reineck, Peter Reineck Associates, UNITED KINGDOM; Massimo Malavasi, Itesa S.p.A; ITALY; Joshua Schmitt, SwRI, USA

Future markets for power are expected to require a larger quantity of load-following power plants which reduce output during the night and early morning, when the demand for electricity is the lowest, and which can respond rapidly to peak loads at any time, a consequence of the variable output of wind and solar power. A coal power plant based on Flameless Pressurized Oxy-combustion (FPO) can go from 5% to 100% of capacity rate in less than a half hour in response to fluctuating demand.

FPO is a proven oxy-combustion technology that was developed to recover energy from low ranking coal, as well as other brown fuels and wastes. Itesa began developing FPO in 2003 on a 5-MWth pilot in Gioia del Colle, Italy, to destroy hazardous industrial waste and as such, design objectives were very high combustion efficiencies and capture of metals in the fuel in the vitreous slag. Pilot plant trials on coal began in 2006. The technology was subsequently deployed in 2009 at the 15-MWth scale at the Jurong Island petrochemical cluster in Singapore for waste incineration.

In the FPO oxy-combustion process, nitrogen is separated from the air and the combustion takes place with oxygen; recirculated flue gas is used to maintain combustion temperatures at acceptable levels. The resultant flue gas is primarily CO₂ and water, which allows for a relatively simple and cheap CO₂ capture process: this is in contrast to air-combustion systems which require a complex and costly post-combustion capture (PCC) process. Coal is fed to the combustor as a slurry in water, and the

combustor operates at elevated pressure (approximately 10 atm), which improves the overall efficiency and reduces the size and cost of the combustor. Notably, the FPO cycle recovers most of the heat of vaporisation of the contained water, maximizing efficiency. The combustor is designed to coalesce the molten ash particles so that they settle to the chamber walls and drain to the outlet, significantly reducing the particulate content in the exhaust gas and allowing the use of coals with up to 40% alkaline ash content.

FPO is a low-emission technology: zero thermal NO_x minimizes overall NO_x; any organic nitrogen is converted to elemental nitrogen (N₂). Total organic content (TOC) at combustor exit is hundreds of times lower than for traditional combustion processes, with dioxin and furans close to zero. Work commenced on DOE Project DE-FE0027771 in October 2016 to provide the design for a 50-MWth FPO pilot plant that can fire a wide range of high-to-low rank coals. The project will investigate updating and improving the cycle for power generation with CO₂ capture by incorporating a turbo-expander as a bottoming cycle, with a principal steam power island that utilizes a heat recovery steam generator, increasing the overall efficiency of the cycle. A cost study will also be performed on the updated FPO design as part of the project. The FPO pilot plant built based on the design would then be demonstrated over a 3-year test program to generate data for the design of a commercial-scale 500 MWth firing module commercial power plant with integral CC which could start operation in 2025. An update on the progress of the project is included.

A discussion of the levelised cost of electricity (LCOE) of various cases is made, including a comparison of established supercritical pulverised coal (SCPC) technology with and without PCC, to FPO fitted with CO₂ compression and liquefaction, and to FPO ready for carbon capture and storage (CCS-ready). This would enable CO₂ capture for use in enhanced oil recovery (EOR) or sequestration when market conditions make it attractive to do so. In addition, a comparison of LCOE of FPO with conventional processes for firing low-ranking coals with high water and ash content will be provided. Through these advances FPO provides a pathway towards affordable, efficient, and clean coal power technology that is CCS ready.

Development of a Cycle for Large Pilot and Commercial Power Plant Using Flameless Pressurized Oxy-Combustion

Joshua Schmitt, Southwest Research Institute, USA. Massimo Malavasi, Itea S.p.A.; ITALY; Brandon Ridens, Adrian Alvarado, SwRI, USA

Flameless pressurized oxy-combustion (FPO) technology, developed by Itea, is providing a pathway for thermally and economically efficient coal combustion with carbon capture and storage (CCS). The technology is being developed into a 50 MWth scale firing loop which will bring the technology maturity closer to a full-scale commercial power plant. As part of the development process, the FPO cycle is modeled in Aspen plus. The model is adapted to match experimental data taken by Itea on a smaller firing loop.

The combustor operates separately at a temperature of 1650 K. The combustion gasses are mixed with a portion of the recycle gas, quenching the flow down to 1093 K. The combustion loop is maintained at a pressure of 12.2 bar. The gas that is not recycled is removed from the loop at high temperature before the boiler. This gas is expanded down to 2.4 bar with a turbo-expander that provides additional power generation. After this point, a scrubber and condenser remove SO₂ and water from the gas stream. This results in a gas stream that is almost entirely made up of 94% CO₂ by mass with 95.5% O₂ purity. The purity of the gas stream and the absence of large particulates eliminate many purification components required for CCS and improves the cost and efficiency of the overall cycle.

The 50 MWth cycle model is tested with varying input conditions. Coals of low rank, including PRB and Lignite coals, are fed into the system. For the different coals, adjustments are made to the flow splits and feed rates in order to maintain the 50 MWth of produced energy. The different coals are compared to each other in terms of their feed requirement relative to thermal output and their CO₂ production.

The 50 MWth cycle model is adapted into a fully commercial model that fires at 1,500 MWth. This arrangement is laid out in a modular configuration which requires three separate combustor-boiler loops. This cycle includes a supercritical steam turbine operating with a single stage of reheat. The power produced by the turbine and the turbo-expander is calculated and offset by the expected parasitic loads from the compressors, blowers, and other parasitic power losses. A comparison of the net produced power for different qualities of coal feeds is made.

Replacing Liquefied Natural Gas with Synthetic Natural Gas in the Energy Mix of Pakistan

Farid Malik, Forman Christian College, PAKISTAN

Energy security is vital for a nation. Pakistan emerged on the world's Natural Gas Map in 1952 with a huge discovery in the Dera Bugti area of Balochistan. At 12 TCF it was one of the largest deposits of its time. Transmission and distribution of this natural resource started in 1955. Today the country has a state of the art gas network spread over 20,000 km covering the length and breadth of the entire land mass.

In order to meet its energy needs the government has signed a binding contract with Qatar to buy 1.3 million tons of LNG every year for a period of 20 years at a varying price of Brent. Even at the current low rates of oil the price of RLNG is higher (Rs. 946

/ mmbtu) and unfeasible compared to local gas supply (Rs. 700/mmbtu). With climbing oil prices RLNG will be out of reach of the local industry. SNG produced from indigenous coal seems to be a more viable option. Worldwide there are three major projects for gasification of coal: Kemper County in Mississippi USA, National Taiwan University (NTU) and Institute of Chemical Processing of Coal Poland. In order to meet both environment and cost considerations SNG should be able to replace LNG in the long run.

SESSION 8

Combustion Technologies – Advanced Technologies

Experimentally Observed Influences of KCl and SO₂ on CO Oxidation in an 80 kW Oxy-Propane Flame

Thomas Ekvall, Klas Andersson, Chalmers University of Technology, SWEDEN.

It is well known that combustion of biomass derived fuels may lead to problems with high-temperature corrosion (HTC). The HTC process is largely based on the release and transformation of chlorine, sulphur and alkali components during the combustion process. However, these components may also interact with other critical parts of the combustion chemistry and the present work focuses on how potassium chloride and sulphur dioxide influence the oxidation of carbon monoxide. This is investigated during combustion of propane (80 kW) applying both air and oxy-fuel combustion conditions. The experiments were carried out in Chalmers 100 kW oxy-fuel test facility in which sulphur dioxide and potassium chloride was added to the flame. The experimental results are also supported by modelling work including a detailed reaction mechanism of the related alkali-S-Cl chemistry. The results show that KCl promotes CO-oxidation in oxy-fuel combustion. However, for the experimental conditions tested in the present work, no significant effect was detected in air-fuel combustion. In addition, when adding water as well as SO₂ to the flames, there were no significant effects on the measured CO concentrations in the respective flames.

Attrition and Reactivity Analysis of Oxygen Carrier Materials under High Temperature Conditions

J.G. van der Watt, Daniel Laudal, Harry Feilen, Michael Mann, University of North Dakota; Srivats Srinivasachar, Teagan Nelson, Envergenx LLC, USA

Chemical-looping combustion is a process whereby carbon dioxide produced during fossil fuel combustion is generated in relatively pure concentration without the need for post combustion capture. The process is based on using a solid carrier material to provide oxygen for combustion with a fuel source. The oxygen carrier material can be regenerated separately in air using an air reactor to replenish the spent oxygen, thus preventing mixing of the combustion products (carbon dioxide and water vapor) and air/nitrogen. The oxygen carrier material continuously circulates between a reducer (fuel reactor) and oxidizer (air reactor). The resultant effluent stream from the combustion process contains predominantly steam and carbon dioxide. The steam can be condensed, leaving an almost pure stream of carbon dioxide ready for storage or industrial use. The combustion process therefore represents an effective method for reducing carbon dioxide emissions from fossil-fuel based energy production systems. The most important aspects related to the adoption of chemical-looping combustion technology are vested in the oxygen carrier material characteristics and efficient exploitation thereof. Oxygen carrier materials represent a significant cost element to the technology due to the high material requirement. The technology must accordingly accomplish high fuel conversion whilst adhering to low energy requirements for material handling throughout the entire combustion process. An important aspect resulting from this is the requirement to accurately project and develop methods to maximize the lifetime of an oxygen carrier in the chemical-looping combustion process, which is primarily determined based on a combination of physical and chemical degradation processes that necessitate replacement. The performance of an oxygen carrier will also influence the design of processes and equipment.

Past research has been related to oxygen carrier performance evaluations comprising either cold temperature attrition testing, or reaction kinetics evaluation via thermogravimetric analysis. Some of the most relevant tests have been conducted in fluidized bed reactors, but such experiments require extensive periods of testing and often large material samples. It is important to rapidly evaluate both chemical and mechanical effects when examining the broad spectrum performance of numerous potential oxygen carrier materials. In the preceding work to this article, an ASTM D5757 test standard, primarily utilized in catalyst attrition testing, was improved for use in assessing both the attrition and reactivity propensities of oxygen carriers. The ASTM standard was improved by incorporating the ability to perform attrition testing at temperatures relevant to chemical looping combustion, as well as to continuously cycle the fluidizing gas between oxidizing and reducing compositions to simulate the chemical reactions occurring in the air and fuel reactors. An additional benefit is that only 30 grams of material is required for initial performance evaluation, which will allow rapid

screening of specialized or new materials developed in the lab at small scales. To validate the advanced methodology and test equipment, an iron oxide-based oxygen carrier material was used and the test method yielded important information. The testing showed that the attrition behavior of the carrier was starkly different under reacting conditions as compared both to ambient temperature and high temperature in inert conditions, and that as a function of time morphological changes to the carrier particles occurred due to the reactions that increased their porosity, and thus resulted in higher attrition as well as better reactivity. These changes were not observed without redox cycling, and thus the importance of the advanced method was validated.

This study is vested in expanding the scope of oxygen carrier analysis to different materials. The goal is to establish attrition and reactivity models to characterize particle abrasion, fragmentation and chemical performance. Such models will be beneficial in progressing the research in the natural and synthetically manufactured oxygen carrier sectors. Synthetically manufactured oxygen carriers are expensive to develop. Inexpensive testing protocols are required to examine small amounts of material.

Various oxygen carriers have so far been tested and the experimental results illustrate the importance of simultaneous data gathering regarding reactivity and attrition. The approach provides a holistic overview when comparing materials and enables an oxygen carrier developer the opportunity to tailor materials and process conditions for specific operating scenarios. In addition to gaseous fuel mixtures, solid fuel has also been tested on the experimental setup and represents an additional performance characteristic whereby oxygen carriers can be assessed. Scanning electron microscopy has been used to evaluate the oxygen carrier transformations resulting from long duration oxidation and reduction reactions. Value adding practices have been identified, but additional research is required to develop and exploit opportunities that can lead to more profitable and resourceful use of oxygen carriers. Such practices are imperative and can benefit industrial communities. This paper will provide results to date and plans for future testing.

The main benefit of this work is advancement of the development of oxygen carriers, equipment and processes for chemical-looping combustion. In addition to chemical-looping combustion, several other potential markets have been identified that can potentially benefit from the technology. The markets include characterization of limestone for fluidized bed combustors, sorbents for carbon dioxide capture, catalysts for fluid catalytic cracking, materials for thermal energy storage and others.

Design of a Methane-Oxygen Pilot Burner for High Pressure Oxy-Coal Combustor Application

Arifur Chowdhury, Ahsan Choudhuri, Norman Love, The University of Texas at El Paso, USA

Oxy-fuel combustion involves burning fossil fuel with oxygen resulting in an exhaust stream which is composed mainly of carbon dioxide and water vapor. The advantages of this system are that higher temperatures theoretically allow for higher achievable efficiencies, the exhaust products are free of NO_x, products can be treated and steam condensed, thereby allowing for capture of as high as 100 % carbon dioxide at the post-combustion stage. A pressurized combustion system reduces component size; consequently, capital and operational cost decreases. Therefore, the integration of oxy-combustion technique in pressurized coal combustor have the potential of achieving efficient power generation and lower cost comparison to existing systems. Motivated by the advantages of pressurized oxycoal power generation system, this paper presents design of a methane-oxygen pilot burner for pressurized oxy-coal combustor application. A commercial computational fluid dynamics simulation tool, ANSYS Fluent, is used to analyze the burner design. The combustor is designed to deliver 1 MW power inputs. The combustor is conceptualized such a way that the pulverized coal is vertically injected into the chamber and ignite using the pilot burners. The proposed system will use two methane-oxygen shear co-axial fuel injector as the pilot burners. Each of the pilot burners are intended to provide 100 kW into the combustor. Nevertheless, the shear coaxial fuel injectors are designed to operate between 75 kW to 150 kW power ranges. The total power in each of the pilot burners are divided into three individual small injectors. The momentum flux ratio is maintained between 12 and 16. The final paper will include a numerical analysis of the pilot burners' fluid mixing properties, flame length and combustion characteristics inside the combustor.

Chemical-Looping Technologies for Solid Fuels

Tobias Mattisson, Carl Johan, Linderholm, Anders Lyngfelt, Chalmers University of Technology, SWEDEN

In chemical-looping combustion (CLC), an oxygen carrier provides lattice oxygen for complete combustion of a fuel for heat and power production. The reduced metal oxide is then oxidized in a separate reactor. The combustion products CO₂ and H₂O are obtained in pure form, without any nitrogen in the gas. As no gas separation work is needed, this could be a breakthrough technology for carbon capture (CCS). Normally, the fuel reactor and air reactor are designed utilizing inter-connected fluidized beds. The same underlying reversible redox reactions of CLC can be used for other fuel conversion technologies. These include fluidized bed processes for gas, solid and liquid fuels for heat, power, syngas or hydrogen production. Some of these concepts were suggested as far back as the 1950's, while others have just recently been proposed. Chalmers

University of Technology has been involved in CLC research for over 18 years, and this paper will provide a review of some recent developments with respect to CLC with solid fuels, including coal and biomass. Further, the paper will provide an overview some related technologies where Chalmers is conducting research including Chemical-looping gasification (CLG) and Oxygen Carrier Aided Combustion (OCAC). Both of these processes utilize oxygen carriers in the form of metal oxide particles for converting solid fuels. In CLG, the fuel is not oxidized completely but rather a pure syngas/hydrogen stream is produced effectively in the fuel reactor, which could be utilized for chemical or fuel production. Oxygen carrier aided combustion (OCAC) uses oxygen carrier particles instead of sand directly in the furnace of a normal fluidized bed boiler. This enables internal oxygen transfer, with positive effects obtained with respect to emissions of nitrogen oxides and carbon monoxide, in addition to reduced corrosion problems when utilizing different wastes and biomass as fuel. This technology was developed around 2012, and is today commercial and employed in several CFB units in Sweden.

Experimental and Numerical Study On Ash Deposition Model in A 35kW Horizontal Coal Reactor: Application to CoalFired Boiler

Seok-Gi Ahn, Pusan National University; Young-Gap Jeong, Korea SouthEast Power Co.; Chung-Hwan Jeon, Pusan National University, SOUTH KOREA

Ash deposition on heat transfer surfaces produce resistances to heat transfer that can reduce boiler efficiency. Hence, the ash deposition seriously inhibits the stable boiler operation. The slagging and fouling that occur in a boiler originate in deposition phenomena. When deposited particles melt and form a sintered layer, the result is called slagging, whereas when ash particles form a layer through condensation at a relatively low temperature at a surface, it is called fouling. It is possible for these two phenomena to occur simultaneously or separately, depending on the temperature and surrounding environment. The ash adhesion experiments for blended coal were conducted to understand the mechanisms of growth of ash deposition. The ash deposition model was applied to estimate the ash adhesion characteristics in a coal-fired boiler. For this study, we used thermo-mechanical analysis(TMA) for predicting ash phase transition according to the ambient temperature. And we used computational fluid dynamics(CFD) to perform a simulation of coal-fired boiler. This numerical study examined the characteristic of combustion in the boiler and explored the boiler's deposition potential.

SESSION 9 Coal Ash Management - 2

CCR Industry Overview: A View from the Websites

Mark Rokoff, AECOM, USA

The presentation will capture two key parts (1) an assessment of the CCR industry through the data available on the CCR websites, and (2) insights on the trends in the business and approaches that can better prepare the CCR market for the coming years and activities. The data will be used to share information related to surface impoundments, inactive surface impoundments and landfills and the trends that can be observed by geography, key actions, and more for closure, qualifications, and more. These trends indicate a means to be proactive and seek efficiencies that exist through measured and well-executed strategic efforts. The presentation will outline key efforts that can be implemented today to result in cost and schedule savings. In addition, the presentation will tie the trends identified above to better draw more conclusions about the future of the industry.

Geophysical Tools and Techniques for Improvement of Coal Ash Management

Nathaniel P. Shields, Thomas B. Brackman, Near Surface Geophysics Innovations LLC; Michael T. May, Western Kentucky University; John Kerr, ATC Group Services LLC, USA

There should be a concerted effort to apply near-surface geophysical tools and techniques to best characterize various coal-ash retention areas. There are many hundreds of coal-ash slurry or coal-combustion residuals (CCRs) in the USA sequestered in various types of landfills (such as lined or unlined) and CCRs and coal ash are retained behind myriad types of impoundments, and in sinkholes and ravines. The variety of geological and engineering conditions at a given site are little known in many cases without extensive drilling of test borings or trenching. We present use of multiple geophysical tools that can, and we would maintain, should be utilized to best characterize coal ash and CCR materials in a relatively rapid, and noninvasive manner leading to the establishment of best management practices (BMPs) for coal ash and CCRs. Electrical resistivity (ER) in 2-D or electrical resistivity tomography (ERT) in 3-D can be used to define fill-material (e.g. ash) and native soil or bedrock interfaces. ER surveys in general can also be used in lined landfills to detect leak areas or in karst or sinkhole areas were fluid carrying CCRs or ash has migrated. Coupled with ER survey are induced potential (IP) surveys that can detect breaches in impoundments or landfills as well. ER/IP

methods are valuable tools for locating suitable onsite or near site materials for landfill caps. Geophysical methods have been shown to demarcate zones of silty clay vs clayey silt and show sand lenses and associated thickness and topography. In addition to using Ohm's Law based geophysical techniques, surface-wave disturbances are useful for demarcating surface to subsurface changes in varying density of landfill or impoundment materials relative to native geological materials via so-called refraction microtremor (termed ReMi). The technique known as ReMi is actually a seismic method that produces a shear-wave velocity profile with increasing depth and provides a shear modulus for seismic site classification. These engineering parameters coupled with borehole data can aid in determining suitability of site repurposing for reuse of coal ash and CCR sites. Use of near-surface geophysics should be an integral part of coal-ash management strategies. We present several case studies illustrating the success of using ER and ReMi in particular for characterizing coal-ash and CCRs in the greater Ohio Valley area.

Reclaiming and Recycling Coal Combustion Residuals for Encapsulated Beneficial Reuse

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The positive economic and technical benefits of utilizing fly ash as a replacement for cement in concrete are well established. However, as ever-increasing environmental regulations on coal-fired plants negatively impact fly ash quality for use as in concrete, increasing percentages of ash are disposed rather than recycled. In addition, while the overall availability of specification-grade fly ash has decreased, its supply has become dramatically inconsistent as coal fired generation no longer compromises base-loaded electrical generation in the United States. At the same time the market demand for high quality fly ash continues to grow due to Alkali-Silica-Reactivity (ASR) concerns and the desire for durability and sustainability. Utilizing reclaimed ash from ponds and landfills will provide continuous feed material and ensure uninterrupted supply for customers. Further, as addressed in the latest coal combustion residual regulations, EPA encourages the encapsulated beneficial use of coal ash.

For over 40 years, The SEFA Group has been a leader in the beneficial use of fly ash in environmentally sustainable ways. For the past two decades, SEFA has been at the forefront of development and commercialization of thermal beneficiation technologies designed to raise low grade ash to meet specification standards. To date, SEFA has recycled more than 20 million tons of coal ash, with nearly 7 million of those tons processed through thermal beneficiation facilities.

SEFA has successfully demonstrated the viability of STAR® Technology through commercialization at three thermal beneficiation plants. The process removes all organics and contaminants from the ash leaving pure mineral matter with no solid waste stream, and improves the quality of ash far beyond previous levels. The most recent plant at Santee Cooper's Winyah Generating Station not only recycles all coal ash generated during normal operations, avoiding the need for disposal, but also has the ability to run solely on coal ash reclaimed from onsite impoundments or ponds. The plant can switch at a moment's notice from the reclaimed ash to dry ash produced at the power plant, or any blend of both. This flexibility allows full load operation at all times without any dependence on operation of the power generation plant now or in the future. This unique independence is particularly important as the supply of fly ash for the construction industry continues to dwindle as more coal fired generation is taken off line.

Since commercial operation in early 2015, the Winyah STAR® beneficiation facility has reclaimed and processed over a quarter of a million tons of Coal Combustion Residuals from onsite ash impoundments and has consistently produced a product ash below 1.0% Loss on Ignition (LOI) while meeting all relevant specifications for use in ready mix concrete as a replacement for Portland cement.

In situations where excavation is required for coal ash pond closure, removal and beneficiation offers a lower-cost option that is a permanent solution where 100% of coal ash is transformed into a new, environmentally-responsible material. STAR® Technology is a self-sustaining, stand-alone solution that is cost-effective, eliminates long-term liability, and the use of its product increases the sustainability of concrete infrastructure. This is a unique environmental success story.

This paper will discuss various aspects of the STAR® Technology, operating experience, and product characterizations.

Application of Best Practices in the Seismic Stability Assessment of CCR Landfills and Surface Impoundments

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The Tennessee Valley Authority (TVA) operates ten coal-fired power plants across the states of Tennessee, Kentucky, and Alabama, which are equipped with disposal facilities to contain the by-products of coal combustion processes: Fly Ash, Bottom Ash, and Gypsum. In April 2015, the Environmental Protection Agency (EPA) passed regulations—generally known as the CCR Rule—that govern the disposal of coal ash (coal combustion residuals or CCRs). The CCR Rule establishes stability requirements for CCR landfills and surface impoundments. This paper focuses on the approach to the

seismic stability assessment for the landfills and surface impoundments at the TVA fossil plant facilities used to assess compliance with the EPA CCR Rule.

Prior evaluations of seismic stability used simplified methods of subsurface exploration and analysis which led to the finding that these sites were unstable for the required seismic loading conditions. As part of TVA's compliance effort, Geocomp recommended an approach we called "Best Practices" in which we employed the best available and applicable methods to run field tests and collect undisturbed samples, used high quality laboratory testing on the undisturbed samples, performed site-specific dynamic analyses and used advanced numerical dynamic analyses to assess the seismic and post-earthquake stability of the landfills and surface impoundments at these facilities. The goal was to remove the overly conservative assumptions and inappropriate practices employed in the previous seismic assessments. Using these "Best Practices" gave results that met or exceeded EPA's CCR Rule without the need of costly remediation measures to achieve compliance.

The geotechnical exploration incorporated drilling techniques that rigorously followed published test methods and maximized soil sample quality. The site explorations were performed with mud rotary drilling methods exclusively and used heavy drilling mud with rigorous density control to minimize disturbance of the soil by heave and running soils. A12-inch spacing between standard penetration test (SPT) samples and undisturbed Osterberg samples was maintained. This provided superior penetration resistance and undisturbed sample quality as compared to previous explorations where hollow stem auger techniques without drilling mud or density control were used. Hammer efficiency tests were performed at every site to provide correction of the SPT values used in liquefaction triggering analyses. These best practice techniques proved vital in the accurate determination of cyclic resistance of the natural soils and CCR materials. In-situ seismic explorations including seismic cross-hole, gamma-density, and seismic cone penetrometer tests with dynamic pore pressure measurements (SCPTu) were incorporated to determine critical dynamic soil parameters such as shear wave velocity (V_s) and bulk density.

Emphasis on measured shear modulus degradation and cyclic resistance of soils and CCR materials was paramount in the stability assessments of the TVA facilities. Modulus and Damping of Soils by Resonant Column Method (RC) tests were performed on high quality undisturbed samples to provide direct measurements of dynamic properties for site-specific, two-dimensional, non-linear, finite element amplification analyses. Cyclic Direct Simple Shear (CDSS) tests followed by monotonic Direct Simple Shear (DSS) tests were used to determine the post-cyclic undrained shear strength of liquefiable materials and soils with the potential for cyclic softening under the maximum design earthquake loading. Laboratory measurements of shear wave velocity with bender element sensors were used to determine whether the shear wave velocity of the specimens had been affected during sampling or transport. X-Ray radiographs were used in the selection of the best quality undisturbed specimens for advanced soil testing.

In-situ and laboratory measured dynamic parameters and laboratory determined monotonic, cyclic and post-cyclic behavior of soils were the primary input source for the site-specific response and amplification and slope stability analyses. The site-specific response and amplification analyses were performed with the finite element program OpenSees and the results were validated with the finite difference program FLAC. The results of the amplification analyses were used to determine the induced cyclic loading from seven representative input ground motions. The amplification analyses provided the horizontal equivalent acceleration (HEA) time histories within the critical sliding mass at each disposal facility. The HEA were used in sliding block Newmark analyses to determine displacement compatible accelerations that correspond to tolerable displacements at these facilities. The displacement compatible acceleration was used as horizontal seismic coefficient in pseudo-static slope stability analyses to determine the seismic factor of safety. The induced cyclic loading, in terms of cyclic stress ratios (CSR), were used in CDSS laboratory tests to determine the cyclic behavior of the soils and CCR materials. The post-cyclic undrained shear strength of critical soils and CCR materials obtained from monotonic DSS after cyclic loading, were used in post-shaking slope stability analyses to determine the post-earthquake factor of safety at each of the facilities evaluated. Following this approach resulted in seismic and post-earthquake factors of safety that exceeded the minimum required factors of safety outlined by EPA's CCR Rule at all the seven facilities assessed.

Synthesis of Zeolite Type X from Coal Fly Ashes and Bottom

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The large emissions of greenhouse gases, mainly CO₂ from power plants, have encouraged many studies about the synthesis of solid adsorbents for the cleaning of gases. Among the by-products of coal, fly ashes and bottom ashes generated at the thermoelectric power plants are produced in large amounts and have few valuable applications, especially for bottom ashes. It is now known that the fly ashes generated has great potential for application in the synthesis of adsorbent materials, such as zeolites, but studies involving the bottom ashes are rarely found. In this context, the

present study aims to evaluate the main chemical, physical and mineralogical differences between fly ashes and bottom ashes and verify the influence of these differences in the synthesis of zeolites type X for CO₂ capture. XRF, XRD, SEM, pore and surface area (BET) analyses were carried out for the characterization of the ashes and zeolitic products formed. Although the SiO₂ and Al₂O₃ contents are similar for both materials, the main differences are the iron content and loss on ignition, presents in higher concentration in the bottom ashes (Fe₂O₃ = 6.19% and LOI = 3.97%). The XRD analyses showed the predominance of the minerals quartz and mullite as majorities and a third mineral of iron, in the fly ashes as hematite and in the bottom ashes as magnetite. Zeolite syntheses were performed by a two-step method (i) fusion step followed by (ii) hydrothermal reaction. Using a fusion temperature of 550 °C for 1h and SiO₂/Al₂O₃ = 3.5 and Na₂O/SiO₂ = 2.0 ratios, a pure Zeolite type X was obtained from the fly ashes. In regards to bottom ashes SiO₂/Al₂O₃ = 3.05 and Na₂O/SiO₂ = 1.92 ratios were applied and a good quality Zeolite type X was obtained. As main results, we can mention the surface areas of the synthetic zeolites. Surface areas of 586.7 m².g-1 using fly ashes and 351.6 m².g-1 with the bottom ashes were achieved. Despite the differences between the fly ashes and the bottom ashes are not so significant, the zeolites synthesis process undergoes enough alterations to influence the quality of the product. These differences can be associated mainly to the higher unburned carbon content in the bottom ashes. However, considering only the raw ashes it is possible to obtain good zeolites for CO₂ capture using both ashes. It was also possible to observe that higher Fe contents have a low influence on the synthesis of zeolite type X using a fusion step.

SESSION 10
Coal Science - 2

Attractiveness of Wyoming Powder River Basin (PRB) Coal as a Valuable Resource from Which to Manufacture NonEnergy and Fuel Products

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Most recent coal research has largely been on comprehending better ways to deliberately and aggressively destruct coal to extract energy in novel and effective ways, or to produce syngas that can be used to manufacture fuel and non-energy products. Sense, suggests that historic coal research and technology development activities (largely related to coal combustion and high-temperature conversion) are reaching a mature technical state. Set in the context of the USA, the techno-economic viability of implementing such technology solutions is increasingly challenging.

If the latent value in coal is to be truly realized, either as a clean-energy product or as a feedstock to make other carbon based products, rethinking the notion of coal utilization migrating from rationale that involves aggressive destruction to deliberate decomposition of coal is offered as a basis to rejuvenate utilization. The understanding and comprehension of molecular structure, physics and chemistry of coal, built upon systems engineering concepts, is required to appreciate and identify the huge potential for investing in transformative ground breaking and pioneering research and technology development, recognizably confronting today’s market and technology need challenges and realities.

This presentation, sets out the compelling proposition for rethinking coal as a value proposition, sharing with participant’s recent research and technology development achievements at the University of Wyoming. This research and technology development pursuit is being funded by the State through the Wyoming Carbon Engineering and Science Initiative. The Carbon Engineering and Science initiative, seeks to explore and investigate conversion of Wyoming Powder River Basin (PRB) coal in ways to both sustain coal as a competitive clean energy resource, and create new carbon product markets that can be leveraged to create economic diversification opportunities. Early successful achievements and findings will be used to highlight the value in thinking about coal differently, justifying investment in improved understanding and comprehension of coal science and engineering.

Dry Sensor-Based Sorting of Coal at Demonstration Plant Level

David M. Powell, Isabel King, Neo Makhalemele, Carl Bergmann Mintek, SOUTH AFRICA

Dry sensor-based sorting of coal, typically x-ray transmission (XRT) sorting, has been successfully implemented in de-stoning applications both locally and internationally (1). The option of using these methods in lieu of traditional dense medium separators (DMS) has become evident particularly for smaller, water-stressed mines in South Africa. Future local resources, that will need to be exploited to replace the aging Witbank coalfields, are also located in arid regions and may benefit from dry upgrading methods. In a unique application of XRT sorting, Mintek investigated the possibility of producing both a low-grade Eskom-specification product and high-grade, niche quality product for the metallurgical sector. Preliminary XRT testwork on samples from the Vlakfontein mine indicated that different qualities of coal could be distinguished by XRT sensors. However, in order to evaluate sorter separation efficiency at industrial throughput rates,

a demonstration scale XRT sorting plant was constructed and commissioned at the Vlakfontein mine with a design capacity of 125tons/hr of sorter feed.

The results of the demonstration tests at Vlakfontein mine are presented for the -50mm +20mm size fraction. Using standard washability analysis, the calculated Ep of the sorters was found to vary from 0.10-0.20 which is high in comparison to the 0.02-0.03 typically expected for DMS circuits. Test work done on two coal seams (4 Upper and 4 Lower) demonstrated that XRT technology is capable of distinguishing and separating various grades of coal at laboratory, pilot and demonstration scale, thus indicating that the use of the technology is not only technically limited to de-stoning applications.

Investigation of Washability of Akcelik Lignite, Tekirdag/Turkey

Ali Ucar, Sevgi Karaca, Ozer Oren, Dumlupinar University; Murat Ozturun, Akcelik Mining; Cem Sensogut, Dumlupinar University, TURKEY

The objective of this study was to examine the washability properties of lignite samples acquired from the open-pit mine in Tekirdağ, Turkey which belong to the Akçelik company. For this purpose, sieve analysis was first carried out thus determining that the particle size is below 75 mm. Afterwards, complete chemical analysis (ash, calorific value, humidity, sulphur etc.) was carried out. It was concluded according to these analyses that the sample was of low quality. This affects the marketing conditions of coal and results in environmental problems. Hence, the coal has to be cleaned in order to improve its quality. Float-sink experiments were carried out for -75+18, -18+10 and -10+0.5 mm dimension groups in order to put forth the washability of the samples in experimental studies. The washability properties of the samples were determined from the Henry-Reinhard Float-Sink and Mayer (M) curves obtained as a result of these studies. Accordingly, it was determined that in case the sample is floated in an environment with a density of 1.6 g/cm³, its floatability is easy in +75 and -75+18 mm size groups according to ±0.1 density separation values, however it was also determined that the floatability became more difficult in the -18+0.5 mm size group. It was observed that ash values decreased as with decreasing particle size as a result of coal washing process which caused an increase in the calorific values.

Study on the Properties of Coal Sludge Slurry Prepared by Lean Coal and Sludge from Coal-to-Oil Process

Yuxing Zhang, Ping Feng, Yanan Tu, Zhiqiang Xu, China University of Mining & Technology, CHINA

The sludge from coal-to-oil process was hazardous to the environment and difficult to handle. In the present study, it was mixed with lean coal to prepare coal-sludge slurry for seeking a safety disposal. The effect of sludge ratios on slurryability, rheological properties and stability of coal-sludge slurries has been investigated. Results show that the addition of sludge improved the stability of slurry and changes the slurry rheological model from the dilatant fluid to the yield pseudoplastic fluid. With the increase of sludge dosage, the pseudoplasticity became stronger. The addition of sludge also increased the slurry viscosity and reduced the maximum slurry concentration. As the sludge to coal ratio increased from 0 to 15%, the maximum slurry concentration drops from 73.08% to 65.38%.

The Spontaneous Combustion Liability of Akcelik Lignite, Tekirdag/Turkey

Cem Sensogut, Ozer Oren, Sevgi Karaca, Dumlupinar University; Halim Demirkan, Akcelik Mining; Ali Ucar, Dumlupinar University, TURKEY

In the present work, the spontaneous combustion liability of the lignite samples obtained from Sahinkoy open pit of Akcelik Mining Company in Tekirdag, Turkey was determined. In order to bring out the susceptibility of the coal samples in concern to self-heating, the method of crossing point temperature (CPT) was utilized. The samples were initially minimized to the required amount by cone and quartering and then their particle size were reduced under 74 µm by the use of jaw crusher and ball mill respectively. During the experimental works, 35 g of coal samples were exposed to the oxidation under the airflow rate of 100 cc/m for a total of 6 CPT tests. For the disclosure of the risk indices of spontaneous combustion inclination belonging to the coal samples exercised throughout the experimental works, an empirical formulae revealed by Feng, Chakravorty and Cochrane was employed.

SESSION 11
Gasification Technologies: General 2

Advances in Coal Gasification R&D

Jai-woh Kim, DOE, K. David Lyons, NETL, Regis Conrad, DOE, USA

Coal has been and will be a major fuel of power generation and industrial energy source in terms of abundance and supply security in USA and developing countries. Even

though the price of natural gas and petroleum is currently low, developing countries such as China and India are developing coal gasification technologies.

The U.S. Department of Energy's Office of Advanced Fossil Technologies Program has engaged in comprehensive efforts to enable the widespread technology improvement of the overall coal gasification systems, in order to promote affordable and reliable power generation, to reduce greenhouse gas, and to create more jobs. These technologies offer a critical pathway for sustaining the electricity generation sectors in a manner that is primary to other renewable energy technologies such as solar and wind.

This talk will highlight an overview of the broad progress that the Gasification System Program has made in these areas: high-pressure dry solid pump feed system for low rank coal and biomass to lower cost of syngas production from reduction of CapEx and OpEx; air separation system to lower oxygen production cost; high temperature/warm syngas cleanup system; water gas shift reaction system for hydrogen-rich syngas production system to produce high valued product of liquid fuel oils and other chemicals.

Characterization of Mineral Matter Transformation in Brown Coal Ashes Processed under Gasification Conditions

Daniel Roberts, Alexander Ilyushechkin, San Shwe Hla, David Harris, CSIRO Energy, AUSTRALIA

Australian brown coals have a wide range of ash compositions with different mineralogy. The characteristics of inorganic species in coal affect ash fusion temperatures and slag viscosity, the parameters which are critical for reliable gasifier operation. Their presence can also impact conversion behaviour; their transformations under realistic gasification conditions is important to support the use of low-rank coals in contemporary gasification applications.

When coals are processed under gasification composition, the inorganic species follow a number of phase transformations at different temperatures. In order to understand these transformations, proper characterisation of the ash and slags is required. This paper describes evaluation of the phase transformation in laboratory-made brown coal ashes processed in simulated gasification atmospheres and temperatures. A number of analytical techniques such as X-ray powder diffraction, scanning electron microscopy and electron-probe microanalysis, have been applied.

It was found that at moderate gasification temperatures (900–1000°C) most of the changes in brown coal ashes corresponds to the transformation of iron- and iron-magnesium oxides in high-iron ashes, while in high-sodium ashes the phase transformation associated with the reaction of sodium and silica-containing phases. These transformations are clearly detected by XRD, but difficult to quantify using EPMA as most of the phase are fine dispersed in porous ash samples.

Analysis of the samples processed at high gasification temperatures (1000°C and above) demonstrates formation of liquid phase (slagging) and formations of new phases due to followed slag cooling and crystallisation. EPMA was a most suitable technique to analyse quenched slag samples particularly to quantify the amount of liquid and solid phases and their composition.

These results are considered in the context of a wider research program into the gasification performance of low-rank coals under conditions relevant to their use in entrained flow gasifiers.

Measurement, Characterization and Market Potential of Tars from British Gas/Lurgi (BGL) Gasification and their Representation in Aspen Plus® Modeling

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A characteristic feature of counter-current moving-bed gasification is a tar/oil fraction in the raw gas, which is produced in the pyrolysis zone of the gasifier and leaves the reactor with the gas due to the comparably low outlet temperatures. This fraction of condensable hydrocarbons was usually regarded as undesired sidestream and recycled to the gasifier. Recently, the tar/oil fraction gains importance as marketable by-product. Therefore, a current project at the Institute of Energy Process Engineering and Chemical Engineering at TU Bergakademie Freiberg focuses on the investigation of tar/oil generation in moving-bed gasification processes. To identify the yield and character of tar from BGL gasification, a hot-gas sampling equipment was installed at the slagging bath pilot gasifier (inner diameter: 0.6 m). The system consists of two condensers and allows to collect all condensable by-products in dependence of operational parameters. The present work introduces the hot-gas sampling equipment and shows tar yields and compositions of test runs. The market potentials of the tar as basis for chemicals or for an energetic use is assessed based on the analysis of chemical and physical tar properties. Furthermore, the results serve to improve modeling of the BGL gasification process. An Aspen Plus® model of the pilot gasifier and the following wash cooler is developed, which reflects the specific characteristics of the tar/oil fraction. The current approach to use pseudo-components as representation of tar is thereby refined. Finally, economic benefits of the marketing of tars from moving-bed gasification are shown based on a conceptual study of a polygeneration route with hydrogen production in China.

Effect of Graphitization Degree of Residual Carbon on Ash Fusibility

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Residual carbon is often found in slag, and it has been proved that the presence of residual carbon significantly influences ash flow properties. In this work, graphite, activated carbon and demineralized coal char prepared at high temperature were selected to simulate as residual carbon to investigate the effect of graphitization degree of residual carbon on ash fusibility under Ar atmosphere. X-ray diffraction (XRD) was used to investigate mineral transformation of the ashes with different residual carbon. It was found that ash fusibility significant increase with increasing the content of graphite, activated carbon and demineralized coal char. The existence of residual carbon led to the formation of high melting point moissanite. When the ash had same residual carbon content, the effect of residual carbon on ash fusibility increased from activated carbon to demineralized coal char to graphite. Mineral compositions revealed that the amount of moissanite formed in slag increased with the graphitization degree of residual carbon. Furthermore, the increase of S/A reinforced the effect of residual carbon on ash fusibility. FactSage calculation implied that reaction between SiO₂, Al₂O₃ and CaO is more likely to occur than the carbonthermic reaction between SiO₂ and residual carbon.

SESSION 12 Rare Earth Elements - 2

Brief Overview of Rare Earth Research at NETL R&IC

Evan Granite, Elliot Roth, Tracy Bank, Ronghong Lin, Bret Howard, Yee Soong, Mac Gray, Chris Wilfong, Ranjani Sriwardane, James Bennett, Jin Nakano, Mary Anne Alvin, Kurt Rothenberger, NETL, USA

Everything that is in the Earth's crust is also present in coal to some extent, and the challenge is always to use abundant domestic coal in clean and environmentally friendly ways. Trace elements present within the coal such as mercury, arsenic, selenium, cadmium, antimony, phosphorus, and chlorine, as well as sulfur and nitrogen, have long been of interest due to their roles in producing pollution emissions from combustion or gasification plants. Critical elements, such as some of the rare earths present within the coal, have recently been of great interest due to their importance in the world's economy. Coal is an important resource, both in the United States and around the world. The United States generates approximately 30 percent of its electricity through coal combustion and, at the current overall rate of consumption, has more than a 250-year supply of coal. According to the US Energy Information Administration, approximately 1 Gt of coal has been mined annually in the United States over the past twenty-five years (1990-2014), although the 2015 total was 896 million tons, and 2016 was 739 million tons. The recent decline in domestic coal production is due to the availability of inexpensive natural gas; regulatory uncertainty with regards to carbon dioxide emissions; and the retirement of older coal-fired power plants.

In the United States, most coal is burned for power generation, but substantial quantities are also used in the manufacture of steel, chemicals, and activated carbons. Numerous industries, such as mining, power, rail transportation, manufacturing, chemical, steel, activated carbon, and fuels, are involved in the production, transportation, and use of coal.

Rare earth elements (REEs), which comprise the lanthanide elements, as well as scandium and yttrium, are present in the abundant coal and coal by-products produced domestically and worldwide. Widely used in high-technology products such as catalysts, cell phones, hard drives, hybrid engines, lasers, fluorescent lamps, batteries, magnets, medical devices, and televisions, REEs are of significant value to US national security, energy independence, economic growth, and the country's environmental future.

Most of the common inorganic lanthanide compounds, such as the phosphates found in coal, have very high melting, boiling, and thermal decomposition temperatures, allowing them to concentrate in combustion and gasification by-products. Rare earths are commercially produced from ores containing monazite (rare earth phosphate mineral) or bastnasite (rare earth carbonate-fluoride mineral), as well as from ion exchangeable clays. The lanthanides are found in coal as well as combustion by-products such as ash, coal preparation residues, gasification slags, and mining by-products. Rare earths have also been found in interesting concentrations in the strata above and below some coal seams, thereby making every process in the mining and utilization of coal a potential source of rare earth elements.

Also of interest, some coal and coal by-products have elevated concentrations of heavy rare earths (HREEs)—which are lowest in supply, rank high in criticality and price, and are projected to increase in demand—making them potentially attractive targets for REE recovery despite their overall lower concentration.

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) recently initiated research to support the measurement of concentration, identification of rare earth compounds, and recovery of rare earths from abundant domestic coal by-products. The NETL Rare Earth EDX Database (<https://edx.netl.doe.gov/ree/>) is a resource for rare earth information related to coal and by-products. Many other research organizations have also initiated efforts for the

analytical characterization and recovery of rare earths from unconventional sources such as coal by-products.

Effect of Pre-Reaction Ball Milling of $\text{LaPO}_4 \cdot \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ on Kinetic Parameters of the LaPO_4 Roasting Reaction

Ward Burgess, Murphy Keller, Elliot Roth, Jonathan Lekse, Bret Howard, Evan Granite, DOE / NETL, USA

Rare earth (RE) minerals comprise the 15 lanthanides plus yttrium and scandium. They are vital to industrial operations and are most widely used in the production of magnets, phosphors for video displays, metal alloys, catalysis, and glass production. The price spike following the 2009 cutback in export quotas by the Chinese government underscored the importance of national self-sufficiency in RE mineral production. More than 2 billion tons of coal refuse and 100 million tons of ash are produced each year, with RE minerals present primarily in the form of monazite and xenotime at concentrations of 1000 ppm or lower.

Rare earth phosphates are very unreactive in their pure state even to temperatures above 1500° C, but are reactive at significantly lower temperatures when mixed with another compound such as Na_2CO_3 . In order to design economic roasting processes for the recovery of RE phosphates from coal derived feedstocks, it is convenient to study model systems of rare earth phosphate plus a reactant. In this work, the kinetics of the high-temperature roasting of LaPO_4 with Na_2CO_3 were studied. It is typically necessary to heat the reaction mixture above the melting point of Na_2CO_3 (851° C) to ensure that the formation of La_2O_3 is complete or nearly complete within 2 hours, but subjecting the sample to a ball milling process prior to reaction reduces the necessary reaction temperature to as low as 625° C. It is believed that this increase in reactivity occurs because the ball milling process ensures that the reaction mixture is thoroughly mixed rather than by reducing the reactant particle size. XRD hot stage results suggest a two-reaction mechanism is the route by which La_2O_3 is produced from the ball milled sample upon reaction. Activation energy and Arrhenius pre-factor for each reaction were determined from TGA experiments

Elucidating Distribution and Speciation of Rare Earth Elements in Coal Utilization By-Products Utilizing Synchrotron Microscopy and Spectroscopy

Mengling Stuckman, AECOM; Christina Lopano, Evan Granite, DOE/ NETL; USA

Rare earth element (REE) binding environments in coal and coal utilization byproducts (CUBs) are not well understood, nor are their associations in post-production byproducts (e.g. fly ash). Well-developed research into the binding environments of the REEs before, during, and after production could be vital in establishing an economically viable extraction method for REEs in these materials. In order to advance the knowledgebase for improved REE recovery from coal and CUBs, this study characterized speciation and distribution of REEs in 24 CUBs collected from various locales. Synchrotron-based X-ray fluorescence (XRF) elemental mapping and X-ray absorption near edge structure at SSRL were utilized to examine different REE distributions, cerium (Ce) oxidation states, and binding environments in CUBs. Differing distributions were identified between light REEs and heavy REEs. Further analysis of cerium identified Ce(III) as the predominant Ce oxidation state in all studied samples. Ce speciation and XRF maps analyses further suggest the presence of REE phosphates, chlorides, oxides, and sulfates in ash samples analyzed. In samples studied to date, the fly ash sample primarily contained Ce(III) sulfate and Ce(III) phosphate phase; while the bottom ash analyzed contained both Ce(IV) oxide and Ce(III) phosphate. The synchrotron-based characterization confirmed the presence of these trace, previously only theorized, phases during the combustion process and ultimately may inform the simplification of separation and extraction processes for REE from different CUBs.

Grain Scale Rare Earth Element Distribution in Coal Fly Ash

Allan Kolker, Clint Scott, U.S. Geological Survey; James Hower, University of Kentucky; Christina Lopano, DOE/NETL, USA

In coal burning for electric power generation, rare earth elements (REEs) are strongly retained in solid coal combustion products (CCBs) leading to total REE enrichment on the order of 5 to 10 times relative to their feed coal concentrations [1]. While enrichment of REEs in coal ash is well documented, the mode in which REEs occur in CCBs is poorly understood. SEM examination of CCBs reveals that REE-bearing trace phases are much less common than in coal and other sediments, leading to the suggestion that REEs are partitioned into the melt/glass phase at boiler temperatures [2]. Determining the distribution of REEs in CCBs requires instrumentation capable of quantifying HREEs at low abundances while providing adequate spatial resolution to select among CCB constituents. In the present study we used the Stanford-USGS SHRIMP-RG ion microprobe [3] to investigate grain scale partitioning of REEs in 19 U.S. and international coal fly ash samples. Instrument conditions included a nominal spot size of 15 micrometers and an oxygen negative-ion primary beam. REE + Y contents of bulk samples range from 192 to 1668 mg/kg. On a chondrite-normalized plot, bulk samples

show characteristic LREE enrichment ((Ce/Yb)_N = 4.8 to 10.8) with corresponding variation in the proportion of critical REEs as defined by Seredin and Dai [4].

Aluminosilicates, the most abundant constituents of fly ash, show considerable variation in REE content. On a grain scale, individual glass cenospheres have ranges that may be above or below the bulk sample REE distribution. Aluminosilicates that are enriched in components other than Al-Si, such as Fe- and Ca-rich aluminosilicate spheres, tend to have REE contents that are similar to or higher than the bulk. REEs are also partitioned into Fe-oxide/glassy magnetospheres, as shown by Yang et al. [5] for bulk separates. Although relatively minor or absent in some samples, co-occurring quartz and/or high-silica glasses generally have much lower REE contents than aluminosilicate glasses, and in many cases are below detection by the SHRIMP. In a few samples, zircon (melting point 1690 °C) was found to survive the combustion process, and these show characteristic HREE enrichment. The finding in the present study that REEs are partitioned into aluminosilicates is consistent with results for a large group of bulk U.S. coal ash samples [6] showing a strong positive correlation between Al and REE contents. Together with the present study, these results indicate that the aluminosilicate fraction hosts a significant portion of the REEs present in coal ash. Our results also show that limited pre-concentration or selective extraction may be possible by removing the most REE-depleted fractions or targeting the most REE-enriched fractions, based on internal variation in REE contents.

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Determination of Rare Earths in Coal Combustion By-Products

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Everything in the earth's crust is present in coal, and combustion by-products, including coal ashes, have long been of interest for potential recovery of valuable metals and trace elements (1-6). The National Energy Technology Laboratory recently initiated research for the recovery of rare earths from abundant domestic coal and coal byproducts (7). The coal burning power plants are a domestic treasure chest for the trace elements, including economically important ones like the rare earths. Most of the common inorganic lanthanide compounds, such as the phosphates found in coal, have very high melting, boiling, and thermal decomposition temperatures, allowing them to concentrate in combustion by-products such as bottom ash and fly ash.

Approximately seven hundred million tons of coal were burned to generate electricity in the United States in 2016 (8). With an average concentration of 62 ppm, it is estimated that 40,000 tons of lanthanide elements are present within the coals burned each year in US power plants. The partitioning of the rare earths across US coal power stations is being investigated through a collaborative research effort between the Electric Power Research Institute and the Department of Energy (7, 9). Figure 1 shows a schematic of a modern coal-fired power plant containing pollution control devices for NO_x, SO_x, and particulates. Early results suggest the lanthanides are mainly present within the coal being burned, the bottom ash, and the fly ash. Recent results for the determination of rare earths in various solid samples obtained across different points within coal-burning plants will be presented, and future research will be discussed.

SESSION 13

Clean Coal Demonstration and Commercial Projects - 3

Techno-Economic Analysis of Battelle's Direct Coal-to-Liquids Process for Jet Fuel & Diesel Using Biomass Derived Solvents

Satya Chauhan, Dan Garbark, Rachid Taha, Rick Peterson, Battelle; Jason T. Lewis, DOE/NETL, USA

Battelle is demonstrating a breakthrough technology for a direct coal-to-liquids (CTL) process for producing jet fuel and diesel using biomass-derived coal solvents. The Battelle process offers a significant reduction in capital and operating costs and a substantial reduction in greenhouse gas (GHG) emissions, without requiring carbon capture and storage (CCS) at coal liquefaction plants. The result of the two-phase project, supported in part by the US DOE and State of Ohio, USA, is the advancement of three steps of the hybrid coal/biomass-to-distillate fuel (jet fuel or diesel) process to the technology readiness level (TRL) of 5. The latest results from Phase 2 testing and associated technoeconomic analysis are covered in this paper. In Phase 2, all major process steps were scaled up to small pilot scale, including: (1) biomass conversion to high hydrogen-donor bio-solvents; (2) coal dissolution in biomass-derived solvents, without requiring molecular H₂, to produce a syncrude; and (3) two-stage catalytic hydrotreating/hydrogenation of syncrude to jet fuel and other distillates. The results were used to conduct a technoeconomic analysis as well as a GHG-emissions-reduction analysis.

More than 40 novel biomass-derived solvents have been tested so far. The raw materials for these, mostly non-edible solvents, are believed to be readily available around the

world. The process has been successfully used with coals from West Virginia, Ohio, Wyoming, and South Africa. The various biomass-derived solvents were compared to tetralin, which is a well-known hydrogen-donor solvent. The results showed that a total of 12 novel solvents met the goal of greater than 80% coal solubility. Most of these novel solvents were as good as or better than tetralin. The coal liquefaction process was scaled up to 1 ton/day. The data show that the solubility and syncrude viscosity from pilot testing were comparable to those attained during bench-scale testing. The CTL syncrude was upgraded in a 2-stage hydrotreatment/hydrogenation process, to reduce the sulfur and nitrogen contents to less than 2 ppm. The resulting distillate had 70% of the mass boiling in the jet fuel range and 90% in the diesel range. A detailed characterization of the jet fuel fraction showed that up to about 30% of it could be blended with a standard jet fuel.

A detailed economic analysis of the process shows it to be competitive at today's crude oil prices. Also, the GHG footprint for the process is much smaller than conventional, indirect CTL processes. The results from the technoeconomic analysis and GHG-emissions analysis will be presented.

Lignite-Plus-Biomass to Synthetic Jet Fuel with CO₂ Capture & Storage: Design, Cost & GHG Emissions Analysis for a Near-Term FOAK Demonstration Project in Mississippi and Prospective Future Plants

Eric Larson, Princeton University, USA; Chris Greig, The University of Queensland, AUSTRALIA; Thomas G. Kreutz, Johannes C. Meerman, Robert H. Williams, Princeton University, USA

We report on a 30-month design study for a first-of-a-kind (FOAK) demonstration plant that would be built at a site near Meridian, Mississippi, to coprocess lignite and woody biomass into jet fuel. The design uses an oxygen-blown TRIG™ gasifier developed by KBR and Southern Company. Fischer-Tropsch conversion of the syngas produces synthetic paraffinic kerosene (SPK) as the primary product, plus naphtha. Other co-products include electricity sold to the grid and CO₂ sold for use in enhanced oil recovery (EOR). Previous studies have identified coprocessing of various coals and biomass with CO₂ capture as promising options for cost-competitive production of low net lifecycle greenhouse gas (GHG) emissions synthetic fuels. The effort reported here goes beyond earlier studies in the level of detail in process design and cost estimation with the aim of improving the understanding of the economic prospects for lignite and woody biomass coprocessing systems. Key objectives in the design of the FOAK lignite/biomass-to-jet (LBJ) plant were to achieve net lifecycle GHG emissions for the SPK that are less than for conventional petroleum-derived jet fuel and to make process design and equipment selections such that the plant could be built and operated in the near term, e.g., before 2025. The process design was developed by researchers at Princeton University and the University of Queensland and validated by engineers at the WorleyParsons Group (WP). Commercial vendors provided design and cost estimates for several major plant components. Bare-erected capital costs and operating and maintenance costs were estimated by WP.

The primary objective in building and operating the FOAK plant would be to demonstrate the technical viability of the LBJ concept as an essential first step toward launching commercial-scale plants in the longer term. With this in mind, the project team developed a set of principles to help guide the process design: the total plant cost should be less than \$2 billion (to limit investment risk); the level of input biomass should be both proportionally significant to reflect biomass/lignite co-gasification and sufficient to achieve GHG emissions goals; process design decisions and vendor/equipment selections should prioritize the likelihood of technical success over minimizing the cost of jet fuel production.

The resulting FOAK plant design capacity is 1,551 metric t/d (45.5% moisture) lignite and 556 t/d (43.3% moisture) biomass, for a total input of 295 MWHHV, of which 25% is biomass. The design output is 1,252 actual barrels per day of liquids, of which 80% is SPK (62.3 MWLHV) and 20% is naphtha (13.9 MWLHV). It exports 15 MWe of electricity after satisfying a 38 MWe onsite auxiliary load. Additional products are 1,326 t/d of pressurized pipeline-quality CO₂ and 49 t/day of sulfuric acid (93 wt% H₂SO₄). With thinnings from sustainably-managed southern pine plantations as the biomass, and with captured CO₂ stored underground via EOR, the net lifecycle emissions for the SPK product are estimated to be about one-quarter of those for petroleum-derived jet fuel. The bare-erected cost (BEC) estimated by WP for this plant is \$588 million (2015\$). The authors' best estimate of total plant cost (TPC) is \$1,230 million, arrived at by assuming engineering, procurement and construction management services (20% of BEC), process contingencies (35% of BEC), and project contingencies (35% of the sum of all other costs, i.e., 35% of 1.55xBEC).

Not surprisingly, an annual discounted cash flow (DCF) analysis determined that it would be impossible to generate a positive net present value (NPV) over a wide range in key input assumptions. An SPK production cost subsidy of nearly \$400/bbl over a 20-year plant life would be required to achieve zero NPV under a baseline set of assumptions (including 3% real weighted average cost of capital and a levelized crude oil price of \$80/bbl). Alternatively, a capital grant in excess of the TPC value would also achieve zero NPV. The poor financial results reflect the small scale of the plant, the design principle to prioritize technical success, the levels of contingencies appropriate for the relatively early stage of project development, and the first-of-a-kind nature of the plant.

Technology innovations, learning via construction and operating experience, alternative plant configurations, and larger scale should improve economics of future plants. To help understand these prospects, a preliminary analysis of Nth-of-a-kind (NOAK) plants was developed, but with the limitation that plants would use only equipment components that for the most part are already commercial today: consideration of advanced, not-yet-commercial technologies and of R&D-driven improvements in existing technologies were beyond the scope of this analysis. The analysis found that a variety of NOAK plant designs that coprocess lignite and woody biomass to make jet fuel are unlikely to be economically competitive without subsidy even in the presence of a high future carbon tax or equivalent greenhouse gas mitigation policy. This conclusion applies to process configurations and input biomass/lignite ratios that result in net GHG emissions as high as those for petroleum-derived jet fuel and as low as zero.

In contrast, encouraging results were found for plants processing only biomass. The economics of these "BECCS" plants (biomass energy with CCS) improve dramatically with the strength of carbon mitigation policies because of their strongly negative net GHG emissions. These findings do not imply that coal/biomass coprocessing strategies for making synfuels with CCS are not economically promising – only that, in the case of lignite, much more than a 25% biomass coprocessing rate would be needed.

However, our analysis shows that all such systems are unlikely to be economic in the absence of a strong carbon mitigation policy. Future R&D driven technological innovations may modify this conclusion. Among other R&D priorities, an emphasis on better understanding and reducing plant auxiliary loads is warranted.

SESSION 14 Combustion Technologies – General I

Liquid Components as Enabling Technologies for Advanced, High-Temperature Power Cycles

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Reconsideration of current combustion systems has illustrated the need for high-efficiency power cycles to mitigate the energy losses required to implement carbon-capture, utilization, and sequestration (CCUS) schemes[1]. Oxy-fuel combustion is one technology under consideration for implementing CCUS and as a side benefit creates much higher flame temperatures than obtained with traditional air-fuel combustion. The high-temperatures can be exploited with the use of magnetohydrodynamic (MHD) power generation [2]. In this work we consider the use of liquid-surface components as an enabling technology for advanced, high-temperature power cycles.

Previous MHD power generation studies found a key technological hurdle in the electrode lifetime requiring about 8000 hours of operation whereas pilot-plant facilities indicated electrode lifetimes extrapolating to less than this quantity due to excessive and/or uneven erosion[3]. The interface between the partially-ionized combustion exhaust stream and the electrode surfaces is essentially a plasma-material interaction zone where non-uniform material phases and compositions co-exist in a small region. A similar material erosion and ablation problem exists in development of nuclear fusion energy systems and one solution is to utilize liquid plasma-facing components[4]. Liquid components are essentially self-healing and replenishable in real-time providing a means of maintaining the overall mass of material on a given component and mitigating arc-based erosion. Capillary forces in metal and dielectric sponges enable production of components to shape with a stable liquid surface. Slow, steady flow of the liquid material through the chamber can replenish the surface and remove deposited materials. Surface reactivity of the liquid with the combustion products is managed by use of an appropriate liquid such as a molten salt. Multi-component salt mixtures can exhibit a range of liquidus temperatures depending on composition (e.g. 898°C vs. 393°C for pure K₂CO₃ and the eutectic mixture of Li-Na-K carbonates respectively)[5]. Replenishing surfaces would also enable a method of managing deposited material on other surfaces such as on high-temperature heat exchangers avoiding fouling. We consider CCS-enabled power cycles leveraging oxy-fuel combustion with an MHD topping cycle and an indirect Brayton cycle via the use of electrodes and high-temperature heat exchangers potentially enabled by these liquid technologies.

Modeling of Mineral Redistribution and Transformation for a Sub-Bituminous Coal

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Ash deposition on heat transfer surfaces in pulverized coal-fired power plant is one of the most important parameter influencing boiler performance. Ash formation during pulverized coal combustion is associated with coal matrix, mineral matter size, mass distribution, chemical composition, boiler design, and operation condition. The objective of this study is to develop a model to predict excluded and included mineral particles number, size, mass, and chemical composition distribution for both before and after combustion.

Mineral matters in coal go through various forms of transformation processes during coal combustion based on type of mineral inclusion. Understanding of physical and

chemical transformation processes for both excluded and included minerals and their lower and upper extreme conditions in terms of composition will assist developing the transformation sub-models exclusively. Physical and chemical transformation of included and excluded mineral particles into ash is the first step in comprehensive and mechanistic approach for predicting ash deposition behavior in pulverized coal-fired boiler. The coal mineral association can be represented as mineral weight percent, coal weight percent, mineral area percent, and coal area percent by Computer Controlled Scanning Electron Microscopy (CCSEM) analysis. The predictive model for ash deposition requires the accurate transformation of surface-based two-dimensional mineral associations into three-dimensional volume based associations where coal particles will be simulated to determine their behavior inside boiler operating conditions. The mineral redistribution model is expected to provide included minerals size, mass and chemical composition distribution into coal matrix.

In this study, KPU, an Indonesian sub-bituminous coal sample was analysed to get Malvern size distribution data for coal matrix, CCSEM analysis for size, mass, and chemical composition distribution of included and excluded mineral particles. Using the data from Malvern size distribution and CCSEM analysis, total number of included and excluded mineral particle numbers before transformation will be calculated. Using the statistical results of previous experimental work done by other researchers, fragmentation and coalescence of char and mineral particles will be calculated to determine the residual ash particles number, size, mass, and chemical composition distribution. Results of residual ash particles number, size, mass, and chemical composition distribution from this study will be used as an input for predicting the ash deposition on boiler and post boiler equipment in a pulverized coal-fired power plant.

Method for Separation of Coal Conversion Products from Oxygen Carriers

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This paper summarizes the development of a technology for segregating fuel-based contaminants (char and ash) from oxygen carrier material in the context of chemical looping combustion application. In chemical looping, the well-mixed solids that flow from the fuel reactor consisting of char, ash, and oxygen carrier particles cannot be completely separated into their constituents before they enter the air reactor. The slip of carbon leads to char oxidation in the wrong reactor and poor carbon dioxide separation efficiency. The buildup of ash that is not rejected necessitates rejection of larger quantities of oxygen carrier material, resulting in a high operating cost penalty. An efficient method to separate char and ash from oxygen carrier material is critical for the deployment of chemical looping technology.

Chemical Looping Combustion (CLC) has emerged as an attractive alternative for carbon dioxide capture, where a near-pure carbon dioxide stream is produced from fossil fuel combustion without the use of oxygen obtained from air separation. In this type of system, a solid oxygen carrier (OC) is used, to bring oxygen to the fuel to convert it to a near pure carbon dioxide stream. During the process, the OC is reduced. The solid is then regenerated (oxidized) separately using air. CLC technology is expected to be more cost-effective and energy efficient compared to oxygen separation from air by other processes and to supply nitrogen-free oxygen for fuel conversion.

In CLC, when a solid fuel is used, only a portion of the fuel is converted in a single pass in the fuel reactor. This necessitates the need for segregation of the material leaving the fuel reactor into unconverted fuel (char) and OC, performed by a char separator. The separated char can be returned to the fuel reactor to increase its conversion. If unconverted fuel is transferred to the air reactor, it would be combusted in air releasing its carbon dioxide with nitrogen-rich gases. Since the primary motivation of chemical looping technology is to achieve a high carbon dioxide capture rate (CCR), an efficient char separator is mandatory. The CCR is the percent of fuel carbon that is converted to CO₂ in the fuel reactor. The design and development of such a char separation device is the objective of our research.

The investigated technology for char/ash separation from oxygen carrier uses a multi-step approach with unit operations that target the specific ranges of particle size and density of the OC and carbon-rich particles relevant to CLC. The OC is "cleaned" through a two-step process to ensure maximum removal of the char and ash. The paper summarizes results from ongoing research and development of the process, obtained during cold (room temperature) testing and hot (1173 K) testing for an oxygen carrier – char mix. Preliminary results demonstrate char rejection potentials of over 80 percent.

An Investigation of Combustion Kinetics of Coal-Microalgae Biomass Fuel

Ejesieme Vitus, Ben Zeelie, Gary Dugmore, Nicole Vorster, Nelson Mandela University, SOUTH AFRICA

Co-firing with biomass has been identified as low cost and low risk option in coal-fired power stations. Combustion of coal-microalgae biomass composite under non-isothermal thermogravimetric TG conditions was studied. The TG data was transformed to differential function, DTG which revealed overlapped processes. The research aim is to study the combustion mechanism of coal-microalgae biomass fuel. The goal is to use microalgae biomass as a renewable component to improve the combustion kinetics of coal.

The Coat-Redfens kinetic model was used on the non-de-convoluted reactions scheme to obtain a set of combustion parameters. While the Fraser-Suzuki equation was used to

de-convolute the overlapped complex combustion into low and high temperature schemes. The solid states oxidation reaction model g (α) was then used to deduce the mechanism while the Arrhenius equation was applied to derive the activation energy E_a and pre-exponential factor A .

Analysis of the combustion kinetics of coal-microalgae biomass composite showed thermal processes which are non-characteristic of coal. The composite showed a different oxidation mechanism relative to coal. At low temperature combustion stage, all the composites indicated a first order reaction O1 mechanism. But 10 % composite was dominated by a phase boundary, R3 and diffusion mechanisms, D3. At the low temperature stage, the phase boundary R2 and R3 mechanisms control the combustion of the coal (dumped fines), to the same degree as diffusion mechanism, D1 and D3. Whereas at the high temperature stage, all the composites indicated second order reaction mechanism, O2. Also, the mechanism, O2 obtained for coal (dumped ultra-fines) via de-convolution is different from the mechanism O1 which is reported for coal in literature though from a non-de-convoluted scheme.

Coal-microalgae biomass forms a homogenous fuel, Coalgae® under temperature treatment unlike linear mix of traditional biomass with coal. The kinetic properties improve as the quantity of microalgae biomass increases. The activation energy showed that coal-microalgae biomass fuel oxidizes more relative to coal. This approach is proposed to be cost effective as it uses of dumped ultra-fines (coal), and microalgae biomass which serves as natural binder for the fines thus making Coalgae® a renewable and sustainable fuel.

Experimental Study On Nitrogen Oxides Formation of Pulverized Coal During Unstaged and Staged Oxyfuel Combustion

Hong-Min Cho, Jeong-Woo Kim, Ho Lim, Chung-Hwan Jeon, Pusan National University, SOUTH KOREA.

Over the past decades, coal has played an important role in producing and meeting the demand for electricity in the world and will continue to be the dominant fuel, in spite of expected reduction in its consumption, for use in power generation in the developing countries. In this circumstance, air pollutants accompanying the pulverized coal combustion, including NO_x, SO_x, and especially CO₂, have become a global concern, as those emissions are the major causes of the atmospheric greenhouse effect. As a solution for the issues, Oxy-fuel combustion technology was suggested and thought to be a promising and near-term option to capture nearly pure CO₂. An important collateral benefit of O₂-CO₂ combustion is a reduction of nitrogen oxides (NO_x) that has been reported by several researchers. The purpose of this study was to investigate the NO_x formation characteristics of reacted pulverized coal in staged oxy-fuel combustion. A series of combustion experiments was conducted in a drop tube reactor named Two Stage Drop Tube Furnace which has several features for the two-step combustion. For the comparison, NO_x and CO concentration at the furnace exit and unburned carbon in reacted char or ash were measured both in unstaged and staged combustion with O₂-N₂ and O₂-CO₂ atmospheric conditions, varying the temperature and the stoichiometric (air-fuel) ratio (SR). The results indicated that, the measured NO_x concentration under O₂-CO₂ conditions was lower than O₂-N₂ atmosphere, with a tendency to be increased as the temperature and SR increased as same as the air condition. In the most case of oxy-fuel conditions, CO emission was much higher than that of O₂-N₂ cases, particularly having a peak at the lowest SR of 0.6 and the highest temperature, reversely with lower NO_x emission than O₂-N₂. These results clearly showed that further char and CO₂ gasification took place in oxy-fuel conditions, where CO products from gasification were reacted with NO to CO₂, having NO reduction effect by non-hydrocarbon fuel reburning. To evaluate the NO_x reduction effect by oxy-fuel-staged combustion, modified fuel-nitrogen conversion ratio (CR) which considered the fractional unburned carbon in reacted char was employed. Overall, CR decreased at the lower SR and temperature conditions and also was likely to be inversely proportional to CO formation, as the CO reburning reaction made a pathway of NO_x reduction. The CR in oxy-fuel-staged combustion was much lower than that under unstaged condition and even air-staged combustion, which indicated that staged combustion was also effective in oxy fuel combustion as well as more effective than conventional air combustion.

SESSION 15 Coal Ash Management - 3

Rapid Solidification of Coal Combustion Residuals (CCR) Leachate & Wet Ash Wastes

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Coal combustion residuals (CCRs) include fly ash, bottom ash, boiler slag and flue gas desulfurization, or scrubber, materials such as synthetic gypsum, which are produced when coal is burned for electricity generation. CCRs are one of the largest industrial

waste streams generated in the United States. In 2012, more than 470 coal-fired electric utilities burned over 800 million tons of coal, generating annually ≈110 million tons of CCRs in 47 states and Puerto Rico.

In the Southeast alone there are around 400 known coal ash storage facilities with a total capacity to hold over 584,234,000 Cys of ash. The Southeast is home to over 50 documented contamination sites where there is known pollution to the ground or surface water along with at least 20 “high hazard” coal ash dams determined by the EPA assessment.

Since its development in the early 1960s, the application of Super Absorbent Polymers (SAP – Sodium Polyacrylate) has been used to solidify liquid industrial /radioactive waste streams, dredge sediments, biosolids and sludges associated with remediation projects, landfill closures, petrochemical spills, and other environmental cleanup projects. ZappaTec (www.zappa-tec.com) SAPs reduce waste transportation and disposal costs from these operations by solidifying liquid waste while minimizing an increase in weight and volume. With the capability of solidifying up to 300x its weight in water, 1# of SAP can solidify ≈36 gallons of water.

Super absorbent polymers have numerous advantages over commodity solidification media like kiln dust, Portland cement or sawdust. Super absorbent polymers:

- Chemically bond with water, and don't biodegrade and release liquid;
- Minimize waste volume;
- Typical expansion is less than 1% mix quickly to improve production efficiency Pass the EPA Test Method 9095 paint filter test. After solidification, many waste streams pass EPA Test Method 1311 for RCRA metals with the addition of SAP alone;
- As SAP is not biodegradable, it is regulatorily approved for landfill use.

Due to the extraordinary pending quantities of wet CCR (>50% moisture) requiring either wet excavation or dredging prior to either dewatering or solidification, a detailed bench-scale evaluation was performed by the Coal Ash Liquid Management Office (<http://epic.uncc.edu/research/research-centers/coal-ash-and-liquid-management-calm>), a part of the University of North Carolina, on six different ZappaTec SAP blends to provide the ideal balance of cost and performance using five wet CCR waste samples from four different power utilities. One of the primary study conclusions was, “As little as 0.5% of SAP by dry weight was sufficient to stabilize the moisture in fly ash containing as high as 70% water”.

Concurrently, Mineral Processing Services (www.mpsmaine.com) has developed a full-scale specialized SmartFeed™ Sequential Mixer/Blending unit capable of metering in >1% ZapZorb admixture, homogenizing/conditioning and delivering a stackable solidified CCR waste by receiving a high-solids (≈45% solids) dredge slurry feed at 300 gpm and delivering ≈88 Cys/hr (≈83 tons/hr) of stackable CCR material. Testing shows that the duration of 0.3% ZapZorb SAP sequential blending of a 65% moisture CCR slurry into a solidified CCR matrix passing EPA Paint Filter criteria is as low as 3 minutes. The large-scale SmartFeed™ Sequential Mixer/Blending unit has a projected capacity of 600 Cys/hr (≈570 tons/hr) by receiving a high-solids (≈45% solids) dredge slurry feed of 2,000 gpm.

Advantages blending as low as 0.3% ZapZorb admixture will ensure the CCR waste or dredged sediment material will pass EPA Paint Filter Test within 3 minutes of blending (expediting direct load-out without the need for interim stockpiles and rehandling expenses), ensure no free liquids are generated during OTR/rail transport prior to arrival at the final destination and will significantly improve strength of the ZapZorb amended material for either support of a final closure cap or to be bladed-out and compacted within a mono-fill.

The sequential addition of 2% EnviroBlend (www.enviroblend.com), a magnesium based pH buffered pozzolan, followed with 0.3% - 0.5% ZapZorb SAP addition has shown to be very effective in stabilizing liquid waste streams, slurries, sludges and saturated sediment containing the following heavy metals:

Arsenic	Barium	Manganese
Arsenate	Cadmium	Mercury
Calcium arsenate	Chromium (tri & hex)	Nickel
Chromated copper arsenate	Cobalt	Selenium
Arsenite	Copper	Vanadium
Antimony	Lead	Zinc

Summary:

Cost, time and volume increase savings for the application of 0.3 - 0.5% SAP versus 8 – 10% Portland cement for the solidification of the millions of Cys of wet CCR will have a dramatic impact on reducing costs, shortening project schedules and minimizing the volume of CCR waste to transported and placed within new impoundment cells.

Ash Pond Closure and Repurposing at Net Zero Discharge Facilities

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Ash pond closures typically require dewatering a significant volume of water. Often, dewatering activities is continuous throughout the project lifecycle which equates to millions of gallons of water being removed. Net Zero Discharge (NZD) facilities face a unique and complex dewatering challenge.

This presentation will offer attendees a case history of converting a wet ash pond into an ash landfill leachate pond and recycle basin. Attendees will gain insight on alternatives to reducing dewatering volumes throughout the project lifecycle. In addition, engineering and construction insights will be offered to attendees related to the impacts of water quantity and quality to these projects, specifically water (surface and

groundwater) management in relation to pond underdrain systems and overall construction activities. Attendees will also be offered a unique look at using cut-off walls in the construction of these new ponds and state-of-the-art sedimentation systems operated in conjunction with these new ponds to mitigate the need for pond dredging.

Design, Installation and Operation of Coal Ash Basin Dewatering Treatment Systems

Charles McCloskey, Evoqua Water Technologies, USA

As more ash basins in both operating and idled coal fired power plants are scheduled for closure and dewatering, best practices have been developed for the design, installation and operation of the wastewater treatment plants that will need to be installed. Good design begins with a thorough understanding of the nature of water needed to be treated, volumes and quality, project timetable, projected ash movement, current and future discharge requirements. Several unit process such as sedimentation, clarification, filtration, and advanced metals removal technologies are available and can be assembled into the right configuration for each application. Proper design will use only the modules needed to accomplish the stated treatment objectives. Installation variables include site location, utilities, access and desired project time frame. Both mobile and permanent systems should be considered and evaluated. Operations and maintenance of the treatment system should be optimized to ensure consistent and reliable results achievement at an acceptable cost to the utility. Several examples and case histories will be presented of designed, installed and operating ash basin dewatering treatment systems.

The Unique Role of Slurry Wall Systems for CCR Impoundment Closure Programs

Dale W. Evans, Kathleen Whysner, Remedial Construction Services, L.P., USA

Since the inception of RCRA, soil-bentonite slurry wall systems have received broad acceptance for managing and protecting groundwater. Impermeable soil-bentonite barrier walls can be used to divert groundwater flow, create subsurface barriers to localized flow, and where full perimeter walls are used, comprehensively isolate impoundments to contain groundwater in contact with CCR materials. Therefore, use of these systems supports application of a unique cost-effective system for managing, controlling, and isolating groundwater that in most cases cannot be duplicated by other technologies. The utility and economy of using this technology to support both near-term impoundment dewatering programs, as well as subsequent containment of impacted groundwater, makes these systems appropriate for consideration for many CCR closure programs.

This paper provides an overview of the broad applications available for CCR-specific slurry wall programs, including the means of application in the field and the parameters requiring consideration to define project-specific efficacy. In particular, the considerations required to address each of the following applications are considered: Impoundment Dewatering – Because many CCR impoundments were not provided with lining systems, the use of a full perimeter alignment supports the capacity to provide complete containment of the water remaining within the impoundment as well as the groundwater within the footprint contained by the alignment. Concurrent installation of an accompanying recovery trench can then be effectively used to convert the base of the impoundment to a sub-drain system to support recovery of groundwater for dewatering the impounded volume.

Corrective Action – Where corrective action may eventually be triggered to address environmental impacts, slurry wall systems can provide containment of groundwater to eliminate the routes of exposure to potential receptors. In effect, such isolation interrupts the connection between source mass and groundwater, thus limiting continued migration of impacts while supporting natural attenuation. This application is supported similar to that outlined for impoundment dewatering through integration with a recovery trench or well-based groundwater recovery system as may be appropriate to create and support an inward gradient to validate containment.

Beneficial Use of CCR Using Geotextile Tubes for Ash Pond Closure

Tom Stephens, TenCate, Water and Environment; Meena Viswanath, Ming Zhu, Geosyntec Consultants; Kirk Foley, Infrastructure Alternatives Inc, USA

This paper presents a case study where geotextile tubes were used to construct a dam to contain and dewater coal ash as part of an ash pond closure. The geotextile tubes were stacked in two layers and formed an approximately 11 ft (3.35m) high, 2,400-ft (730m) long dam with the majority of the geotextile tube dam structure constructed in a 3-2 pyramid structure. The dam separated the ash pond into two areas – a pool area, which continues to serve as an operations area to receive sluiced coal ash, and a construction area where final closure grades will be constructed. Coal ash from the pool area was dredged and pumped into the geotextile tubes, reducing the amount of coal ash that might otherwise need to be stabilized in place during the final closure. The dam also serves as a buttress to improve slope stability during interim construction. At the end of the closure, the entire pond will be filled to final closure grades and the geotextile tubes will be buried in place.

Geotechnical slope stability and settlement analyses were performed during the engineering design phase. Based on design recommendations, piezometers were installed underneath the geotextile tubes to monitor porewater dissipation in the ash. To evaluate the effectiveness of dewatering coal ash using geotextile tubes, ash samples were collected from the site and sent to a laboratory for dewatering testing to determine polymer type and dosage. This paper presents details of the engineering design, laboratory testing, field construction, and observed field performance of the geotextile tubes.

SESSION 16
Coal Science - 3

Fractionation of Wyoming Coals to Produce Intermediates for Non-Fuel Products

David A. Bell, University of Wyoming, USA

Coal production in the United States is falling due to competition in the electric utility market from natural gas and renewable energy. To continue to derive economic benefits from Wyoming's abundant coal reserves, we are exploring alternative markets. Non-fuel products are attractive, because, compared to electricity and fuels, non-fuel products have high unit values that may allow coal processing to be economically viable. Potential non-fuel products include paving materials, soil supplements, aromatic chemicals, polymers, and carbon products (activated carbon, carbon fiber, graphite, and graphene). The State of Wyoming is sponsoring a Carbon Initiative to seek new markets for Wyoming coal. A key concept in this initiative is the "coal refinery." Much like a petroleum refinery, the process would fractionate the raw material, coal in this case instead of crude oil, and the fractions would be processed to make final products. This presentation describes our efforts to fractionate coal.

Our coal fractionation research is taking two basic approaches. The first approach is solvent extraction, in which a portion of the coal is dissolved in either an organic solvent or in an alkaline aqueous solution. We have also started to investigate flash pyrolysis in which the feed to pyrolysis will be either raw coal or the insoluble residue from solvent extraction.

Substantial Upgrading of a High-Ash Lignite by Hydrothermal Treatment with Calcium Hydroxide

Jie Wang, Xueping Liu, Xuanta Wu, East China University of Science and Technology, CHINA

Hydrothermal treatment has been widely investigated as an approach for upgrading lignite. However, this approach has a limited effectiveness for high-ash lignite because inorganic minerals are generally little affected by this treatment. The aim of this study is to explore a new method by a first hydrothermal treatment followed by a subsequent Ca(OH)₂ digestion/acid leaching to substantially improve the properties of lignite. We found that the O/C molar ratio was reduced from 0.30 for a raw lignite to 0.07 for a treated lignite, with a reduction in the ash content from 24.1% to 3.5%. The high heat value increased from 17.4 MJ/kg for the raw lignite to 29.7 MJ/kg for the treated lignite. The lignite contained abundant clays and quartz, which are appreciably removed by this treatment. The first step of hydrothermal treatment was found to be important for improving the demineralization. This treatment also removed many trace elements such as Li, Be, V, Mn, Ga, As, Se, Cr and Pb to a large degree. The upgraded lignite may have not only a high efficiency in coal transport and combustion but also a smaller risk of the emissions of hazardous air pollutants (HAPs) when it is used as a fuel in place of the raw lignite.

SESSION 17
Gasification Technologies: UCG

In-Situ CO₂ Capture During A UCG Process by Simulating Possible CO₂ Absorption On Roof, Floor and Coal Mineral Structures

JC van Dyk, J Brand, FB Waanders, African Carbon Energy, SOUTH AFRICA

UCG is a gasification process used to produce gas from coal in situ (underground in the coal seam) by injecting air or oxygen, with or without steam, into coal seams and extracting the product gas via surface wells. This may also be thought of as a thermochemical mining process. The burning front results in high temperatures (>1000°C) that cause the coal ahead of the front to effectively re-form into gas. A UCG cavity is also directly in contact (physical and chemical) with the surrounding roof and floor strata. CO₂ recycling into a UCG cavity will not only improve the effectiveness and carbon efficiency of the process, but will also open the added advantage of CO₂ capture on the mineral structure of the minerals in the coal, roof and floor strata.

The mechanistic behaviour of minerals such as Mg, Fe, Ca-containing species towards the in-situ capture of CO₂ during gasification, as well as understanding the chemistry and the interpretation of the mechanism involved, as measured by means of high temperature X-ray diffraction (HT-XRD), in combination with FACTSAGETM modelling, is known. The CaO content of a South African and another coal source investigated previously ranged from 6 mass % to 30 mass % respectively. The basic components present in the coal, or specifically the CaO and MgO, only act as fluxing components (lowering of the melting temperature) up to a specific percentage, where after the AFT of the coal starts to increase again.

The principle aim of this study is to validate the possible advantages and CO₂ capture on the mineral matrix inside a UCG cavity by means of a FACTSAGETM equilibrium simulation. The study will be an in-depth focus on the mineral composition of the coal, roof and floor as it will be processed (gasified) during the South African Theunissen UCG project.

Evolution of the keySeam UCG Process

Burl E. Davis, Carbon Energy Limited; Cliff Mallet, CUMT International UCG Research Centre and Carbon Energy Limited, AUSTRALIA

Carbon Energy, CEL, has advanced Underground Coal Gasification Technology from a small-scale batch gasification process to a continuous multi-year operation process with proven environmental safety. The results of the U.S. Department of Energy UCG program culminating in the Rocky Mountain 1 demonstration of a Parallel CRIP concept were integrated with the Geotechnical expertise of CSIRO to develop a unique UCG process. Carbon Energy (CEL) demonstrated at the keySeam UCG Process at the Bloodwood Creek site outside of Dalby in Queensland Australia. The full-scale two Panel operations were between 2008 and 2012. The site is now in restoration phase with no significant environmental impact. The paper will describe contributions of the various field programs to the finished keySeam process.

The Gas -Coal Interface in Underground Coal Gasification

Cliff Mallet, Jianmin Zhang, CUMT International UCG Research Centre and Carbon Energy Limited, AUSTRALIA

Underground coal gasification (UCG) occurs in a cavity at depth with extreme temperatures and it is not easy to obtain direct observations of the processes. Models for the underground gasification process have been developed based on various analogues and post-burn studies. The challenge for these models is that there are many different physical and chemical phenomena interacting simultaneously in an unknown physical cavity shape, a large range of reactions are possible depending on temperature, pressure and gas composition, with various mixes of chemical feedstock comprising injected gases, groundwater inflow and in situ coal.

There are several guides to understanding of UCG. These include the reactions observed in surface coal gasification plants and UCG is considered to involve high temperature oxidation reactions, lower temperature reduction reactions and pyrolysis of coal down to a few hundred degrees centigrade. Many gasifier designs have been used, all based on this idea of a declining temperature profile of the gases flowing through the gasifier. The gasifier cavity continually changes shape as coal is gasified and removed. A successful gasifier design has to maintain contact of the hot flowing gases with coal and water as the coal/gas interface shifts, and preserve a flow path for injected gases into and through the reaction chamber to finally deliver product gas at the surface.

Some direct and indirect evidence is available of conditions at various times in an underground gasifier. Pressure is usually known, and occasionally the temperature at specific points is available. Analysis of product gases provides a guide to the reactions that have occurred, but as the product gas is the result of a whole series of reactions at different sites, it cannot provide definitive interpretations of reactions at specific sites in the gasifier. Post-burn analyses of remaining ash give some insight to temperatures that have operated at some time during gasification.

A critical controlling factor is the behavior of the gas/coal interface which moves as the cavity expands. Gas compositions and reactions change continuously, coal which is naturally fractured is gasifying and heating, the cavity shape is changing with the in situ stresses responding to the excavation and heating. The caving or spalling of coal at the gasification face has been suggested to be a major factor in cavity growth. However, the results of theoretical modelling with typical thermal properties of coal and associated rocks, and experience in some UCG field operations suggest that the gas/coal interface moves primarily as a result of in situ coal gasification, with minimal influence of coal caving or spalling.

The Effect of the Roof and Floor Geological Structures on the Mineralogical Composition of Ash Produced from Coal at UCG Operating Temperatures

JC van Dyk, African Carbon Energy; R.C. Uwaoma, C.A. Strydom, R.H. Matjie, J.R. Bunt, North-West University, SOUTH AFRICA

The mineralogy of the ash and slag formed at typical UCG operating temperatures were investigated using a bituminous coal from the Theunissen UCG site in the Free State province of South Africa. The ash and slag samples were produced at 1000, 1100, 1200

and 1300 °C, and were subjected to XRD, XRF, FTIR, surface area (CO₂) and SEM-EDX analyses. XRD results show an increase in crystalline phases, with a decrease in the amorphous content as the temperature increases, with mullite and quartz found to be the dominant minerals in the crystalline phase. FTIR spectroscopy results reveal the appearance of peaks related to the crystalline phase of mullite with increasing temperature. SEM results showed the formation of spherical particles, with the appearance of cenospheres, as the temperature increases. The surface area results showed a decrease in surface area and porosity as the temperature of the ashing increases, with the slag at 1300 °C having the lowest surface area and porosity. It was concluded that the higher the gasification temperature, the less leaching of inorganic species is predicted. A UCG process temperature of 1300 °C and higher will minimize leaching of inorganic species from the remaining cavity.

Fundamentals in Environmental Management for Underground Coal Gasification

Cliff Mallet, CUMT International UCG Research Centre and Carbon Energy Limited;
Burl E. Davis, Carbon Energy Limited, AUSTRALIA

Enough underground coal gasification (UCG) sites have been operated around the world to achieve an understanding of the geological site characteristics, design specifications, operating conditions during production, and the shut down and clean up procedures which are necessary for safe and environmentally acceptable UCG projects. Geological conditions must provide an overlying gas seal that prevents loss of syngas into overlying roof rocks. Groundwater pressure within the target coal seam must be high enough to allow the gasifier to operate efficiently at a lower gas pressure, which provides continuous groundwater inflow to the gasifier cavity, preventing the escape of potentially contaminating coal pyrolysis by-products. Boreholes for oxidant injection and syngas product removal must retain their integrity during high temperature phases of operations, with appropriate temperature tolerances for borehole casings, liners and cements. During production, gasifier pressure is kept within the specified range in relationship to surrounding groundwater pressure and adjusted to match changes in groundwater conditions to ensure containment of gas in the gasifier cavity. On decommissioning, groundwater inflow is maximized to limit further production of coal pyrolysis products, and to use the heat in rock surrounding the gasifier cavity to convert groundwater into steam which cleans the cavity as it is vented. The example of Bloodwood Creek UCG trial in Australia which successfully applied these processes will be described. At the conclusion of decommissioning at this site the small amounts of pyrolysis derived contaminants present in water filling the gasifier cavities do not affect the environmental values of the water resource and will naturally attenuate to non-detect levels in a few decades.

SESSION 18 Rare Earth Elements - 3

Organic and Inorganic Association of Rare Earth Elements in Coal

Ronghong Lin, Tracy L. Bank, Evan J. Granite, Yee Soong DOE / NETL; Elliot A. Roth, AECOM, USA

Coal contains trace amounts of rare earth elements (REE). They are either in the form of discrete minerals or chemically bound to organic matter. The mechanism of bonding REE by organic matter has not been fully understood. Quantitative characterization of organically associated REE is still very challenging. Methods of distinguishing the organic and inorganic associations of REE in coal have been mostly based on the correlations of REE concentration with ash yields. In this presentation, we will report the first quantitative analysis of REE distribution in the organic and inorganic phases of coal. Particle size and density separations of low-ash Appalachian coal were performed, and the resulted samples were characterized using ICP-MS, ICP-OES, and TGA methods. The results showed that the REE concentration on the whole coal basis increased with increasing ash yields while the REE concentration on the ash basis reduced as the ash yields increased. Based on the correlation of REE concentration with the ash yield as well as the REE distribution pattern, a simple model was developed to quantitatively determine organic associated REE. The model predictions showed a very good agreement with experimental data. The result suggested that approximately 25% of REE in the low-ash Appalachian coal used in this work is associated with organic matter and the organically associated REE are relatively enriched in heavy REE.

Application of a Hand-held XRF Unit to Establish the Lineal Extent of Rare Earth Element Concentration in Investigative Cores

Robert Uhrin, David C. Uhrin, Eugene Uhrin, XLight Corporation, USA

Rare earth elements (REEs) represent an important commodity that is not readily available from US resources. While rare earth elements (REEs) aren't exactly rare, their appearance in high, minable concentrations is unusual. The observation that power plant coal ash contains relatively high concentrations of REEs was an important discovery, and residues from coal combustion are now being studied as a possible economic source

for extraction of REEs. Since coal contains a relatively small fraction of inorganic material, a related issue is the actual coal-related strata from which the REEs originate and the extent of a particular the stratum.

During the course of sampling various coals and coal-associated materials, it was observed that the REE concentrations in samples vary from low (<50 ppm) to relatively high (>300 ppm). It is found that two or more adjacent coal seams can also contain high concentrations of REEs. Generally speaking, the overburden of a single coal seam may be the source of the REEs, while the intervening strata between adjacent seams may also be a source. The distance between seams varies and can become many feet in some cases. One would like to know the extent of a given REE source.

Chemical analysis of coal and coal-related materials is costly and time consuming. Therefore, a suitable technique to quickly analyze a particular sample is of great benefit. It is hoped that x-ray fluorescence (XRF) can meet that challenge, and a hand-held unit would be extremely useful. Chemical analysis by induction coupled plasma mass spectroscopy (ICP-MS) has become a standard technique to accurately measure REEs in coal and coal-related samples. Simultaneously, it is known that XRF is not as accurate per se. This can be circumvented by comparison of XRF data with corresponding ICP-MS data as well as data obtained from standard samples. Suitable NIST standards are not available, so the intent here is to prepare standards using co-precipitation and solid-state reaction.

XRF has been found to provide good semi-quantitative data, and, in many cases, quantitative values (< ±20%) with respect to an XRF database. Cores from coal exploration drilling are widely available, so this offers a good opportunity to determine the continuous extent of high REE concentrations within an existing drilling core. Subsequently, a Niton XL3t-500 hand-held XRF unit was utilized to obtain an extensive data set from an uninterrupted length of a core related to a known Middle Kittanning coal seam. The initial results indicate that the REE concentrations are not only continuous but also extensive. XRF results will be presented and will be presented along with a cross-correlation with ICP-MS and standard sample values.

Influence of Temperature on the Recovery of Metal Elements from Coal Ash – FACTSAGE™ Simulations

J.C. Van Dyk, North-West University, African Carbon Energy; A.C. Collins, C.A. Strydom, J.R. Bunt, North-West University, SOUTH AFRICA

Recovery of K-, Al- or Ti-containing minerals or inorganic compounds from coal ash, formed during thermal processing of coal may have economic value. The minerals, quantities, and the thermal conditions to which the coal is subjected to will have an influence on mineral transformation and slag formation and, importantly, the type and quantity of minerals that can be recovered. FACTSAGE™ Thermo-Equilibrium Software and associated databases supply the option to scientifically predict mineral transformations during thermal treatment and, thus, possible recovery yields and forms of specific minerals. The main aim is to report the mineral transformation of K-, Al- and Ti-containing minerals, to predict whether these species were evaporated as gas or captured in the slag at various temperatures, and to predict if these species can be recovered via hydrometallurgical leaching. Using FACTSAGE™ modeling software, the mineral transformations of four coal samples were investigated under specific gasification conditions. It was determined that the slagging behaviour of the coal was influenced by the addition of potassium to the coal, and also by the minerals, specifically the basic components (yield or composition), in the sample. The theoretical percentage of potassium available for recovery decreased with increasing operating temperatures and increased with potassium loading to the coal. This suggests that potassium either formed part of a stable mineral phase (eg. potassium feldspar) or was captured in the melt. Theoretical recovery of aluminium and titanium from the coal ash decreased with increasing operating temperatures.

Characterization of Rare Earth Element Minerals in Coal Utilization Byproducts and Associated Clay Deposits from Appalachian Basin Coal Resources

Scott N. Montross, Circe A. Verba, Amy Falcon, James Poston, Mark McKoy, NETL, USA

Rare earth elements (REE) are necessary for advanced technological and energy applications. With limited economically viable domestic REE resources, supply remains a major concern for domestic energy security. Efforts to secure a domestic REE source require the advanced development of efficient and cost effective methods for REE extraction from stockpiled domestic materials, such as coal utilization byproducts (CUB) and geologic deposits associated with coal resources. This study focuses on the characterization of REE-bearing minerals in coal source rock, combustion byproducts, and underlying clay-rich rocks associated with Central Appalachian coal resources. Multimodal analytical techniques were used to characterize mineralogical and geochemical relationships (e.g., bulk ICP-MS, electron microscopy) intended for resource evaluation. This study demonstrates a novel technique to identify and quantify REE mineral grains in bulk samples using automated electron microscopy and advanced image analysis. These techniques allow for the scanning of large areas of material (up to 1 cm²) and quantification of REE mineral phases in a variety of matrices. Specific mineral volumes and bulk concentrations are calculated through the analysis of three-dimensional images acquired by FIB-SEM. The coupled results of SEM-EDS and FIB-

SEM analyses provide qualitative internal geometry of rare earth mineral grains and the matrix rock.

The samples examined contain minerals such as quartz, calcite, plagioclase, and various clay minerals. The clay minerals identified are saporite, illite/mica, kaolinite, halloysite, chlorite, and smectite. Trace minerals included: pyrite, zircon, siderite, rutile, gypsum, and barite. We identified primary REE-bearing phosphate minerals – monazite ((Ce,La,Nd,Th)(PO₄,SiO₄)), xenotime (YPO₄,SiO₄), and apatite (Ca₅(PO₄)₃(F,Cl,OH)) – in all samples. Some clay-rich samples are found to contain REE-bearing hydrous aluminum and calcium phosphate minerals, likely formed during diagenesis. Samples from extensively paleo-weathered horizons contain the clay minerals saporite, illite, and kaolinite. REE concentrations in clay-rich samples range from 250-450 ppm and have a HREE/LREE ratio >20%. Study results provide insight into the affinity of REE for specific ligands and colloids, and how the rock and ligands may respond to different physical and/or chemical treatments for the recovery of REE from CUB and clay-rich layers from coal seams.

SESSION 19 Carbon Management – Technology Development Status

Regional Impacts of Carbon Capture and Sequestration (CCS)

Joshua Stanislawski, Steve Schlasner, Bruce Folkedahl, Mike Swanson, Melanie Jensen, University of North Dakota, USA

Regional impacts for carbon capture are a critical piece of the decision process surrounding carbon capture and storage (CCS) implementation. Switching to natural gas-based operation is one option available to utilities for reducing carbon emissions and meeting local regulations; however, the negative economic impacts of this change must also be considered. Significant loss of employment is anticipated when a plant switches to gas because of closure of coal mines and a reduced support staff at the plant. On the other hand, significant job growth and positive economic impact are expected if CCS technology is implemented at a coal plant and at an oil field. A significant number of jobs are created during the construction period, which results in additional job creation through indirect and induced effects. Local suppliers will see an uptick in sales due to the high demand for construction materials, which is considered an indirect impact on the economy. Workers spend money locally on housing, food, and entertainment that can induce additional job creation. The ripple effects of a project such as this can last for many years and result in increased tax revenue to the state and other localities. Permanent jobs are created during the operational phase at both the plant and oil wells that are ready for enhanced oil recovery operations. The incremental oil production can also increase tax revenues.

The EERC has been working to evaluate the economic impact of both natural gas switchovers and implementation of CCS technology in the state of North Dakota. This presentation will review the results of these studies to date and provide a path forward for other regions to conduct similar studies.

CO₂-SCREEN: Application to the Oriskany Sandstone

Sean Sanguinito, AECOM; Angela Goodman, NETL; James Sams III, AECOM, USA

The ability to accurately predict the CO₂ storage resource in saline formations is required to make high-level, energy-related government policy and business decisions. CO₂-SCREEN (Storage prospective Resource Estimation Excel aNalysis) is a tool developed by the United States Department of Energy National Energy Technology Laboratory (US-DOE-NETL) to screen saline formations for prospective CO₂ storage resources. CO₂-SCREEN uses DOE methods and equations to serve as a consistent mechanism for calculating prospective CO₂ storage resources. CO₂-SCREEN is comprised of two files: an Excel file used for inputs and outputs and a GoldSim Player file used to run Monte Carlo simulations. CO₂-SCREEN requires input of physical geologic parameters (i.e. thickness, porosity) as well as efficiency factor ranges (i.e. net-to-gross thickness) to calculate a mass storage probability. An application of CO₂-SCREEN is demonstrated here using well log data from the Pennsylvania portion of the Oriskany Sandstone. The Oriskany Sandstone is divided into 20 km x 20 km grids in which 151 grids contain well log data. CO₂-SCREEN calculates prospective CO₂ storage resource for each grid based on the well log data and uses lithology and depositional environment information for efficiency factor ranges. The Oriskany Sandstone CO₂ storage resource estimate for Pennsylvania, calculated by CO₂-SCREEN, ranges from 0.07 to 1.28 gigatons (Gt) with a mean value of 0.32 Gt. This analysis is done to demonstrate the use of CO₂-SCREEN and results are comparable to previous studies. This successful demonstration encourages an expansion of this tool to other storage reservoir formations such as shale and depleted oil and gas reservoirs.

Status of Technology Development at the National Carbon Capture Center

Doug McCarty, Southern Company Services, USA

The National Carbon Capture Center (NCCC) is a key component of the U.S. Department of Energy's strategy in promoting the United States' economic, environmental, and energy security through reliable, clean, and affordable power produced from coal. The NCCC provides state-of-the-art facilities and support for technology developers to evaluate and advance the most promising post- and pre-combustion CO₂ capture and gasification technologies for future commercial deployment. Since CO₂ emission reduction is a global issue, the NCCC encourages international participation in the technology development at the center.

The NCCC facilities include the Post-Combustion Carbon Capture Center (PC4), located at Alabama Power's E.C. Gaston power plant, and a pilot coal gasification plant which houses precombustion CO₂ capture test sites. Evaluation of developing technologies using coal-derived gas under industrial conditions provides critical information on material and process suitability for scale-up to commercial applications. Because of the ability to operate under a wide range of flow rates and process conditions, research at the NCCC can simultaneously evaluate a number of technologies at various levels of maturity, thereby accelerating the pace of development.

Operations at the PC4 have included more than 47,000 hours of bench- and pilot-scale technology evaluations, with over 6,200 hours under simulated natural gas flue gas conditions. Testing has included operation of the PC4's Pilot Solvent Test Unit with technology developers' solvents, as well as operation of independent processes employing solvents, membranes, enzymes, and sorbents. For gasification and pre-combustion CO₂ capture technologies, the center has accommodated more than 46,000 hours of developer technology testing since 2009. These include catalysts, solvents, sorbents, fuel cells, membranes, biomass co-gasification, instrumentation, pressure-swung adsorption, syngas chemical looping, and membrane-assisted liquefaction.

Results from NCCC's testing have proved the facility's usefulness in accelerating the development of advanced CO₂ capture and power generation technologies. This presentation will detail the NCCC's capabilities, recent test results, and future plans.

Greenhouse Gas Emissions in the U.S. Coal Industry and the Market for Emission Offsets

Clark Talkington, Advanced Resources International, Inc; Felicia Ruiz, EPA, USA

Methane is a greenhouse gas (GHG) with a global warming potential (GWP) 28 to 34 times greater than that of CO₂ and contributes 16 percent of global GHG emissions. Reduction of methane emissions has, therefore, become an important policy priority in the United States and around the world over the last 25 years. Efforts to quantify and reduce methane emissions have focused on the highest emitting economic sectors, including the coal industry, which accounts for 8% of global anthropogenic emissions. This is especially relevant for the United States because it is the world's second largest coal producing country and also the second largest coal mine methane (CMM) emitting country. In 2015, U.S. active mines liberated 77 million metric tons of carbon dioxide equivalent (tCO₂e), and abandoned mines liberated another 9 million t CO₂e in 2015.

In 2010, the U.S. Environmental Protection Agency (EPA) issued the Mandatory Reporting of Greenhouse Gases Rule (40 Code of Federal Regulations Part 98) to collect accurate and timely GHG data to inform future policy decisions. The Rule was adopted in response to the Fiscal Year (FY) 2008 Consolidated Appropriations Act (H.R. 2764; Public Law 110-161), which required reporting of GHG data and other relevant information from large sources and suppliers in the United States. Within the coal mining sector, active underground coal mines liberating at least 36.5 million cubic feet (mmcf) per year are the only segment required to report to the Greenhouse Gas Reporting Program (GHGRP). The first year of reporting was 2011, and typically 110 to 130 mines report emissions in a given year.

Although facilities must report their greenhouse gas emissions to the GHGRP, there are no requirements at either the federal or state level in the U.S. to abate CMM emissions through controls or utilization schemes. U.S. mines, however, have had very good success in capturing and using CMM. Many U.S. projects have relied on energy commodity markets, especially the natural gas market, to derive economic benefits from the projects, but voluntary carbon markets and the California Cap-and-Trade Program are also incentivizing CMM project development. Significant support has also come from EPA's Coalbed Methane Outreach Program which has played an integral role in furthering CMM projects.

This paper will: (1) review CMM emissions in the United States including recent and future trends; (2) introduce EPA's Greenhouse Gas Reporting Program and summarize data from the first five years of reporting; (3) provide an overview of the voluntary and compliance carbon markets for U.S. CMM projects and the outlook for those markets; and (4) discuss the EPA Coalbed Methane Outreach Program's support of the U.S. coal industry and CMM project development.

Hydrothermal Co-carbonization (HTCC) of Coal-Biomass Blend

Toufiq Reza, Akbar Saba, Ohio University, USA

A 7.5 billion current population of the world is expected reach nearly 10.3 billion in 2040 while energy consumption for electric power is projected to reach 42 quadrillion BTU in 2040. Meeting these energy demands requires high output from our existing energy technologies as well as introduction of emerging technologies. In the US, coal-fired plants accounted for approximately 40% of electricity generation in 2015 and coal consumption has been expected to increase by 17.6% quadrillion BTU by 2040. To meet the projected energy demand without contributing additional greenhouse gas emission, co-combustion of biomass with coal is a viable solution. However, very low bulk density, energy content, and wet nature implements severe risks on co-firing biomass with coal.

Hydrothermal carbonization is one of the thermochemical processes, where biomass is treated with a hot compressed water. As the reaction medium is water, there is no need to dry the feedstock. Therefore, the expensive drying process can be eliminated by applying this technology. Now, sub-and supercritical water, unlike water at ambient condition, are very reactive due to its high ionic product, low density, and low dielectric constant. As a result, hot compressed water reacts with biomass components and release oxygen and ash from the biomass structures. The resulted solid product, often called hydrochar, is hydrophobic and energy dense, just as bituminous coal. Moreover, hydrochar can be further densified by palletization. Energy density via pelletization of hydrochar can be reached much higher than energy density of raw coal.

In this project, hydrothermal co-carbonization (HTCC) of coal-biomass blend was studied at various water temperatures (200, 230, and 260 °C) at water saturation pressures. For coal samples, Ohio's Clarion #4a was used, where, Ohio grown miscanthus (*miscanthus x giganteus*), a perennial grass was used as biomass source. The main objective of this study was to produce a homogeneous hydrochar product in terms of density, fuel properties, and elemental composition. Resulted hydrochar produced from blend (50:50 wt %) was compared with control miscanthus and coal hydrochars. Furthermore, hydrochar pellets were produced using bench-scale single press pellet-press. Pellets mass and energy densities were measured and compared with control biomass or coal pellets.

Hydrochar produced from HTCC reveals that, coal's elemental carbon content was not effected by water temperatures in the tested temperature range. However, sulfur and chloride content are reduced significantly. Hydrochar produced from biomass is located at the surface of the coal, which ensures the homogenization in the micro-level. The resulted hydrochar was hydrophobic, contains high energy (30-33 MJ kg⁻¹), lower ash, sulfur, chloride, and nitrogen than raw coal. The blend hydrochar pellets have very high mass and energy densities compared to their raw feedstocks. For instance, the blend hydrochar pellets can reach as high as 38 GJ m⁻³ energy density, when biomass-coal blend was treated at 260 °C.

Therefore, HTCC technology can be applied as an upstream processing to feasible co-combustion of coal-biomass mixture. This technology produces homogeneous feedstock with superior fuel quality and low pollutants.

Raman Spectroscopy for the On-Line Analysis of Oxidation States of Oxygen Carrier Particles in Chemical Looping Combustion

Hergen Eilers, John Kirtley, Victoria Lechner, Washington State University, USA

The need for cleaner energy systems, including CO₂ capture technologies, is driving the current development of new combustion approaches such as chemical looping combustion (CLC). This process is based on using oxygen carrier particles (OCPs) such as iron oxides, copper oxides, calcium sulfates, etc. to provide the oxygen for the combustion process.

In order to optimize the overall process performance, it is critical that the properties of the oxygen carriers are well-defined and maintained for their specific purpose during the different stages of the CLC process. One of the critical properties of the oxygen carrier is its oxidation state (e.g., content of Fe₂O₃ vs. Fe₃O₄) as it affects the fundamental operation of the CLC process. Unfortunately, the ability to make on-line measurements of the oxidation state of oxygen carriers is lacking and new sensors need to be developed. Our goal is to develop a sensor for the on-line analysis of the oxidation state of oxygen carrier particles and to demonstrate its feasibility. Oxygen carrier particles (OCPs) of interest include iron oxides, copper oxides, and calcium sulfate, with particle sizes typically less than 0.5 mm diameter. The expected operating conditions of the sensor include OCP temperatures in the range of 800 °C to 1000 °C, and pressures of about 10 atm. The expected results are to be of a statistical nature, providing relative concentrations of the different oxidation states. These requirements make a strong case

for using non-contact, stand-off, pulsed Raman spectroscopy as a sensor for the high-temperature on-line analysis of oxygen carrier particles.

In order to achieve our goal, we have set up and tested a pulsed Raman spectroscopy system in combination with a pressurized high-temperature sample chamber, and have taking initial Raman spectra of various materials at high temperature. We are now in the process of optimizing the operating parameters such as laser wavelength, laser intensity, collection optic design, focal spot size, data acquisition, etc. We will also develop an analysis procedure for the interpretation of the Raman spectra. Typical Raman spectra consist of a convolution of background signal and multiple individual spectra. In order to extract relevant information such as the concentration ratio of a material in different oxidation states, we need to process (background subtraction, deconvolution, fitting, etc.) the measured data. In addition, statistical modeling and multivariate calibration need to be performed to correctly analyze the Raman spectra.

Co-Firing of Biochar and Lignite under the Oxy-Fuel Combustion Mode

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Controlling the emission of CO₂ to the environment is one of the most practical solutions now available for tackling the problem of global warming and climate change. This involves utilising alternative energy sources like biomass such as woodchip and woodchip char by blending them with coal. These fuels are highly potential yet not exploited properly so far due to the lack of understanding of their combustion behaviour. In this study, co-firing characteristics of lignite with woodchip char was conducted in a lab-scale drop tube furnace by blending in three varying proportions (10%, 20%, 30%) and combustion at 1000 °C. For comparison, blends between sub-bituminous coal and woodchip powder were also studied for the co-firing test. Experiments were conducted in air and oxy-fuel (27% O₂), and unburnt char and ash were collected and analysed to determine the char content after combustion and flue gases were analysed throughout the experiment to determine the gas composition. Combustion behaviour of lignite and its various blends were much different than that of corresponding blends with sub-bituminous coal in both air and oxy firing conditions. Apart from experimental investigation, computational fluid dynamics (CFD) modelling was also conducted which in further explains experimental findings. Homogeneous reactions used Jones and Lindstedt (JLT) global reaction mechanism where the volatile molecule is assumed to contain a mixture of gas species and a CH_x molecule. A UDF was written which defines the heterogeneous reaction of char oxidation, CO₂ gasification and steam gasification using intrinsic reaction model (Smith, 1971). It was assumed that during char reaction, there is a decrease in both particle size and density. Lignite blended with woodchip char at lower ratios showed significant synergy in terms of ignition point and peak average particle temperature, resulting in average particle temperature plot to be almost similar to lignite but with worsening burnout. It was interesting to note that synergy in terms of ignition point and peak temperature were observed only at lower blending ratios with biomass fuel. Using CFD analysis, it was found that contribution of gasification in oxy firing combustion for woodchip blends were much higher than woodchip char blends which was further explained using experimental results. Conclusions from this study were summarised and gives a deep insight into the combustion behaviour of low grade and high grade coal with woodchip and woodchip char with their varying proportions in the blend.

Instrument Model for Narrow Angle Radiometers

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Narrow-angle radiometers based on the International Flame Research Foundation design have been used to measure the incident radiative heat flux in a coal-fired combustion furnace located at the University of Utah. This method of heat flux measurement uses a probe that limits the field of view, allowing radiation measurements of relatively precise locations. The probe contains a Wheatstone bridge with two thermistors, one that is irradiated and one that is not. The measured voltage difference between the two thermistors is used to determine the heat flux based on calibration curves obtained in a blackbody furnace. This calibration produces a curve of measured voltage vs. blackbody temperature. The heat flux is calculated from the blackbody temperature and corrected for the view angle.

Using the concept of an instrument model, we have conducted an extensive analysis of the errors associated with using this radiometer design to measure incident heat flux. The purpose of an instrument model is to identify how the measured signal (in this case mV) is converted to the variable of interest (incident heat flux) and what possible sources of uncertainty might contribute to the calculated heat flux. We have identified many sources of uncertainty in the construction, operation, and calibration of the radiometers, including transient ambient temperature effects on the Wheatstone bridge, view angle variation, lens refractive index variation, blackbody temperature, and target size. We discuss how each source of uncertainty is managed (determined to be negligible, eliminated, or included in the analysis). The major contributor to the total uncertainty is the use of the thermistor in the Wheatstone bridge. There is also unexplained drift in the calibration curves. We present new maximum and minimum calibration curves that account for all identified uncertainties. The overall uncertainty could be greatly reduced

by modifying the construction of the radiometers for future tests. Specific changes for future radiometer design are suggested.

Combustion Characteristics of Coal in A Pilot-Scale Oxy-Circulating Fluidized Bed Combustor System

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The oxy-circulating fluidized bed combustion (oxy-CFBC) has been increasingly focused on a promising power generation technology for carbon capture utilization and storage (CCUS). As well-known, CFBC has some outstanding merits for high efficiency-low emission (HELE) process; 1) high combustion efficiency due to uniform heat flux in combustor and the longer residence time by circulation of solid fuels, 2) fuel flexibility and diversification along with no severe pulverization of solid fuels, 3) low thermal NO_x content due to low combustor temperature at about 900 °C and 4) high desulfurization efficiency in the combustor. From COP 21 Paris agreement in 2015, South Korea should be achieved to reduce CO₂ emission by 37 % (about 850 million tons) in 2030. By this national demand, the project on development of OXY-CFBC-USC (ultra-supercritical) has been recently emerged. The challenges of this project are mainly to those, optimize oxy-CFBC process for production of high CO₂ purity and small amount of flue gas, develop applicable materials of ultra-supercritical (USC) for efficiency improvement of power plant and recover water, usable from emitting flue gas. Therefore, in this work, it is to investigate characteristics of oxy-fuel combustion through newly constructed a pilot-scale oxy-CFBC test rig that consisting of LNG pre-heating chamber, FD fans, CFB riser (I.D.: 0.15 m, height: 10 m), two cyclones, loop-seal, two heat exchangers, bag-filter unit, flue gas condenser, flue gas recirculation units (FGR fan and mixing tank for mixture of oxygen and flue gas as combusting agent), ID fan and stack.

The detail results on combustion characteristics, removal efficiency of pollutants, NO and SO₂ in flue gas, unburned carbon content in ashes sampled at the 2nd cyclone, bag-filter unit and bottom of riser box and the purity of CO₂ with different operating conditions will be presented in the conference.

SESSION 21 Coal Ash Management -4

Emerging Issues in Coal Ash Management: A Panel Discussion

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Coal ash ponds across the coal-fired utility industry are currently being planned for closure. This panel discussion will include panelists from industry, academia, and regulatory agencies involved directly in the closure of ash ponds across the midwest US. Options such as in-situ closure and removal of ponded ash will be discussed. In particular, the panel discussion will focus on post-closure use of these sites for a variety of end-use options such as grassland / tree reclamation, sites for solar panel installations, landfill overfills, etc.

This state-of-the-art panel discussion will be held as a part of the Coal Combustion Residues Symposium being held at the Pittsburgh Coal Conference and will provide utility owners, design engineers, and regulatory agencies with specific information about the technical feasibility and probable cost of using these methods for remediation and reclamation of coal ash ponds.

SESSION 22 Coal Science - 4

Pyrolysis Characteristics of a Sub-Bituminous Coal with Char Solid Heat Carrier at Different Initial Temperature

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A sub-bituminous coal (Shengdong, SD) pyrolysis with char solid heat carrier (SHC) was carried out in a free-fall reactor to investigate the mechanism. Char SHC was pre-loaded in the reactor and heated to the programmed temperature for heat storage, then coal material was added into the reactor through the feeder with a certain ratio. The liquid products were recovered by the ice-salt condenser maintained at around -15 °C, and pyrolysis gas was collected in gas sampling bag. The hot char provided the heat for coal pyrolysis, meantime, it had cracking effects on the released volatiles. Quartz sand (QS) was used in the control group for the thermal cracking effect of solid heat carrier. Through GC-MS analysis of the light tar components and characterization of physicochemical properties of the char SHC before and after the pyrolysis reaction, the interaction of volatiles and char SHC with different initial temperatures was studied. It was supposed that reverse water-gas shift reaction (RWGS) took place during the

pyrolysis process with char SHC. Phenols and alkyl substituted phenols in coal tar tended to crack and convert into aromatics with the increasing of char SHC initial temperature. The cracking of volatiles occurred on char SHC, which led to the decrease of its specific surface area and pore volume and certain high C/H species deposited. Isothermal CO₂ gasification of the char SHC were conducted with thermogravimetric (TG) analyzer, the results exhibited that carbon deposits from the cracking of volatiles on char SHC could promote the gasification reaction, which outweighed the adverse effect caused by the decrease in specific surface area.

SESSION 23 Gasification Technologies: Gas Cleanup

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

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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. Eleven 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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Coal Gasification on a Pilot Scale System for the Application of Liquid Fuel Production

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Within the frame of clean coal technologies, gasification technologies are extremely important in order to produce energy efficient and environmentally friendly clean synthetic gas for IGCC, coal to liquid, coal to chemical and carbon capture applications. The properties and composition of the synthetic gas depend on many factors such as the reactor type, the properties and flow rates of feedstock materials and gasifying agents, pressure and temperature in the reactor. In the recent decades, several research based on the modeling, simulation and experimental studies has been performed to investigate the effect of gasifying agents such as air, oxygen, steam and their combinations on the gasification process. Most of the experimental research carried out on the bench-scale and/or laboratory scale systems to understand and/or to determine the kinetic parameters of gasifying process. The validation of modeling and simulation studies has also been mostly performed considering these experimental results. However, pilot scale systems provide us valuable insights into the gasification process and the only necessary scalable data for designing and operation of larger scale systems in practical usage. Within this frame, the aim of this study is to present the outcome of test results of a pilot scale pressurized bubbling fluidized bed (PFBF) gasifier with a 750 kWth of fuel feeding capacity and operable from atmospheric pressure up to 10 barg. The system was designed and installed as a part of the project entitled "Liquid Fuel Production from Biomass and Coal Blends-TRIEN (contract no:108G043)" funded by Turkish Scientific and Technological Research Council. The system consists of the PFBF reactor, cyclone separator, syngas cooler, quencher, syngas burner, fuel feeding system, ash removal system and gasification agents (air, steam, O₂, CO₂) preheating systems. The PFBF reactor is 3500 mm high, and 300 mm and 450 mm inner diameters for dense bed region and freeboard, respectively. The mixture of air, steam, oxygen and CO₂ was used as gasification agents with different ratios. The operating conditions used to control the gasification reactions are composed of the flow rates of feedstock materials, the flow rates of gasifying agents and its composition, temperature and pressure. The system was monitored and controlled with a distributed control system. The gas analyzer was used for measuring the syngas composition of CO, H₂, CH₄, CO₂, N₂, H₂S, COS, NH₃ and C₆₊ molecules. The effects of equivalence ratios (ER), steam/carbon ratios and CO₂/carbon ratios on synthetic gas composition, carbon conversion ratios and cold gas efficiencies were investigated and evaluated. It was obtained that the lower heating value (LHV) of product gas and the cold gas efficiency of the reactor could reach to 10 MJ/Nm³ and %75 depending on the operational conditions respectively. The results show that the system efficiency highly depends on operational conditions. The results were also compared with the results of simulation performed. This comparison provides valuable insights into the differences between the results of experimental and simulation on the gasification process with different operational parameters.

Catalytic Reduction of Ammonia in Syngas

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Clean coal technologies and polygeneration applications are important alternatives in terms of producing clean fuels acceptable for energy and environment and providing fuel diversity. Within the scope of the project "Liquid Fuel Production from Biomass and Coal Blends (TRIEN)" funded by Turkish Scientific and Technological Research Council, catalytic reduction of ammonia in syngas was investigated since ammonia leads to the poisoning of the Fischer-Tropsch (FT) catalysts shortly. Ammonia concentration in syngas produced from gasification of lignite is about 2000-3000 ppm but its threshold level is below 1 ppm regarding its effect on the loss of FT catalytic activity. Catalytic Reduction of Ammonia and Selective Catalytic Oxidation (SCO) are two important catalytic routes. The selective catalytic oxidation reactions take place in partial oxygen environment and between 300-550°C operation temperatures. In this catalytic oxidation process, hydrogen losses occur due to its concurrent oxidation with ammonia and the syngas composition is unfavorably affected. Therefore, the catalytic reduction of NH₃ was believed to be more attractive since it enables to increase the calorific value of the syngas via H₂ production. An increase in H₂/CO ratio of the syngas is an advantage for the processes like Fischer-Tropsch (FT) and methanol production. In the scope of this research, the most convenient gas analysis technique of ammonia measurement in syngas was investigated firstly. Since ammonia is a very reactive gas and can easily interact with its flowing surfaces, special care must be taken. Four different measurement techniques, namely thermal conductivity detector, nitrogen

chemiluminescence detector, ultraviolet-visible detector and gas measurement tubes, were compared. It was shown that UV-VIS process spectrometry was the best available technique for online NH₃ measurements in syngas among the investigated methods. Then, the catalytic activities of some natural minerals with iron and calcium content were screened for catalytic reduction of NH₃ at 700-800°C. These minerals (limonite, dolomite and olivine) were provided from different regions of Turkey. Silicon carbide and silica were the other two minerals tested as well. Limonite was the mineral showing the highest catalytic activity and this was attributed to the easy reducibility of its goethite phase (α -FeOOH). For the reference use, three different types of commercial catalysts were screened. These were nickel oxide catalyst, unsupported iron oxide pellet and alumina supported noble metal catalyst. Zeolite supported iron and nickel catalysts with different silica/alumina ratios were synthesized as well. Zeolite supported iron catalysts were found to be more active in catalytic reduction compared to zeolite supported nickel ones. For zeolite supported iron catalysts, it was shown that FeO_x cluster size was dependent on both the textural properties and Si/Al of the zeolites. The steric restrictions offered by the cages of the zeolites might also limit the sizes of iron clusters giving the best coordination environment for active iron species and improved iron cluster interactions. Finally, the catalytic activities over zeolite supported iron catalysts were compared for both two catalytic routes, namely SCO and catalytic reduction. It was seen that catalytic reduction over iron based zeolite catalysts was less sensitive to the presence of H₂ in the reaction environment in comparison to SCO reaction. Although relatively higher NH₃ conversions can be attained via SCO under inert atmosphere, the presence of H₂ inhibits the conversion considerably.

SESSION 24

Clean Coal and Gas to Fuels - 1

Spontaneously Activatable Iron-Based Catalysts in Fischer-Tropsch Synthesis: Application to High Temperature Processes

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FTS (Fischer-Tropsch synthesis) has received much attention as an attractive way to produce clean liquid fuels or chemicals from syngas (H₂+CO). Iron-based catalysts are particularly promising for FTS using hydrogen-deficient syngas (H₂/CO ≤ 1) potentially obtained via coal gasification, due to their additional activity to water-gas shift as well as their high activity to FTS and low cost. Conventionally, iron-based FTS catalysts need to be subjected to a proper activation pre-treatment using CO or low-pressure syngas (≤ 0.3 MPa) as they are barely activated in general FTS conditions using high-pressure syngas (≥ 1.0 MPa). In the previous International Pittsburgh Coal Conference (August, 2016, Cape Town, South Africa), we reported spontaneously activatable iron-based catalysts in the LT-FTS (low-temperature FTS) condition from lab-scale study to pilot-scale demonstration. In this study, we report application of the spontaneously activatable iron-based catalysts to HT-FTS (high-temperature FTS). In a lab-scale test using a plug flow reactor, we found that the spontaneous activation can hold true for HT-FTS above 300 °C. Furthermore, we successfully demonstrated the HT-FTS using the spontaneously activatable iron-based catalysts in a pilot-scale slurry bubble column reactor (5-15 bbl/d).

Highly Selective FT Synthesis for Production of JP-8 Jet Fuel from Coal and Coal/Biomass Mixtures

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An indirect liquefaction process employing advanced process intensification approaches is being developed to reduce costs and accelerate commercialization of a coal to liquid (CTL) process for converting coal and coal-biomass mixtures to JP-8 jet fuel. In this Air Force and DOE/NETL sponsored cooperative agreement, Southern Research is leading a team consisting of IntraMicron, Inc., Southwest Research Institute, and Nexant, Inc., along with Chevron as selective Fischer-Tropsch (FT) catalyst supplier and the National Carbon Capture Center (NCCC) as the host site. The process reduces the number of parasitic syngas cleaning steps and eliminates costly upgrading of wax produced in conventional indirect liquefaction processes, resulting in improved economics and lower lifecycle greenhouse gas (GHG) emissions for CTL-based jet fuel production. These improvements directly reduce capital costs of indirect CTL processes, resulting in significantly improved economics and cost competitiveness of CTL when compared to petroleum refining. Specific objectives for FT experiments are to demonstrate a selective and active second generation cobalt-zeolite hybrid Fischer-Tropsch (FT) catalyst from Chevron that predominantly produces liquid range C₅-C₂₀ hydrocarbons with high productivity (5X conventional FT catalysts) and jet fuel selectivity while eliminating the production and associated handling of solid C₂₁₊ wax. In fall of 2015, Southern operated a bench-scale FT reactor with a 2" diameter heat exchange reactor tube using IntraMicron technology in a nominal 5 gallons per day skid-mounted fixed-bed installed at NCCC. In those experiments, both productivity and selectivity goals

were achieved during a 300 hour experiment. Another experiment has just been completed in spring 2017 with the reactor diameter increased to 4". This work will compare the results from the two long-term tests of the hybrid FT jet-selective catalyst using the skid-mounted fixed-bed FT reactor system at NCCC.

Simulation of a Fischer-Tropsch Fluids Refinery using Aspen Plus

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The production of petroleum products from a low temperature Fischer-Tropsch fluid was simulated in Aspen Plus using a pure component approach and conventional petroleum refining processes. Three cases were examined. The first two maximized diesel and jet fuel production, respectively. The third emphasized lubricant base oil production. The feedstock for each of these simulations was a waxy Fischer-Tropsch fluid produced by a cobalt catalyst. In the first case, the feedstock was hydrocracked to get maximum diesel production and the naphtha fraction was isomerized to meet gasoline specifications. The hydrocracker yields were matched to experimental yield data. Diesel products had high cetane number and the predicted pour point was -56°C. Isomerization of naphtha fraction increased the octane number to 87.8. For maximum jet fuel production, the estimated pour point exceeded the freezing point specification by a wide margin, which suggests that lower severity hydrocracking conditions could be used, thereby improving the selectivity to jet fuel. The naphtha product in this case, had high volatile content. For the third case, an isomerization reactor was modeled to convert FT waxes to lubricating base oils. This reactor had a much higher isomerization/hydrocracking selectivity than the hydrocracker used for the first two cases. Three base oils are produced. Two have nominal viscosities of 2 and 4 cSt at 100 °C. The viscosity of the third base oil was not estimated because this product consists primarily of C33+ hydrocarbons, which are not in the Aspen properties data base.

SESSION 25 Carbon Management: Modeling and Optimization

Integration of Heat Recovery Unit to Reduce CO₂ Capture Costs

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Electricity generation from fossil fuels power plants is accounted for one third of the U.S. greenhouse gas emissions. Carbon capture and sequestration is regarded as an essential part of the technology for carbon mitigation, as it can significantly reduce CO₂ emissions while ensuring electricity generation from fossil fuel power plants. With current technology, post-combustion removal of CO₂ by use of absorption with chemical solvents (typically monoethanolamine MEA) is considered to be the most cost-effective and viable option. However, the cost and energy requirements of amine solvents are the dominant components of CO₂ capture costs, due to high heats of regeneration associated with aqueous amine solvents. The regeneration energy is supplied from a low-pressure steam, reducing turbine power production and increasing electricity costs. For these reasons, there is a strong interest in new developments for reducing CO₂ capture costs. One method is to integrate available heat with sufficient temperature to reduce regeneration steam load from the LP turbine. A location within the power plant where such heat can be found is in the flue gas upstream of the desulfurization unit. In this work, a new heat recovery technology is proposed which can directly recover flue gas energy, which is then utilized to lower CO₂ capture costs and increase overall power plant efficiency. To evaluate the feasibility of the new heat recovery methodology, non-aqueous heat transfer fluid(s) (HTFs) were identified for use in the direct heat recovery technology based upon fluid properties. The interactions between HTFs and flue gas were evaluated independently using thermogravimetric (TGA) and spectroscopy (FTIR) methods. Preliminary results suggested that the HTF was thermally stable and does not interact with the flue gas. Further studies are underway to identify interactions between HTF/rich CO₂ solvent using lab-scale testing and develop heat recovery models and power plant simulations to identify the most attractive designs and heat integration schemes with commercial CO₂ capture technologies.

Cost-Effective Post-Combustion Carbon Capture from Coal-Fired Power Plants

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Post-combustion capture of carbon dioxide from the flue gas of fossil fuel-fired electric power generation power plants via amine-based absorption-desorption is a proven technology. One attractive feature of this technology is its amenability to being a "bolt-on" addition to existing power plants. However, its commercial deployment on a large scale has not been possible due to its significant detrimental impact on total installed cost and net power delivered to the grid. This impediment has been especially severe for coal-fired power plants with large carbon dioxide content in their exhaust.

This paper describes a novel approach to amine-based post-combustion capture of carbon dioxide from the flue gas of a coal-fired power plant, which is aimed to maximizing net power output when it is most needed and, thus, commands the highest market price. The capture system in question retains all features of the proven amine-based stripping technology (i.e., equipment and process) with (i) a modification of the operating philosophy and (ii) addition of balance-of-plant equipment to facilitate the implementation thereof. Cost and performance benefits of the proposed approach are demonstrated using a case study drawing upon recent Bechtel experience in carbon capture system front-end engineering and design.

Technical and Economic Feasibility Analysis of Integrating Activated Carbon Plant with Heating Plant

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The University of North Dakota Institute for Energy Studies has teamed with technology development partner Envergen LLC, to develop the technical and economic feasibility of integrating activated carbon production with steam generation for application to heating plants operating in North Dakota University System (NDUS) campuses. The production of activated carbon integrated with steam generation plants is a disruptive technology, with dramatically lower cost carbon production than compared to conventional carbon production plants. The proposed coproduction offers numerous advantages over traditional steam generation methods currently deployed within NDUS. The key advantage is the opportunity to generate revenue from selling the activated carbon products, thereby operating the heating plant as a profit center for the university. This is in contrast to the existing arrangement where the plant is strictly a cost incurrance. Additionally, the proposed plant allows for opportunities in education and research to educate the next generation of energy experts and provide a platform for testing of novel energy-related technologies. Further, due to the unique steam generation method, the proposed concept has dramatically lower emissions of carbon dioxide and other harmful pollutants when compared to conventional methods. In fact, the coproduction concept results in the ability to meet the carbon dioxide emissions requirements of the Environmental Protection Agency's recently released Clean Power Plan, which requires extremely challenging reductions of 45% for the state of North Dakota, compared to traditional coal-fired power generation.

A technical assessment of the concept involved developing mass and energy balances, process flow sheets and, equipment sizing and selection. Aspen Plus process modeling software was used to develop the process flow sheets. Two modes of operation of the carbon plant were evaluated during this project, aimed at identifying the best method to overcome the challenge of seasonal steam demand for campus heating. A first mode consisted of seasonal operation of the carbon plant, in which the entire plant is operated during the high steam demand winter months, but only a portion of the plant is operated during the summer months. However, due to multiple reasons including lack of sufficient on-site carbon storage and loss of revenue, this option was eliminated. It was determined that year-round, steady operation of the carbon plant was most appropriate for this application. However, with this strategy, in the warmer months, where the VCSU steam plant is not in operation, the carbon plant produces combustible gases that must be utilized or safely exhausted. A waste heat recovery system such as Organic Rankine cycle (ORC) was evaluated to generate electricity by recovering heat from the hot combustion flue gases.

An economic assessment was performed for the down-selected option that included capital and operating costs, revenues and annual cash flows. Given the early stages of design, this assessment is considered to have an accuracy of about +/- 40% for the capital costs. The capital cost for integration of a carbon plant to the VCSU steam plant is about \$15.3 million. For a combined facility, sized for VCSU, the total cost of the carbon and steam plant would be about \$ 32 million. For the carbon plant, the annual operating cost, including fuel, O&M, labor and utilities is estimated at about \$5 million. Total revenues from the sale of activated carbon and electricity is about \$9.4 million. The annual cash flow for the carbon plant is \$2.5 million in the years 1-10, and \$4.3 million after initial debt is retired. Based on a discounted cash flow sheet with a 20-year plant life and hurdle rate of 4%, the net present value (NPV) of adding a carbon plant to the existing VCSU facility is about \$43.4 million, with a capital payback time of about 3.5 years. We have defined capital payback time as total capital investment divided by non-discounted annual profit. Independent sensitivity analyses on the capital cost and the activated carbon sale price were also evaluated to determine economic risks. With a 40% increase in capital cost, the NPV decreases to about \$37.2 million, with a capital payback of 4.9 years. Decreasing activated carbon sale price from the projected value of \$0.73/lb to \$0.55/lb results in an NPV of \$18.1 million and a capital payback of 6.2 years. With the baseline capital cost and carbon sale price, a more conservative hurdle rate of 15% results in an NPV of \$3.4 million.

The project team is working closely with administrators from VCSU as well as NDUS Facilities Management. An advisory group has been formed by VCSU that includes key members of the technical team, representatives from VCSU, NDUS, the State Board of Higher Education, as well as private industry representatives who have experience in setting up public/private partnerships such as the one required to deliver this technology.

Combined CO₂ Capture /Water-Gas Shift with Integrated Heat Management for IGCC Applications

Andrew Lucero, Shen Zhao, Santosh K. Gangwal, Southern Research, USA

As one of the 16 transformational carbon capture technologies projects selected by Department of Energy (DOE), Southern Research is developing a combined CO₂ capture water-gas shift (WGS) process for integrated gasification combined cycle (IGCC) applications. Here we present a laboratory-scale combined sorbent/catalyst reactor system with advanced integrated heat management to capture 90% of CO₂ from simulated Transport Reactor Integrated Gasifier (TRIG) syngas at warm gas conditions (250 – 400 °C). A highly efficient regenerable magnesium based sorbent was developed to remove CO₂. It offers high and stable CO₂ capacity with minimum requirement for temperature and pressure swings. Under optimized conditions, the sorbents achieved up to 6 mmol/g of CO₂ working capacity and remained stable over 250 cycles of adsorption and regeneration. The selected WGS catalyst achieved around 95% CO conversion under both continuous feed and combined cycle tests and remained stable during the test duration that lasted over 200 hrs. The approach has potential to reduce costs and increase efficiency for electricity generation from IGCC. Upon successful completion of bench-scale integrated test program, the process will be ready to test at pilot scale. This presentation will examine bench-scale results on combined CO₂ capture/WGS experiments.

Computational Fluid Dynamics Modeling and Optimization of Absorber Design for Pre-combustion CO₂ Capture

Omar M. Basha, ORISE/U.S. DOE/NETL; Isaac Gamwo, Nicholas Siefert, NETL, USA, Badie Morsi, University of Pittsburgh, USA

The optimum design of packed column absorbers for pre-combustion CO₂ capture using physical solvents is crucial to enhance the performance of both the unit and the overall process. However, widely used empirical design strategies inherit severe limitations in terms of scale-up, flexibility, and optimization of the packed column; primarily due to the multiphase hydrodynamics coupled with the complex internal structure of the packing, which increases the uncertainty in using such empirical strategies, resulting in startup delays and cost overruns. Computational Fluid Dynamics (CFD) offers an advanced prospect to move beyond empirical design strategies, and provides an exceptional opportunity to gain detailed time- and space- dependent information about the local hydrodynamics and the overall behavior and performance of the packed column.

This presentation will cover ongoing activities at the National Energy Technology Lab to develop highly resolved, and experimentally validated multi-scale CFD models for CO₂ capture using physical solvents in absorbers with both structured and random packings. The multiscale CFD model structure consists of: (1) Two-dimensional Volume of Fluid (VOF) simulations of the gas-liquid flow rate at the scale of the packing surface or packing corrugation, (2) Three dimensional multi-eulerian simulations of the smallest periodic element representative of commercial structured packing geometries, in addition to various random packing configurations. (3) Large scale simulation of the overall column behavior by considering the packed bed as a porous media characterized by hydrodynamic and pressure drop coefficients obtained at the previous scales. The overall model would then be used to study the gas-liquid interactions and behavior when using different combinations of packings and gas or liquid distributors, to achieve the optimum column design.

SESSION 26 Power Plants: Advanced Technologies

Discussion of Using Aspen Plus Vs Thermoflex to Model NGCC and IGCC Power Plants

Henry A. Long, Ting Wang, University of New Orleans, USA

For a research project for developing new clean coal processes for power plants, Thermoflex®, from Thermoflow, Inc., was used. To validate the results from Thermoflex, a Natural Gas Combined Cycle (NGCC) and an Integrated Gasification Combined Cycle (IGCC) were modeled first in order to be compared with similar plants modeled in Aspen Plus by the National Energy Technologies Laboratory (NETL) of the United States Department of Energy (U.S. DoE). Thermoflex is a program within the Thermoflow software suite, which is mainly used for modeling general thermal-flow components/processes, gas turbines, and power plants, while Aspen Plus is mainly used for designing thermodynamic and chemical components/processes/reactors and modeling chemical plants.

Throughout the study, the two different software programs are analyzed through their treatments of various plant parameters, including the HRSG & deaerator design; the effects of low calorific value gas on the total gas turbine mass flow rate, turbine inlet temperature, and turbine polytropic efficiency; and mass balance capabilities (especially with regards to the steam cycle). Multiple modeling issues are also discussed, such as

local temperature matching, the use of syngas heating during gas cleanup, determining the deaerator operating state, and verifying the deviation of the GT's operating performance from the spec data.

The convenience of using built-in modules in Thermoflex is also discussed in comparison with Aspen Plus: for example, an air separation unit, an acid gas removal unit, a carbonyl sulfide hydrolysis reactor, etc. The conclusions are: (a) the Thermoflex results match the Aspen Plus results within a 1% difference in power outputs and efficiency, and (b) Thermoflex is more convenient for modeling the various subsystems, particularly with regard to its comprehensive capabilities involving the gas turbine system's performance, but is less versatile in modeling chemical processes, particularly those involving chemical reactions; whereas Aspen Plus is more robust in terms of modeling chemical reactions but requires extensive prior knowledge of the detailed design of all relevant subsystems, and a significant amount of effort must be spent to model them accurately. The capability of Aspen Plus for simulating the gas turbine system's performance is limited to using individually separate components: i.e., a compressor, a combustor (modeled as a generic reactor), and a turbine.

Progress of Coal Direct Chemical Looping Development at The Ohio State University (OSU)

Yitao Zhang, Dikai Xu, Tien-Lin Hsieh, Cheng L. Chung, Yaswanth Pottimurthy, Cody Park, Mingyuan Xu, Andrew Tong, Liang-Shih Fan, The Ohio State University, USA. Coal is one of the main source for electricity production. Coal-fired power plants account for a large portion of global CO₂ emission. Several CO₂ capture and sequestration (CCS) techniques can be integrated to conventional integrated gasification combined cycle (IGCC) and pulverized-coal (PC) power plants to reduce CO₂ emission. However, the integration will also decrease the energy efficiency and increase the cost of power plant. The Ohio State University (OSU) has developed coal direct chemical looping (CDCL) technology, which combusts coal with circulated iron-based oxygen carrier particle, mitigating the influence on energy efficiency and cost of power plant due to CCS. CDCL based power plant avoids the usage of air separation unit (ASU) and/or complex CO₂ purification unit, the expensive and energy-intensive parts in conventional coal-fired power plant with CCS. The model of CDCL system was built and experimental results from sub-pilot scale unit were used to validate and improve the model. A commercial scale (550 MW_e) CDCL based power plant with CCS has been configured and designed to investigate the limit of electricity production. Aspen Plus is used to build the comprehensive model of power plant including CDCL unit, CCS unit, steam cycle for electricity production and other auxiliary facilities. Potential heat recovery source and energy-intensive equipment were identified for process energy assessment. Heat exchanger network with pneumatic equipment of the power plant was then carefully designed and optimized. The optimized heat exchanger network was used to perform exergy analysis for the power plant. The presentation will initially focus on the construction of the model of CDCL system and then the optimization on energy efficiency of CDCL based power plant.

High Performance Computing Design Exploration for a 500 MW Oxy-coal Fired Boiler Design

Michal Hradisky, Derek Har-ris, N. Stan Harding, Philip J. Smith, University of Utah, USA

The mission of the Carbon-Capture Multidisciplinary Simulation Center (CCMSC) at the University of Utah, a five-year \$21M Department of Energy funded program, is to demonstrate the use of exascale uncertainty quantification (UQ) predictive simulation science to accelerate deployment of low-cost, low-emission electric power generation to meet the growing energy needs in the United States and throughout the world. The two main objectives, advancing simulation science to exascale with UQ-predictivity in real engineering systems and use of high-performance computing (HPC) and predictive science to achieve a societal impact, are linked together through an overarching problem: simulation of a design 500 MW oxy-coal advanced ultra-supercritical (AUSC) horizontal boiler. The simulation of oxy-coal AUSC horizontal boiler is motivated by the emergence of oxy-combustion systems as a low-cost technology solution for both carbon capture utilization and storage and simultaneous reduction of NO_x and SO_x emissions. Using a high-performance computing platforms, we explore a range of scenarios and designs to predict and quantify heat flux distribution inside the design boiler, aiding in material science research of steam tubes that are able to withstand the high temperatures and pressures of oxy-fired AUSC systems. We employ the use of both Large-Eddy Simulation (LES) as well as Reynolds-Averaged Navier-Stokes (RANS) models for our study. Using 128,000 cores on Lawrence Livermore National Laboratory's (LLNL) Vulcan super-computer, we perform a series of scoping runs using time-resolved high-fidelity LES models for the initial design scenarios. However, to explore a wide range of design scenarios, such as overall boiler dimensions, relative lengths of radiant and convective sections, burner placement, hopper and nose dimensions, as well as geometric features for reduction of temperatures on the walls, we use the lower-order steady RANS models to perform hundreds of simulations to map out a large design space and quantify the effects of design parameters on boiler design and performance. By performing a multi-objective trade-off study and cross-correlation analysis, we are able to narrow down the number of design parameters with the highest

impact on the local temperature and local heat flux distributions inside the design 500 MW oxy-coal AUSC boiler.

Integrated Process to Lower Emissions and Increase Efficiency

Donald W. Collins, Western Research Institute; Alan Bland, Ash Management Engineering, Inc., USA

Western Research Institute (WRI) with industry partner, Ramaco Carbon, LLC, developed a multi-pollutant reduction technology that also increase coal power efficiency while reducing local water consumption. The WRI Thermal Enhanced Coal (WRITECoal™) is a thermal process for extracting multipollutant emission components (arsenic, mercury and selenium) and water from low-rank coals, such as subbituminous and lignite coals, and creates a significantly more reactive coal with faster reaction kinetics compared to raw low-rank coals.

The WRITECoal process is a two-step thermal-based coal upgrading and emissions (mercury) control process that removes water in the first stage and captures it for plant use, followed by the volatilization and capture of volatile metals species such as mercury prior to combustion or gasification at the plant site using in part waste heat from the plant. In this process, raw low-rank coal is heated to a temperature not exceeding 300°F wherein the free water and some of the more tightly bound water is evaporated and removed from the zone by the heated inert sweep gas. No evolution of mercury and other volatile metals occurs in this zone allowing for water recovery without treatment for mercury or phenol removal. The coal is then heated to a temperature of 500-600° F, wherein 75 to 80% of the mercury in Powder River Basin (PRB) subbituminous coal, for example, is volatilized and removed by an inert sweep gas. The sweep gas stream, containing the evolved volatile mercury, passes into the mercury removal equipment and the mercury is captured via a high loading capacity non-transport sorbent bed that efficiently captures the evolved mercury contained in the relatively low volume sweep gas. The smaller volume of gas and higher concentration allows the sorbents to be more efficient than activated carbon use in post-combustion.

When coupled with native capture with the fly ash and an oxidizer, the WRITECoal integrated retrofit process has been shown capable of 87-92% mercury removal without the need for post-combustion activated carbon injection (ACI)-based Hg control. With physical separation technologies added to the WRITECoal integrated retrofit process, such as air jig, mercury removal is expected to consistently exceed 90% mercury removal.

Starting with a subbituminous coal, the WRITECoal process produces a low-moisture (<1.5%), low-sulfur (<0.6%), high heating value (11,800 Btu/lb), low-mercury (<0.03 ppm) coal that achieves a high volatile matter content and a high O₂ content compared to bituminous coal, important for integration of the process with oxy-combustion and gasification / IGCC. Water removed from the coal is usable after minor filtration for plant water needs. By increasing boiler efficiency by 3 to 5%, overall plant output is increased by 30-34 MW_e (570MW_e net plant). This increase in power generation can be used to offset parasitic power consumption associated with carbon capture.

WRI developed the WRITECoal technology with the support of the U.S. Department of Energy, Office of Fossil Energy and numerous other state and governmental agencies (State of Wyoming and State of North Dakota) and a wide range of utilities and industry organizations (Electric Power Research Institute, Basin Electric Power Cooperative, Detroit Edison, Montana-Dakota Utilities, Alliant Energy, Southern Company and SaskPower) has developed a novel patented and patent-pending coal treatment/upgrading and emissions control technology.

Dynamic Corrosion Testing of Alloys for Supercritical CO₂ Cycles

Joshua Stani-slowski, John Kay, Jason Laumb, Michael Swanson, University of North Dakota; Xijia Lu, Brock Forrest, Mike McGroddy, 8 Rivers Capital, USA

The Allam Cycle is a high-pressure, highly recuperative, oxygen-fired, supercritical CO₂ cycle that makes carbon capture part of the core power generation process. This cycle utilizes supercritical CO₂ as a high-pressure working fluid through a very compact high-pressure turbine. Cycle efficiencies are capable of reaching up to 47% on a higher-heating-value basis for a lignite feedstock while producing a near-sequestration-ready CO₂ stream requiring some O₂ reduction and dehydration.

A team consisting of the Energy & Environmental Research Center (EERC), 8 Rivers Capital, LLC (8 Rivers), and the North Dakota Industrial Commission (NDIC) Lignite Energy Council (LEC) is working to develop lignite-based Allam Cycle technology in support of an industry team comprising ALLETE, Inc., and Basin Electric Power Cooperative (BEP). This work is building on the development of the natural gas-fueled Allam Cycle while addressing challenges to coal-fired applications. The team is addressing potential technology barriers requiring further research and development for lignite-based applications. Potential barriers include corrosion, impurity management, gasifier selection, and syngas combustor design.

This paper addresses bench-scale testing of potential metal alloys and their corrosion potential in a supercritical CO₂ cycle. To enable this assessment a dynamic corrosion system capable of simultaneous testing of six alloy types was developed. Alloy coupons can be exposed to a flowing gas mixture while experiencing temperatures up to 750°C and pressures up to 300 bar. A series of tests are being conducted on 740H, 625, 617, 347H, 282, and 230 alloys for their corrosion resistance at these temperatures and

pressures for an exposure time of 1500 hours. Preliminary results of the corrosion tests will be given that will include mass loss determinations and chemistry of the reacted surface layer via scanning electron microscopy (SEM). Relative costs and material availability will also be discussed.

Additionally, the system allows for testing of alloy tubes exposed to the flowing gas at pressures up to 300 bar and temperatures ranging from 27° to 390°C along the sample tube. Two alloys, Inconel C-276 and 316 stainless steel, were used for this testing. Results of their behavior and resistance to selective acid condensation will be discussed.

SESSION 27 Coal Ash Management - 5

Evaluation of Compressibility Characteristics of Fly Ash under Constant Rate of Strain

Jaime A. Mercado, Luis G. Arboleda-Monsalve, University of Central Florida; Tarunjit S. Butalia, The Ohio State University, Pedro J. Amaya, American Electric Power, USA

Coal combustion processes produce large volumes of fly ash. This material has been used in civil engineering applications including concrete production, base or subbase for road constructions, and bridge embankments. Compressibility behavior of fly ash is studied in this paper placing the material using moist and dry pluviation methods to achieve different stress states in terms of relative density before subjecting the material to compressive oedometric Ko-loading. The fly ash used in this research was produced at a US Midwest power plant. The material is initially characterized with hydrometer and specific gravity tests. Maximum and minimum realizable void ratios are determined. The compressibility characteristics of the fly ash material are studied at four strain rates: 1, 10, 40, and 100% and three different initial void ratios. Changes in pore water pressures of the fly ash are continuously measured when the material is subjected to different strains and loading rates representing different on-site depositional or construction loading processes. The Ko compressibility and consolidation behavior of this fly ash is rather insensitive to the tested strain rates and very small values of pore water pressures were generated regardless of the testing rates. The measured compressibility behavior of the material was very similar under constant rate of strain and incremental loading tests. Compressibility engineering parameters and indices are presented to understand the behavior of this fly ash compared with other soils.

Control of Leaching Characteristics of Heavy Metals for Utilization of Landfilled Coal Ash to Geomaterial

Hirokazu Murata, Motoyuki Asada, Masato Kawaguchi, Hiroyuki Tochiyama, Shimizu Corporation, JAPAN

The ratio of electrical power supplied by coal-fired thermal power plants has increased since the Great East Japan Earthquake on 2011. As a result, the production of coal ash (the combustion residue of coal) has increased and landfill disposal sites are having to accept greater quantities of ash. This points to a need for discussion about the effective use of buried coal ash (aged ash) from such sites, which has so far not been utilized.

Leachate from aged ash is found to have lower concentrations of heavy metals compared with that from fly ash (coal ash before burial). This suggests that aged ash offers reduced risk and greater stability. Another advantage of aged ash is that its characteristics can be confirmed before use simply by collecting samples from the landfill site. Consequently, there are expectations that aged ash may find application as an effective geo-material for urban infrastructure maintenance.

This report clarifies the variability of heavy metal elution from coal ash materials destined for such applications as urban infrastructure maintenance. 20 samples of fly ash collected from electrical power plants of all over Japan are subjected to simulated aging through humidification and tests are carried out that demonstrate reduced heavy metal leaching with aging. It is found from tests that leachate from aged ash is correlation with main ingredients ratio or pH of the coal ash before burial.

Beneficial Re-Use of CCRs for Coal Mine Reclamation

Kathleen Whysner, Dale W. Evans, Remedial Construction Services L.P., USA

The CCR Rule specifically exempts CCRs from regulation if placed in a coal mine. This distinction does not mean that coal mines can in effect become unregulated dump sites, but instead, through pragmatic analysis and thoughtful processes, coal mines may represent an optimally sustainable and environmentally sound life-cycle solution for the management of CCRs through legitimate beneficial re-use. As the EPA previously defined the beneficial re-use of CCRs subject to defined placement and management criteria as very different from land disposal, this paper examines the technical and regulatory applicability of CCR beneficial re-use for reclamation of both above and below ground coal mines associated with the following applications.

Above Ground Coal Mines – Unencapsulated Form

Major surface mine operations were used to extract very thick coal seams leaving some reclamation footprints with vastly different topography than what originally existed. Given a sufficient volume of CCR materials, the ability to develop regrading templates coincident with lining and capping systems to provide environmental isolation supports land restoration to approximate pre-existing contours.

Below Ground Coal Mines – Encapsulated Form

Underground coal mines represent a substantial long-term potential for mine subsidence as well as methane and acid mine drainage production. In fact, backfilling of mines has been historically used within western Pennsylvania and West Virginia to limit potential mine subsidence. Through using encapsulated CCR material as backfill, the substantial network of subsurface voids within these mines can also be sealed which provides the benefits of minimizing methane and acid mine generation while offering significant protection against mine subsidence.

Beneficial Use of Fresh and Legacy CCBs in Maryland

Paul Petzrick, Maryland Department of Natural Resources Power Plant Research Program, Tawes State Office; Robin Lee, Environmental Resources Management, Inc; Jason Litten, Western Maryland Regional GIS Center, USA

Encouraged by Maryland's enlightened Pozzolan Act of 1974 Maryland utilities have become national leaders in the beneficial management of the coal combustion by-products (CCBs) also referred to as Coal Combustion Residuals (CCRs). This Act required that pozzolan ash in particular be treated as a resource rather than as waste. Maryland's seven coal-fired power plants produce a full range of CCRs include: both alkaline and non-alkaline fly ash as well as bottom ash, boiler slag, and flue gas desulfurization material. In addition to the fresh material produced each year, there is an enormous tonnage of legacy ash buried or stored across the State. This presentation is an update and progress report on the dynamic CCR activities in Maryland. These activities are greatly abetted by the presence of two ash beneficiation plants in Maryland and the existence of both a robust concrete ready-mix industry in the area as well as a significant cement manufacturing industry in the region. The result is 80 percent or higher utilization of our utilities' active production of CCR and an aggressive approach to mining legacy ash.

A 1982 report catalogued legacy CCR sites across the State. This report is being updated to assess just how well stored ash in Maryland can support the above industries in the coming decades as active production of CCR in the State declines. At the same time, an industry venture starting in 2004 that now mines over 400,000 ton per year of legacy ash at the decommissioned R. Paul Smith Power Plant is being closely observed to identify the economic and environmental issues associated with the transport of the recovered material by truck from the landfill to users.

The Role of Work Area Quantification for CCR Construction Efforts

Dale W. Evans, Kathleen Whysner, Remedial Construction Services, L.P.; Joseph Scalia, Christopher Bareither, Colorado State University, USA

Conventional geotechnical engineering practice routinely provides the analytical tools necessary to address civil construction issues for defining the performance of foundations, embankments, and related soil and rock mechanics applications. However, since the advent of environmental regulation, conventional geotechnical practice has had limited focus on linking the specific physical mechanics of various waste materials, including those associated with materials such as CCRs, to the materials handling prerogatives required for closure. The primary issues to be addressed are most often associated with facilities that employed sluice-based placement methods. These methods have historically left impounded CCRs with heterogeneous distributions, high moisture contents, and limited available bearing capacity. Left unquantified, such conditions, represent the potential for both dangerous as well as costly field operating conditions as access by production-oriented heavy equipment may be limited. To best understand field conditions and predictively assess those actions necessary to improve safety and optimize production, a pragmatic field quantification method has been developed to support predictive analysis and evaluation of field-based responses associated with construction. This quantification methodology supports the field-based capacity to better define the variabilities common in the field as well as key relationships between moisture content, void ratio, effective stresses, and shear strength.

As described within this paper, the applied geotechnics process developed provides the ability to establish a functional link between the field conditions present and the construction means and methods appropriate to support safe and optimally cost-effective impoundment closure. Accordingly, using the field and laboratory quantification efforts noted herein, the physical mechanics of CCR materials can be used to define those construction methodologies capable of addressing the oftentimes difficult and variable site conditions associated with CCR impoundment closure.

SESSION 28 Coal Science - 5

Cold Strength of Coal Briquettes for Finex®

Wooil Park, Hyeonsu Kim, POSCO, SOUTH KOREA

Finex® has been developed for an ironmaking process based on the direct use of fine ore and non-coking coal. Through trial and error the process has been successfully scaled-up from demo plant, 0.6MTPA in 1999 to two commercial plants, 1.5MTPA in 2007 and 2.0MTPA in 2014. At the same time, coal briquettes process also has been intensively studied to use fine coal directly. In this study, cold strength of coal briquettes for Finex® was investigated using a numerical calculation and experimental methods. In the numerical calculation, the relation between compressive strength and breakage probability was evaluated from DEM simulation based on the loaded weight in the storage bin. And impact strength was calculated from impact force on transferring routes. As a result, the requirements of cold strength for Finex® Coal Briquette was proposed and supported by real operation test. In the experiments, various parameters on the cold strength were investigated by varying binder content and species, moisture content of coal, drying condition and so on. Among them, the binder content and species was the most important factor on the cold strength. In this study, cellulose ether was mainly concerned as a binder for coal briquettes.

SESSION 29 Gasification Technologies: General - 3

R-GAS Technology Development and Testing of High Ash, High Ash Fusion Temperature Chinese Coals

Don Stevenson, Andrew Kramer, Derek Wissmiller, Gas Technology Institute, USA

The Gas Technology Institute (GTI) is maturing an innovative and compact gasification technology, R-Gas™, leveraging decades of investment from both U.S. aerospace and energy sectors. R-Gas™ was developed from concept to pilot scale by Aerojet Rocketdyne and was acquired by GTI in July, 2015. GTI has signed an agreement with Yangquan Coal Group Company in China to cooperate on the scale-up, design, development and operation of a commercial demonstration plant project in Taiyuan, China to demonstrate the technology at commercial scale of 800 MTPD. In addition to an active market for coal gasification, China has significant coal resources, in provinces such as Anhui, Henan, and Shaanxi, that are characterized by a >20% ash content with very high ash fusion temperature (AFT). These coals have properties that make them highly challenging for existing gasification process technologies. The high AFT make it a difficult feed for entrained flow gasifiers, especially for membrane wall designs that may not have sufficient thermal margin to manage the high outlet temperatures required to run the coal, unless it is blended with other coals or flux. The relative low reactivity of the coal makes it difficult to achieve high carbon conversion with fluidized bed technologies, which are often preferred for coals with high ash and/or high AFT. This presentation will summarize the recent long-duration (>100 hr) test campaigns of GTI's compact R-Gas™ gasifier technology on two anthracitic Chinese coals with ~25% ash and AFT >1500°C. Test results showed high carbon conversion (85%-98%), excellent slag coverage throughout the liner wall, and continuous slag discharge after installation of a slag bath system to deal with the challenging thermal environments posed by high AFT coals. Pilot plant test results are used to predict performance for commercial scale GTI gasifier technology on these difficult-to-process coals, and indicate that GTI's R-Gas™ gasifier technology provides an attractive approach to monetize the challenging coal resources.

Chemical Looping Coal Gasification Using CO₂ as a Co-Feedstock for Chemicals Production (with 100% carbon efficiency) and its Modularization Scaling Strategy: Thermodynamic Analysis, Techno-economic Assessment and Experimental Proof of Concept

Peter Sandvik, Mandar Kathe, Gabriel-le Grignonis, Charles Fryer, Fanhe Kong, Yitao Zhang, Liang-Shih Fan, The Ohio State University, USA

The prospect of CO₂ capture and utilization as a feedstock in an iron-titanium composite metal oxide based chemical looping process for coal gasification and reforming offers numerous advantages to conventional coal gasification and reforming. Given the projections for sustained global coal usage in the near future, the opportunity to reduce CO₂ emissions and improve process efficiencies has the potential to be disruptive in the global energy market, global chemical market and in overcoming the challenges presented by stricter global emission standards. A modularization chemical looping strategy that leverages two or more reactors operating in parallel can enhance syngas quality beyond what a single reactor performance and approach the thermodynamic limitations for syngas production. This study quantifies the advantages of a chemical

looping modularization strategy that leverages two or more reducer reactors operating in parallel to enhance syngas production beyond what is achievable by a single reducer reactor or conventional processes. The modularized system incorporates CO₂ capture and utilization as a feedstock in an iron-titanium composite metal oxide based chemical looping system to enhance coal-based chemical production. Simulations conducted in ASPEN Plus software suggest that adopting a concurrent moving bed reducer reactor based modularization strategy can improve syngas yield by greater than 12% over a single chemical looping reducer reactor. Experiments conducted on a bench-scale reducer confirm the findings of the simulations. The modularization simulation is scaled up and incorporated into a commercial sized methanol and acetic acid production plants. Chemical looping modularization demonstrates the ability to reduce coal consumption by 25% over Shell's conventional coal gasification process (compared to 15% reduction if a single chemical looping reducer reactor is used instead of the modular strategy) for 10,000 ton per day methanol production. Integration into a commercial scale acetic acid plant shows conditions in which the process can operate as a CO₂ neutral or negative system, where the process was consuming more CO₂ than it produces. These results indicate the potential for significant feedstock reduction in large-scale coal to chemical processes.

Catalytic Gasification of a Powder River Basin Coal with CO₂ and H₂O Mix-tures

Maohong Fan, University of Wyo-ming, USA; Fan Zhang, National Institute of Clean and-low-Carbon Energy; Xin Huang, China University of Mining and Technology, CHINA; Morris D. Argyle, Brigham Young University, USA; Bo Zhang, China University of Mining and Technology; Yulong Zhang, National Institute of Clean and-low-Carbon Energy, CHINA

This work studied the catalytic gasification of a Wyodak low-sulfur sub-bituminous coal from the Powder River Basin (PRB) of Wyoming using CO₂ and H₂O mixtures. Na₂CO₃, an inexpensive mineral widely available in Wyoming, was chosen as the catalyst. The experiments were conducted between 700 and 900°C in a fixed-bed laboratory gasifier under atmospheric pressure. Results show that the variation of H₂O/CO₂ mole ratio in the feed gas from 1:9 to 5:5 could increase the H₂ yields in the gas products by a factor of ~3. With the addition of 3 wt% Na, the H₂/CO mole ratio in the gas products decreased compared to the uncatalyzed gasification by ~37% at 800°C, while this decrease became not so notable when the gasification temperature increased to 900°C. The disposition of the sodium during gasification and its form in the ash were characterized by scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) mapping. The results suggest that part of the sodium combined with minerals from the ash, including calcium, silicon, and aluminum, while the remaining sodium formed sodium oxide domains. Integrated model was employed to fit the kinetic gasification data, and the results show that the addition of 3 wt% Na led to a 28.0% reduction in the activation energy during gasification with a H₂O/CO₂ mole ratio of 3:7. Na₂CO₃ can be a cost-effective catalyst for gasification of the PRB coal with CO₂ and H₂O mixtures.

Effects of B-site Substitutions on BaFeO_{3-δ} Perovskites for Oxygen Separation from Air

Elliot Roth, NETL/AECOM; Jonathan Lekse, Evan Granite, NETL, USA

Sorbents for oxygen separation from air can have applications in oxy-fuel combustion and coal gasification technologies. Perovskites, which have an ABO₃ formula, are widely studied materials, due to their tunable properties utilizing A and B site substitutions. In this study, the effects of partial B-site substitution for BaFeO_{3-δ} were investigated using a simultaneous TGA/DSC instrument. The partial B-site substitution of 10% Fe consisted of first row transition metals, Ti, Mn, Ni, Co, and Cu, as well as an alkali earth metal Sr, to form a perovskite with the formula of BaFe_{0.9}M_{0.1}O_{3-δ}. Isothermal cycles using air and nitrogen were conducted at temperatures ranging from 400°C to 900°C. In general, the perovskites demonstrated rapid adsorption of oxygen in air with a relatively slow desorption, and no degradation in uptake capacity over three cycles. The highest uptake was observed for the BaFe_{0.9}Cu_{0.1}O_{3-δ} and BaFe_{0.9}Ni_{0.1}O_{3-δ} perovskites at 700°C, with exceptional weight gains of 1.46 wt.% and 1.31 wt.% respectively. A comparison of the oxygen uptake, desorption, and the heat flow curves for the substituted perovskite sorbents will be discussed.

Chemical Looping Coal Gasification Sub-Pilot Unit Demonstration and Economic Assessment for IGCC Applications

Fanhe Kong, The Ohio State University; James Simpson, WorleyParsons; Mandar Kathe, Dikai Xu, Tien-Lin Hsieh, Yitao Zhang, Chunyi Li, Robert Statnick, Andrew Tong, Liang-Shih Fan, The Ohio State University, USA

Coal accounted for 29% of the worldwide energy demand in 2016 and is therefore an essential energy source. An integrated gasification combined cycle (IGCC) provides a conversion pathway from coal to electricity with higher energy efficiency and easier pollutant control compared to pulverized coal (PC) boilers. The capital and operating costs of the IGCC process, however, are high due to the expensive gasification

equipment and energy-intensive air separation unit (ASU). To address these disadvantages of the conventional IGCC processes, The Ohio State University (OSU) has developed a novel chemical looping-based IGCC process which utilizes an iron-based metal oxide oxygen carrier (OC) to indirectly supply oxygen to carbonaceous fuel. The novel chemical looping-based IGCC process produces high purity syngas while eliminating the need for a gasifier or ASU. The Environmental Protection Agency has issued New Source Performance Standards that limit CO₂ emissions from coal based electricity generating units. The proposed regulations limit CO₂ emissions to 1400 lbs/MW_e-gross. Depending on the conversion efficiency of the chemical looping IGCC unit, the unit could meet the NSPS without additional CO₂ control equipment. Three different process configurations have been designed for the conversion process including a two-reactor system utilizing the efficiency of the chemical looping IGCC to comply with the CO₂ emission limit, a two-reactor system with 90% CO₂ capture and a three-reactor system with 90% CO₂ capture. Aspen Plus is utilized to study the thermodynamic properties and simulate the process system of the chemical looping IGCC process. Operating conditions including temperature, pressure, OC flow rate and steam injection rate are varied in the Aspen models to investigate their influence on syngas yield and composition. At the optimal operating conditions, syngas yield reaches 1.55 mole of (H₂+CO) per mole of carbon in coal, which is 5.4% higher than the 1.47 mole of (H₂+CO) per mole of carbon in coal produced using the conventional IGCC processes. Along with the thermodynamic calculations, experiments have been conducted in a bench scale moving bed reactor to verify the thermodynamic calculation results. The results obtained from the bench-scale experiments showed a close match between experiments and simulation. A 15 kW_{th} sub-pilot unit was constructed for larger scale experimental verification of the thermodynamic simulations. The experimental results are scaled and integrated into a techno-economic analysis of the chemical looping IGCC process, conducted in collaboration with WorleyParsons. This presentation will initially focus on the thermodynamic calculations and process simulations of the chemical looping IGCC process. The results obtained from bench scale and sub-pilot scale experiments will also be discussed. Finally, a comprehensive techno-economic analysis and sensitivity study analysis on critical technology parameters will be presented.

SESSION 30 Clean Coal and Gas to Fuels - 2

Near-Completion CO-Conversion and Total H₂-Recovery by One-Step Water Gas Shift Reaction in Zeolite Membrane Reactor

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Water gas shift reaction (WGS) is a key operation for hydrogen production from coal and other fossil fuels. The WGS reaction is moderately exothermic, $CO + H_2O \leftrightarrow CO_2 + H_2$, $\Delta H_{298.15K}^\circ = -41.2 \text{ kJ/mol}$, and is thus kinetically favored but thermodynamically limited at high temperatures. In this presentation, we report the establishment of a zeolite membrane reactor packed with ferrite based nanocrystalline catalyst for WGS membrane reaction at high temperature and high pressures. The zeolite membrane reactor has been demonstrated to be capable of achieving nearly complete CO conversion (>99.9%) and almost total hydrogen recovery (>99.5%) in the permeate product stream at an operation temperature of 500°C and reaction pressures of >20 bar with some compromise in H₂ product purity. The H₂ purity however can be readily increased to meet the requirements for use in IGCC and >90% of CO₂ capture through low-cost polymeric membrane separations.

The Impact of Copper Oxidation States on H₂ Production from Partial Oxidation of Methanol

Hao Chi, Christopher Andolin, University of Pittsburgh; Jonathan Li, State University of New York; Matthew Curran, University of Pittsburgh; Guangwen Zhou, State University of New York; Judith Yang, Götz Vesper, University of Pittsburgh, USA

To mitigate the impact of climate change and pollution, we need to search for sustainable and clean energy production methods, such as fuel cells. Methanol is of particular interest due to its relatively high energy density and safe handling. Hence methanol can be used to replace H₂ as a storage fuel to power fuel cell directly or indirectly. The partial oxidation of methanol (POM, $CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2$) catalyzed by a copper based catalyst can provide on-board generation of fuel-cell ready H₂ streams. Although POM activity of copper-containing catalysts has been studied for decades, the reaction mechanism and the catalytically active sites are still poorly understood. In particular, the chemical nature of the active phase (Cu⁰, Cu⁺ or Cu²⁺) is unclear and their impacts on activity and selectivity of POM are unknown.

In the present contribution, we present results from a study of partial oxidation of methanol (POM) catalyzed by Cu/ZnO powder catalysts with the aim to identify correlations between POM reactivity and Cu oxidation state. We prepared a 30wt% Cu/ZnO nanoparticle catalyst by a co-precipitation synthesis. The catalytic performance was measured at different O₂/methanol molar ratios in a home-built micro-reactor. The

Cu oxidation state was assessed at different time-points via ex-situ X-ray photoelectron spectroscopy (XPS). We found that the reactivity for POM and the oxidation state of copper changes with reaction time and with O₂ to methanol feed ratio. Most importantly, we observed a strong correlation between H₂ selectivity and (metallic) Cu⁰ content of the catalyst. Surprisingly, the CO₂ selectivity was not significantly impacted by the oxidation state of the catalyst, but showed a strong correlation with the O₂ partial pressure. Based on the observed correlations, we propose a mechanism for POM including different bonding configurations of intermediates between metallic Cu and Cu₂O surfaces. We are currently in the process of verifying key reaction steps by first-principle calculations. The knowledge we gain from this study will benefit the optimization of current Cu-based catalysts which may lead us to a promising methanol based energy economy.

New Mechanistic Insights into Oxidative Coupling of Methane

Gizem Ozbuyukkaya, Götz Vesper, University of Pitts-burgh, USA

The recent increase in recoverable natural gas resources has renewed interest in using this resource beyond combustion, in particular via conversion to higher value and easily transportable chemicals. One target process is oxidative coupling of methane (OCM) to ethylene, an important feedstock for the chemical industry. Achieving high ethylene yields in OCM is challenging since competitive total oxidation is thermodynamically favored at typical reaction temperatures (800-900°C). In OCM, a metal oxide catalyst provides its lattice oxygen via a Mars-Van Krevelen mechanism to activate methane, while the carbon-carbon coupling reaction is widely accepted to occur in the gas phase after desorption of methyl radicals from the catalyst surface. Among the large number of catalysts that have been studied over recent decades, manganese oxide-based catalysts have shown highest C₂ yields (<24%), although falling short of economically viable targets (>30%). The present work therefore revisits the reaction mechanism over Mn oxide catalysts in order to identify reaction pathways and thus gain insights for optimization of process.

Supported Mn oxide-based catalysts were synthesized via simple wet-impregnation and were characterized via thermo-gravimetric analysis (TGA) combined with X-Ray Diffraction (XRD) and Transmission electron microscopy (TEM). Catalytic performance was evaluated in fixed-bed reactor experiments. We found that although lattice oxygen in unpromoted Mn catalyst is able to activate methane, C₂ yields were poor since intermediates and products are quickly oxidized further to CO₂ on the carrier surface, i.e. the undesired total oxidation seems to occur on the catalyst surface. The addition of Na₂WO₄ as a well-known promoter for OCM was found to improve reaction selectivity by suppressing CO₂ formation and increasing C₂H₄ yield. Remarkably, while Na₂WO₄ alone was found to be essentially inactive for OCM, significant improvement in C₂ selectivity was observed when separate Mn and Na₂WO₄ catalysts were physically mixed (rather than being alloyed in a single catalyst formulation). Product distribution and performance of alloy catalysts and the physical mixtures were found to be indistinguishable, in contradiction to the prevailing mechanism in the literature that requires directly exchange of lattice oxygen between the two oxide phases.

Overall, the present study hence provides new insights into the reaction mechanism and points towards new directions for further process improvements.

Efficient Syngas Upgrading with High Flux Zeolite Membranes

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Upgrading of synthesis gas and natural gas is often one of the most expensive parts of the production process. Membranes are considered one of the most promising sustainable and cost-effective separation technologies. Consequently, polymeric membranes have contributed to cost and energy reduction in these applications, however, there is still much room for improvement in terms of membrane properties. High flux zeolite membranes may offer a disruptive change in gas upgrading as the membrane properties may be orders of magnitudes better than for polymeric membranes. Luleå University of Technology has been conducting research in the area for many years and is preparing to commercialize the technology. The present paper highlights the current technological standpoint and the status of commercialization.

Zeolites are inorganic porous materials and there are more than 200 different zeolite structures with different pore size, e.g. the MFI zeolite has a pore size of ca 0.5 nm. Zeolite has been successfully commercialized for alcohol/water separations for more than 10 years but the technology has not yet been applied for industrial gas separations. We have evaluated the performance of high flux MFI membranes for different gas separations. The highlights for CO₂ separation from syngas are summarized in this paper and we also show how these membranes may be employed to reduce the cost for CO₂ separation in syngas processes.

High flux MFI membranes with a selective layer as thin as 500 nm were prepared on disc and tubular shaped porous alumina supports. The membranes have been evaluated for various gas separations over the last 15 years, ranging from the lightest molecules i.e. H₂ and He up to C₈ hydrocarbons. Most separations are based on selective adsorption and therefore the optimum performance of the membrane is observed at different temperatures depending on the separation. For CO₂ separation from syngas the CO₂

permeance was as high as about 80·10⁻⁷ mol/(m²·s·Pa) ca a factor 10-100 times higher than for polymeric membranes while the CO₂/H₂ membrane selectivity was at par or better (26 and 210 at 300 and 235K, respectively) than for polymeric membranes (ca 10-20 at room temp). These performance indicators suggest that very compact processes may be achieved with zeolite membranes, while the robustness of zeolite membranes allow operation at a wide range of temperatures and pressures, even at high CO₂ pressures where polymeric membranes may suffer from plastization.

To summarize, MFI zeolite membranes can be applied in a very broad temperature range enabling separation of a great range of gas mixtures. The robustness of zeolite membranes enables operation at conditions where both permeance and selectivity is high. Consequently, the membranes have great potential for application in industrial gas separation processes

Comparison of Integrated vs. Non-integrated Processes for Coal to Synthetic Natural Gas (SNG) Application to Produce Power

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Since mid-2016, the “energy transition policy” has been launched in Taiwan to establish low-carbon, stable and sustainable energy systems, during the next decade. The target of electricity from renewable energy is set as 20 %, and the portfolio of natural gas (NG) in electricity generation increases significantly as well. In Taiwan, the price of natural gas is relatively higher than that of coal; moreover, the limited receiving and storage capacity of liquefied natural gas (LNG) poses concern for energy security on the island at present, while commissioning of additional LNG terminals can relieve the situation in the future. Starting from 2014, the costs of fossil fuel keep descending. Especially, the seasonal average prices per mBtu for LNG drop from \$15.51 to ~\$8.5, due partially to massive production of shale gas; nevertheless, the cost of LNG is subject to variation, while the unit price difference between LNG and coal remains around \$4.5. The target of electricity out of LNG in 2025 is 50%, ascending from 31.38% in 2015, which means that the safety issue of electricity supply needs to be solved as the usage of natural gas increases greatly. Moreover, lack of long-term LNG contracts might cause deficiency of gas supply and the impact of price fluctuation of LNG on the cost of electricity. Hence, it would be beneficial to convert coal to synthetic natural gas (SNG) that can feed the NGCC units in Taiwan, provided that the SNG price is comparable with that of LNG. This would help stabilize the price of electricity by softening the impact of high LNG price.

The objective of this study is to model the whole system of coal to SNG via gasification, and then feed into NGCC plants to avoid the shortage of LNG, owing to unexpected political or environmental situation. The analysis model consists of three systems: a syngas plant, an SNG plant, and a combined cycle plant. The commercial chemical process simulator, Pro/II® V8.1.1, is implemented to build the analysis model in the study to simulate two scenarios, i. e., integrated and non-integrated configurations. The energy integration and performance analysis of process are investigated. The pros and cons between an integrated and non-integrated SNG plant with the application of supplying SNG for power generation in a combined cycle plant were discussed in the study. In the integrated configuration, different grades of energy are effectively utilized through steam integration and waste heat recovery, and the power system can produce the power for internal usage, resulting in higher efficiency than the counterpart of non-integrated system. On the other hand, the non-integrated system preserve flexibility of supplying multiple products that may be utilized as alternative fuel for power sector or feedstock to petro-chemical industry. The study shows a possible way of using SNG that could be a backup source to feed combined-cycle plants, and softening the impact of possible LNG shortage on stable supply of electricity in Taiwan.

SESSION 31 Carbon Management - Chemical Analysis and Characterization Studies

Characterizing the Geochemistry of the CO₂-Fluid-Shale Interface using In-Situ Infrared Spectroscopy and Feature Reloca-tion Scanning Electron Microscopy

Sean Sanguinito, AECOM; Angela Goodman, NETL; Mary Tkach, ORISE; Barbara Kutchko, NETL, USA

Traditionally, shale formations have been studied as sealing layers to contain vertical migration of CO₂ due to their low permeability and fracture porosity. Recently, research is being conducted focused on the potential to store CO₂ in shales that have been hydraulically fractured. Hydraulic fracturing introduces chemically diverse fracturing fluids, some of which are left behind in the shale formation and will interact with CO₂ and shale components (i.e. clays, organic matter) affecting rock properties through chemical alteration, matrix swelling/shrinkage, and related geomechanical effects. As these changes in rock properties will impact storage of anthropogenic CO₂, it is imperative to increase our understanding of the fluid-CO₂-shale interactions occurring at the molecular scale.

In-situ Fourier Transform infrared (FT-IR) spectroscopy coupled with subsurface high temperature and pressure capability was used to examine the interaction for CO₂ at the molecular scale and characterize vibrational changes of sorption bands sensitive to the gas-fluid-solid environment. Shale samples were also analyzed for chemical and physical changes before and after exposure to CO₂ fluids at storage conditions using surface relocation techniques via high-resolution field-emission scanning electron microscopy (FE-SEM).

Specifically, two initial scenarios were examined: 1) conditions expected near the injection wellbore where in-situ fluids, left behind from hydraulic fracturing, are displaced during injection and 2) conditions away from the wellbore where in-situ fluids are not fully displaced by the CO₂ and a thin film of fluid remains on shale surfaces. Vibrational spectroscopy indicates carbonate formation and dissolution occurs in hydrated shale samples exposed to CO₂ at storage conditions. Preliminary, feature relocation via FE-SEM results show precipitation of carbonate species as well as increased fracture spacing.

The Effect of Topology of Lewis Pair Functionalized Metal Organic Framework on CO₂ adsorption and Hydrogenation

Lin Li, Jinyun Ye, Karl Johnson, University of Pittsburgh, USA

Metal Organic frameworks (MOFs) are a class of porous materials having unique potential for both gas adsorption and catalysis. Functionalizing MOFs with catalytic moieties results in heterogeneous catalysts having active sites similar to those of molecular catalysts. We have shown that inclusion of Lewis pair (LP) moieties into UiO-66 and UiO-67 gives effective catalysts for hydrogenation of CO₂ to formic acid and methanol [1, 2]. The reaction pathway in this system has a lower barrier than the barriers reported for the reduction of CO₂ on traditional heterogeneous catalysts [3]. MOFs have a similar structure topology to zeolites, where the effects of confinement on the transition states and intermediates are well documented [4]. Here, we focus on how the effects of pore size could be applied to improving catalysis in MOFs. We do so by comparing and contrasting results from UiO-66, (largest pore) MIL-140C, and MIL-140B. (smallest pore)

The MIL-140B/C structures were functionalized by replacing a C-C group from the 2,6-naphthalenedicarboxylate linker with the NBF₂ moiety. We computed reaction pathways for H₂ dissociation, CO₂ chemisorption, and CO₂ hydrogenation. The transition states were found by using the climbing image nudged elastic band method and verified with vibrational mode calculations.

The effects of pore size on the chemisorption energies of H₂ and CO₂ were examined by contrasting energies for the UiO-66 and MIL140 systems. The calculated adsorption energy for H₂ is very similar between the three MOFs, ~ -0.6 eV. Furthermore, in all cases, H₂ heterolytically dissociates and generates a hydridic hydrogen bound to B and protic hydrogen bound to N. Additionally, the hydrogen dissociative adsorption energy does not appear to vary with the concentration of LPs inside the pore. However, the effect of having a limited pore size was much more pronounced for CO₂ chemisorption. The adsorption of CO₂ in functionalized MIL-140B (0.17 eV) was much weaker than the adsorption in functionalized MIL-140C (-0.62 eV), and UiO-66 (-0.93 eV). More importantly, the weaker binding of CO₂ relative to H₂ implies that the activation of H₂ in MIL-140B-NBF₂ will be further enhanced, by reducing the poisoning of the Lewis acid-base sites by CO₂.

We found that confinement significantly affects the hydrogenation of CO₂ in MIL-140B-NBF₂. Confinement in the small pore allows the physisorbed CO₂ to adopt a bent structure that activates the CO₂ prior to hydrogenation. We found that the hydrogenating this coadsorbed bent CO₂ has a much lower barrier than linear CO₂. We believe this is due to the decrease in the energy of LUMO of the bent CO₂, which facilitates the electron transfer from HOMO of the functionalized ligand with 2H*. (HOMO-LUMO gap is 3.26 eV for bent CO₂ and 4.24 eV for linear).

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CO₂ Capture on Li₂CuO₂ Under Different Physicochemical Conditions

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Carbon dioxide (CO₂) emissions are one of the most threatening pollution problems in the world. Most of CO₂ emissions come from the use of fossil fuels for energy production, and this is the main contribution to the global warming. In order to reduce the greenhouse gases concentrations, several strategies have been proposed. Among the different solutions, Carbon Capture and Storage (CCS) is a possible way to reduce the concentration of this gas in the atmosphere. In this regard, different materials have been studied as a possible CO₂ captors. These materials must have certain properties in order to be considered ideal captors, such as large capacity of capture, adequate kinetics, thermal stability and cyclability, among others. Alkaline ceramics are one of the most studied materials. These ceramics present some of the previously mentioned properties, which convert these materials in an option for CCS. Moreover, capture of CO₂ could be improved by some modifications in the conditions of the capture, such as the

microstructural changes of the captor, the addition of some gases or vapors in the inlet gas, variations in the pressure or concentrations of the inlet gases, etc.

On the other hand, Lithium cuprate (Li₂CuO₂) has been reported as a material capable to trap CO₂ in a wide range of temperatures (120-650 °C). The maximum theoretical CO₂ chemisorption capacity is 9.11 mmoles of CO₂ per gram.

Thus, in this work, lithium cuprate has been widely studied as captor of CO₂ under different physicochemical conditions. Li₂CuO₂ was synthesized by solid-state reaction. Afterwards, in order to modify the microstructural characteristics of the sample, the powder was processed by dry ball milling in air atmosphere, the milling time was varied between 10 and 60 min. All the samples (including the solid state sample) were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂ adsorption-desorption measurements.

CO₂ capture was evaluated, as mention above, in different physicochemical conditions, which could be separated in three sets of experiments. It is worth noting that these sets of experiments were performed with the solid state sample and the sample with the largest surface area (after the milling process). First, the CO₂ capture was evaluated in the presence of water vapor at low temperatures (40 to 80 °C). Then, the capture was evaluated at moderate temperatures (30 to 350 °C), under moderate pressures of CO₂ (between 5 Pa to 2.5 MPa). Finally, it was tested in a wide range of temperatures (350 to 750 °C) under dry conditions, varying the inlet gas: a) in a saturated atmosphere of CO₂, b) under different partial pressure of CO₂, and c) adding oxygen.

All these experiment showed that the modifications in the microstructural properties of lithium cuprate change the CO₂ capture. In some physicochemical conditions as the low temperature in presence of water vapor, and under moderate pressure the capture was improved by these variations. On the other hand, in dry conditions, the surface area increment resulted in a CO₂ capture decrement. However, Li₂CuO₂ prepared by solid state sample is capable to trap large amounts of carbon dioxide, even under low partial pressures of CO₂ in the inlet gas. Finally, the addition of oxygen improves the capture under these conditions, reaching an efficiency of 95 %, additionally the presence of oxygen allows the cyclability in this material.

Sorption of Flue Gas Mixture on South African Bituminous and Anthracite Coals under Feeds of Supercritical Conditions: CO₂ Sequestration Study

Major Mabuza, Kasturie Premllal, Maurice Onyango, Tshwane University of Technology; Michael O. Daramola, University of the Witwatersrand, SOUTH AFRICA

Over the past two decades, greenhouse gas (GHG) emissions have increased; hence the earth is facing the issue of global warming with carbon dioxide (CO₂) being the main contributor. One possibility being seriously considered to mitigate this effect is to capture CO₂ from emission sources, liquefy and store it in deep unmineable coal formations. The objective of this research was to investigate the effects of flue gas impurities in relation to physicochemical properties and CO₂ sorption capacity of South African coals. Two coal samples from two coalfields were analyzed for pure CO₂ and flue gas sorption capacity using a high-pressure volumetric sorption technique at 30-60 °C and pressures up to 9.0 MPa. The measurements were performed on 10 g samples with a grain size of passing through 2 mm sieve. A simulated industrial flue gas from a coal-fired power plant with 12% CO₂, 5.5% O₂, 82% N₂, 0.38% SO₂, and 0.12% NO₂ was used to investigate the effect of impurities. The sorption experimental data was fitted on existing adsorption isotherm models. The adsorption capacity of the coals ranges from 2.25 to 4.16 mmol CO₂/g-coal for pure CO₂ and 1.41 to 1.55 mmol CO₂/g-coal for flue gas. CO₂ sorption capacity is positively correlated to the vitrinite and inertinite maceral contents. Microporous coal exhibit high sorption capacity than macroporous coal. The Langmuir adsorption isotherm model conventionally fits the pure CO₂ gas experimental data better than Freundlich and Temkin. The Extended Langmuir gives best experimental data fit for flue gas.

SESSION 32 Power Plants - General

Performance of Ion Selective Electrodes (ISE) on Wastewaters from Power Plants

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Ion selective electrodes (ISEs) were tested for their feasibility as a sensor array to detect specific species in flue gas desulphurization (FGD) wastewater samples. Selected ISEs for calcium, chloride, nitrate, and nitrite were tested along their entire range and it was determined that the ideal Nernst equation does not properly describe the performance of the electrodes. The ISEs examined had varying sensitivities to changes in temperature, with nitrate and calcium being the most sensitive. In addition, samples from an FGD wastewater treatment plant were analyzed, and it was determined that the high ionic strength indicates that additional non-ideal correction factors are needed in order to properly use ISEs as sensors in these wastewater systems. Future work will be focused

on determining the correction factors needed for specific treatment equipment to account for high ionic strength and pilot scaled testing of ISEs using FGD wastewater samples

Theoretical Modeling for Thermophoretic Ash Deposition Ash In Gas-To-Gas Heater

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Ash deposition is a major concern in the coal power plant industries because it causes reduced efficiency and material damage to the heat exchangers in form of corrosion and erosion. There are factors such as coal properties, boiler design, and operating condition influencing the ash deposition in the heat exchangers. The fly ash transport mechanisms by which the deposition takes place include inertial impaction, thermophoresis, chemical reaction, and condensation. The objective of this research is to predict thermophoretic deposition rate of ash in Gas-to Gas Heater. Thermophoresis depends on the temperature gradient between the flue gas and the heat exchanger surface. The temperature gradient has been determined initially using the basic heat transfer equation. The temperature of the flue gas at inlet is 393.1 K. The typical range of particles (0.1-10 μ m) undergo deposition by this effect. There are also cases when the ash particles beyond this size range go through deposition by other forms. The study takes into account the chemical composition and the temperature of the flue gas to calculate the mean free path which is used to calculate Knudsen number. The calculated Knudsen number is constructive for distinguishing the flow regimes as continuum region, free molecular region, and the transition region. This theoretical study helps to estimate the thermophoretic ash deposits on the heat transfer surfaces in low temperature region. The thermophoretic velocity was calculated at 4.76 $\times 10^{-4}$ m/s and the mass deposition per unit length per unit mass concentration was 5.69 $\times 10^{-5}$ m²/s. The greater thermophoretic velocity results the more ash to be deposited on the surfaces. The thermophoretic deposition modeling will benefit for the efficient heat exchanger designs and control the use of the soot blowers to remove the ash deposits making the power plants run with improved efficiency.

Opportunities for Existing Coal Infrastructure

Angelos Kokkinos, DOE; Peter Rozelle, Churnside Technology Management, LLC; John Rockey, Advanced Combustion Systems; John Wimer, DOE / NETL, USA

Coal power generation has essentially changed from a baseload electricity provider to a load-following mode of operation, caused by an increase in renewable generation coupled with low natural gas prices. Cycling of these units has increased maintenance costs, and is making many units less competitive with lower capacity factors. Opportunities exist to reverse cycling damage and improve efficiency, both of which will improve dispatch.

In addition to cycling, many plants are older, and upgrades to equipment have been deferred. Recent DOE/FE analysis shows that efficiency upgrades can improve the heat rate of existing plants by up to 6-7 percent. Updated plants will operate at reduced operating costs, resulting in greater utilization and longer lifetime. Many older coal-fired generation assets use sub-critical steam power cycles, which exhibit significantly lower plant efficiencies. Repowering with an advanced supercritical steam cycle can increase plant efficiency by 20-25%, with an attendant improvement in plant economics. Retaining the existing plant infrastructure minimizes costs associated with a repowering, largely to boiler, turbogenerator, and control system components.

Analyses indicate that a modest efficiency improvement of 2% across the existing fleet of coal units would result in a slightly lower coal consumption, however by 2030, the retirement of 15GW of older units may be prevented, as these units would be more economic and less costly to operate.

MRC DICE: Flexible, Efficient, Low Emissions Power from Coal

Daniel Roberts, Louis Wibberley, CSIRO Energy, AUSTRALIA

There is increasing global demand for cost-competitive, reliable, low-emissions energy. The use of modified engines with coal-based feedstocks is a relatively-old concept, that through advances in engine technology and the development of new coal-water and biochar-water fuels, is becoming closer to technical and commercial reality.

CSIRO, with support from the coal and engine industries, is undertaking a RD&D program to develop a coal-water feedstock that is suitable for use in a modified diesel engine. So-called 'MRC DICE' (micronised refined carbon, direct injection carbon engine) provides a reduced-emissions means of using all grades of coal:

- Flexible and responsive, supporting increased grid stability and security
- Capable of providing base, intermediate and peaking capacity within a grid
- High efficiency – 50%

DICE provides an ability to utilise waste coal fines and can potentially be coupled with CCS for very low emissions. Furthermore, there is the potential to create MRC from biochar materials derived from woody biomass waste streams, offering the opportunity for net-negative carbon emissions.

This presentation will give an overview of some of the drivers and applications of the MRC-DICE technology, and some insights into the RD&D program that is currently underway. This program is focussed on MRC characterisation and fuel system

development, with work underway to adapt a 1 MW single cylinder test engine in Japan for pilot tests.

SESSION 33 Coal Ash Management - 6

Project Delivery Method Selection: A Prescription for Success in CCR Construction

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Selection of a project delivery method for CCR projects is often complicated by a variety of factors that must be considered to ensure "Best Value" execution can be recognized in spite of the high degree of site variabilities common with such projects. Broadly characterized, these project delivery methods may include the following:

- Design-Bid-Build
- Design-Build

Selection of an appropriate method specific to meeting a "Best Value" objective depends upon which contract format will be best to appropriately apportion client-contractor interests. In general, contractors typically value projects based on the certainty provided by the design and the production rates achievable given the resources allocated to the required work elements. Therefore, uncertainties in site conditions and the production rates possible during construction create the potential need to consider financial contingencies to bridge project risks. Accordingly, other than luck, the quantification of risks to production rates and cost represent the only viable means to provide a realistic surety of outcome.

One option for risk quantification is to perform front-end loaded efforts as part of the design process. These efforts may provide certainty within baseline site conditions provided that such conditions remain unchanged during the project, thus avoiding a basis for change of conditions. Conversely, consideration can also be given to contractors means and methods such that a front-end understanding of site conditions becomes the contractor's responsibility as the basis for defining means and methods capable of meeting design prerogatives subject to the contractor's cost and schedule basis. Each of these approaches apportion the elements of control and responsibility such that financial risks for changes in site conditions are either placed on the client or the contractor. Each has risks for the client depending upon the evaluations performed and the resultant value of contingencies applied to pricing by contractors. Therefore, assuming contractors are properly vetted to have the requisite capabilities to understand site conditions as the basis to define pricing, "Best Value" recognition is possible through development of a rigorous evaluation process tied to the selected project delivery method. Given the wide array of site variabilities common, regardless of project delivery method, the "Best Value" will most likely be obtained through assigning contractors the obligation to define means and methods specific to the site conditions present as the basis for pricing while providing a bid schedule that allows data compilation, investigation, and analysis, specific to their approach.

This paper examines these project delivery issues from a contractor's perspective to support the development and selection of a procurement basis capable of supporting the selected project delivery method that best represents the decision-making criteria for a given project.

Theoretical Modeling for Thermophoretic Ash Deposition

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Ash deposition is a major concern in the coal power plant industries because it causes reduced efficiency and results in the material damage to the heat exchangers in form of corrosion and erosion. There are factors such as coal properties, boiler design and operating condition influencing the ash deposition in the heat exchangers. The vital fly ash transport mechanisms by which the deposition takes place include inertial impaction, thermophoresis, chemical reaction and condensation. The objective of this research is to predict the ash deposition via thermophoresis. Thermophoresis depends on the temperature gradient between the flue gas and the heat exchanger surface. The temperature gradient has been determined initially using the basic heat transfer equation. The typical range of particles (0.1-10 μ m) undergo deposition by this effect. There are also cases when the ash particles beyond this size range go through deposition by other forms. The study takes into account the chemical composition and the temperature of the flue gas to calculate the mean free path which is used to calculate the Knudsen number. The calculated Knudsen number is constructive for distinguishing the flow regimes as continuum region, free molecular region and the transition region. This theoretical study helps to estimate the thermophoretic ash deposits on the heat transfer surfaces. The thermophoretic velocity was calculated as 4.76 $\times 10^{-4}$ m/s and the mass deposition per unit length per unit mass concentration was 5.69 $\times 10^{-5}$ m²/s. The greater thermophoretic velocity results the more ash to be deposited on the surfaces. The thermophoretic deposition modeling helps for the efficient heat exchanger designs and control the use of the soot blowers to remove the ash deposits making the power plants run with improved efficiency.

Using a Tufted Geosynthetic Final Closure System to Effectively Close Ash Impoundments & Landfills

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Recently passed federal environmental regulations are now requiring electric and industrial utilities to evaluate and address final environmental closure for coal ash storage areas. This paper focuses on using an engineered synthetic turf cover system (ClosureTurf®) to provide final environmental closure to large saturated ash storage areas. The paper describes the engineering strategies used to replace traditional soil closures with lightweight engineered synthetic final covers, thus reducing substantially the amount of ash stabilization efforts and dewatering of the ash.

The original project design called for a clay cap using geosynthetics and two feet of vegetated soil cover. Due to the low bearing capacity of the saturated ash, there were concerns that the additional geotechnical loading of the clay cap and vegetated soil cover would produce excessive surcharge stresses of 600 to 800 psf, which could create geotechnical instability (i.e. sloughing) conditions often associated with very low CBR value subgrades.

Additionally, due to the very large size of the closure area, which included distances exceeding 1,500 feet in width, it would be necessary to add significant additional soil materials in order to achieve the minimum 3% grade, after settlement, to provide surface water drainage. This additional geotechnical loading would be realized throughout the entire ash profile, resulting in settlement values on the order of a few to several feet, depending upon the ash thickness. Of major concern was the possibility that these settlements would result in reversing the final grades of the cover due to the additional surcharge type loading after the geomembrane installation.

A lightweight, engineered geosynthetic final cover system using engineered synthetic turf, a structured geomembrane and specified infill for the turf was then selected to improve geotechnical stability and minimize surcharge loading of the final cover system. The final cover system described in this paper consisted of lightweight engineered synthetic materials producing geotechnical loads of less than 8 pounds per square foot in total.

This paper highlights the benefits realized through the use of the lightweight engineered geosynthetic final cover system, including: elimination of borrow soils necessary for traditional final cover design; acceleration of project schedule by enabling the final cover system to be constructed before final dewatering was completed, as well as accelerated installation rates of the final cover system; geotechnical stability of the final cover system due in part to the lightweight profile and the high interface shear stress between system components and the subgrade; as well as environmental benefits including storm water quality improvements, reduced carbon footprint, and land preservation.

COAL ASHES AS A VALUABLE COMMODITY FOR FIXATION OF TOXIC WASTES

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Several recent studies have shown that coal fly ash (produced as a residue in Israeli utilities) is an excellent scrubber and fixation reagent for acidic wastes both for inorganic and organic toxic reagents. Moreover, the aggregate product formed via the scrubbing process could be used as a partial substitute to sand and aggregates in industrial concrete and the resulting concrete was strong enough for concrete standards, and even stronger than regular concrete. The concrete product was qualified as a green product according to the European Compliance Test 14257.

The largest acidic waste producer in Israel is the phosphate industry, which is using either sulfuric acid (Rotem Ampfert Plant) or hydrochloric acid (Haifa Chemicals Plant) for dissolution of the phosphate rocks. At present, the acidic wastes are transferred to large settling ponds and the acid capacity is neutralized by either CaCO₃ or CaO addition. When the pond reaches full capacity, it is covered by soil.

In this investigation, we have determined the fixation mechanism occurring at the surface of the fly ash particles and its potential economic value compared to the present processes used.

SESSION 34 Value-Added Products from Coal - 1

Anode Coke from Low Ash Coal

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Domestic coal reserves are a potential alternative carbon resource for anode production, primarily for the aluminum industry, provided coke specifications can be economically achieved. Previous work suggested solvent refining of coal could produce carbons suitable for aluminum production. However, to meet coke specifications (e.g. metals content), it was necessary to remove mineral matter in the coal by a costly filtration step.

This added cost and complexity made coal derived anode coke uncompetitive with petroleum derived coke. In this work, we explored working with natively low-ash coal sources, and omitted the filtration step.

Reported here are the results of our investigation into using low-ash coals (1–2 wt.%) from the southeastern Kentucky coalfield to produce anode-grade cokes. Milled coal was extracted in a solvent to produce a coal digest. The conditions for extraction were systematically explored and optimized. The digest was then coked and calcined. The conversion yields to green and calcined coke were tabulated, and the final calcined cokes were characterized by optical microscopy, XRD, and chemical analyses. The structures of the coal derived cokes showed a fine mosaic of anisotropic domains, which likely stemmed from the small amount of mineral matter in the coal digest. These domains were mixed with larger domains which suggested incomplete dissolution in the coal digest.

Carbon Fiber from Coal Tar Pitch

Matthew Weisenberger, Rodney Andrews, David Eaton, Nik Hochstrasser, Aaron Owen, Ashley Morris, University of Kentucky, USA

Demand for carbon fiber is growing at approximately 10% CAGR. Over 90% of it is derived from polyacrylonitrile (PAN) precursor fiber, as it offers a high toughness carbon fiber for structural applications. Yet pitch offers some key advantage over incumbent PAN-based carbon fiber. First, pitch can be melt spun, whereas PAN is solution spun. Melt spinning is significantly more economical and quite a bit faster than solution spinning – which requires immense amounts of solvent and energy for its recovery from water. Second, pitch typically has superior carbon yield, up to 80 wt.% conversion, while PAN offers approximately 50% conversion. There is key future interest in the utilization of pitch for a low-cost carbon fiber.

Here we report on our work utilizing coal tar pitch as a precursor for carbon fiber. We will discuss the coal tar extraction, and pitch upgrading processes. Then, the melt spinning process will be discussed, followed by general oxidation and carbonization process review. The resultant carbon fiber properties and yields will be discussed in the context of existing carbon fibers.

Production of High-Quality Precursor Feedstocks from Coal

Donald W. Collins, Western Research Institute; Alan Bland, Ash Management Engineering, Inc.; Charles A. Atkins, Ramaco Carbon LLC; Garrett W. Lin-demann, USA

Western Research Institute (WRI) with industry partner, Ramaco Carbon, LLC, is adapting a clean coal power plant technology to produce high-quality precursor materials for use as feedstocks for a number of coal to carbon products manufacturing facilities. In its original incarnation, the WRI Thermal Enhanced Coal (WRITECoal™) is a two-stage process deployed prior to feeding coal into a power plant. The process extracts multipollutant emission components and water from low-rank coals, such as subbituminous and lignite coals.

In the first stage, WRITECoal extracts water from low-rank coals in a form that is easily filtered to provide clean water for power generation and manufacturing process water needs. Heavy metals, such as arsenic, mercury, and selenium, found in coal are extracted during the second stage, thereby producing a very clean carbon resource from which to produce precursor feedstocks for manufacture of carbon fiber, regenerable activated carbon, carbon nanomaterials, graphene, etc. For example, utilizing WRI's saturates, aromatics, resins and asphaltene determinator (SAR AD™) patented technologies, third and fourth stage process stages are being developed to selectively extract volatile matter compounds for use as pitch precursors for making carbon fiber.

A number of coals and processed coals have been studied to determine the chemistry composition overall and to identify the specific chemistry of the multiple constituents. Understanding the specific chemistry of the constituents and how their chemistry varies between different coal resource is important for developing processes that produce consistently high-quality precursor feedstocks regardless of the starting raw coal. The overarching objective is remove the variability uncertainty of feedstock materials for carbon product manufacturers to aid lowering their production cost and increasing the performance and quality of the carbon material products produced. We will highlight work and results achieved to date.

WRI developed the WRITECoal technology with the support of the U.S. Department of Energy, Office of Fossil Energy and numerous other state and governmental agencies (State of Wyoming and State of North Dakota) and a wide range of utilities and industry organizations (Electric Power Research Institute, Basin Electric Power Cooperative, Detroit Edison, Montana-Dakota Utilities, Alliant Energy, Southern Company and SaskPower) has developed a novel patented and patent-pending coal treatment/upgrading and emissions control technology.

Understanding the Chemical Composition of Coal Oils, Tars and Pitches

Donald W. Collins, Jeramie J. Adams, Jean-Pascal Planche, Western Research Institute; Charles A. Atkins, Ramaco Carbon LLC, USA

With financial assistance from the U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, Western Research Institute (WRI) successfully demonstrated combining chemical data, including spectra, with chemical compositional saturates, aromatics, resins and asphaltene determinant (SAR-AD) data and correlating physical and performance data (using Explifit) predictive models for paving grade asphalts and air blown asphalt shingle materials. WRI successfully predicted coke formation and fouling during refining and upgrading. These approaches are now being used to relate chemical, compositional, and mechanical properties of precursors and intermediates to carbon fiber (CF) mechanical properties.

WRI's automated SAR-AD technique is a combined precipitation and chromatographic analysis that separates a sample of petroleum, heavy oil, or asphalt into solubility fractions. Four analytical-size columns are used in the separation, and unlike other SARA procedures, the columns do not have to be repacked or replaced between separations. In addition to measuring the conventional SARA fractions, the asphaltenes are further separated into three asphaltene sub-fractions. For the automated SAR-AD analysis, a 10.0 percent (w/v) solution of asphalt is prepared in chlorobenzene. A 20 μ L aliquot is injected into a high performance liquid chromatography (HPLC) system equipped with 4 columns packed with polytetrafluoroethylene (PTFE), glass beads, aminopropyl bonded silica, and activated silica in series. Peak elution is monitored by optical absorbance at 500 nm and an evaporative light scattering (ELS) detector. The asphaltenes precipitate on the PTFE column using n-heptane as the mobile phase. The maltenes in n-heptane elute through the glass bead column where some polar resins molecules adsorb; then through the aminopropyl bonded silica column where the remaining resins and some aromatics adsorb; then finally through the silica column where aromatics adsorb, and from which the saturates elute in two peaks. Three subfractions of precipitated asphaltenes are then selectively dissolved with cyclohexane; toluene; and finally, methylene chloride:methanol (98:2 v:v). The aromatics are split into two fractions: a less polar fraction is first desorbed from the activated silica column followed by a more polar aromatics fraction eluting with a backflush from the aminopropyl bonded silica and glass bead columns. The cut between the two aromatics fractions may lack precision from month to month as it is very sensitive to the activity of the bonded columns and other factors such as subtle impurities in solvents. Therefore, typically the total aromatics (1+2) fraction is reported. The resins/polars are eluted from the aminopropyl bonded silica and glass bead columns. The cut between resins and aromatics can be tuned to match historical databases. ELS detector peak areas are used to determine the relative percent values of the fractions.

SAR-AD data highlight how different materials can be fingerprinted for a petroleum vacuum residue, an asphalt, a coal tar used for CF production, a coal liquefaction residue, a super critical CO₂ (sCO₂) coal liquefaction residue, and used motor oil vacuum residue. Other SARA methods and solvent fractionation methods have been reported to be beneficial for characterizing and understanding petroleum and coal materials in light of CF starting material properties, reactivity, and product quality.

SESSION 35 Gasification Technologies: Modeling - 1

CFD-Simulation of a Fluidized Bed Coal Gasifier Under Reactive Conditions using a Two-Fluid-Model

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Fluidized beds are widely used in large scale industrial applications, e.g. fluidized bed drying, fluid catalytic cracking and coal gasification. Especially in reactive systems, the uniform temperature and improved solid-fluid contact in fluidized beds is beneficial for process control and efficient fuel utilization. Numerical simulation in particular can provide an improved understanding of the underlying phenomena of reactive fluidized beds, which can lead to advanced process development.

The Two-Fluid-Model describes the gas and solids as interpenetrating phases. The particle behavior is described by the Kinetic Theory of Granular Flow. The phase interactions, e.g. drag force, heat transfer, particle collisions and mass transfer significantly influence the hydrodynamics of the fluidized bed and therefore need to be modeled carefully. Different model assumptions are used in the literature among several validation data for the hydrodynamics. For reactive systems numerical investigations are focused only on global conversion rates not accounting the hydrodynamics. Furthermore, a comprehensive Two-Fluid-Model, which is validated for multiple fluidization regimes, can not be found in literature.

The present work focuses on developing a numerical setup for a reactive fluidized bed coal gasifier using ANSYS Fluent. The numerical model is validated against experimental data taken from the literature and in-house experiments.

The influence of model parameters and the heterogeneous reaction model are investigated in terms of reliability of the numerical results.

Towards a Validated CFD Setup for a Range of Fluidized Beds

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The present work aims to conduct CFD simulations of different types of fluidized beds with a single simulation setup. For this, a suitable validation experiment from literature must be identified that mimics the different states of fluidization that are of interest. The experiment chosen from the literature review covers fluidization regimes from bubbling to core annular flow of Geldart A class particles. It provides measurement data in the form of pressure, pressure fluctuations, voidage profiles, and contour plots of the particle velocity derived from magnetic tomography for validation of the simulation. As a first approach, use is made of only out-of-the-box models already included in the software of ANSYS Fluent 14.5 as well as typical parameters widely used in the literature with the Two Fluid Model. For the simulation a simple modification of the drag model is carried out to match the minimum fluidization velocity of the simulation to the value given in the experiment. A critical discussion about the potential limitations of the experimental setup in terms of proper gas distribution is conducted together with a discussion of the limits of the selected modeling approach. The influence of the inlet velocity profile on the voidage profile is investigated. Furthermore, the transition from bubbling to turbulent fluidization regime is evaluated by pressure fluctuation curves and solids concentration contour plots and shows good agreement to the experiment. Finally, the validated simulation setup is applied to a lab-scale gasifier in order to visualize its solids concentration profile.

DOE/NETL Multiphase Flow Science Impact and Benefits Analysis for Gasification Applications and Beyond

Madhava Syamlal, Chris Gunther, William Rogers, DOE / NETL; Christopher Munson, Massood Ramezan KeyLogic Systems, USA

The U.S. Department of Energy (DOE) National Energy Technology Laboratory's (NETL) Multiphase Flow Science (MFS) Group is engaged in (1) development of physics-based modeling tools, (2) controlled experimentation across multiple time and size scales using advanced diagnostics, and (3) application of high-performance computing, with these activities targeting accelerated development and deployment of advanced multiphase flow reactors for chemical process and energy conversion. The MFS Group's work in these areas has resulted in the development, validation, and application of widely used open-source software, including the Multiphase Flow with Interphase eXchange (MFiX) suite, publication of scholarly papers in the multiphase flow field, and notable outreach activities such as the annual MFS Workshop. MFS Group work continues to solve critical national problems, supports the mission of DOE, and provides multiphase flow expertise that crosscuts many technology areas. MFiX, an open-source suite of reacting multiphase computational fluid dynamics (CFD) software, is internationally used for problem solving in chemical process and energy conversion devices such as gasifiers, fluidized bed combustors, chemical looping reactors, and carbon capture reactors. MFiX has nearly 5,000 registered users worldwide as of 2017. MFiX and other CFD codes have been applied on challenging industrial-scale problems. Modeling and simulation using CFD tools such as MFS Group's MFiX have been shown to provide significant time and cost savings to industry, reducing technology development time and costs from 30 to 90 percent over traditional build and test methods. More specifically, DOE's investment in the MFS Program has resulted in a five- to six-fold return on the investment.

This presentation will provide an overview of the MFS Group's work, including an evaluation, with specific examples, of the beneficial impacts and value that have resulted from the work.

SESSION 36 Coal Bed and Shale Gas - 1

Coal mine and Coalbed Methane Development in India

Jonathan Kelafant, Advanced Resources International, Inc; Felicia Ruiz, EPA, USA

India is the world's third largest coal producer and is ranked fifth in terms of overall coal reserves. While many countries have begun to ramp down the use of coal for power generation, the Indian government has set a goal of doubling the country's coal production by the year 2020 to meet their ever growing need for electricity. Along with the goal of increasing coal production, the Government of India recently enacted several policies to increase coalbed (CBM) and coalmine (CMM) methane production. In 2016, the Cabinet granted Coal India (CIL) the rights to explore for and develop CBM and CMM within CIL's existing coal mine leases (they were previously prohibited from doing so without the consent of the Ministry of Oil and Gas). In early March of 2017, the Cabinet decided to exempt CBM and CMM from government imposed price controls and allow them to sell at market rates which should provide a major catalyst for CBM

and CMM development; the government set price for natural gas in India is currently \$2.50/Mcf whereas a true market price in the country is in the \$8.00 to \$10.00/Mcf range. This presentation will review the history of CBM and CMM development in India, summarize the major active and planned CBM/CMM projects, and discuss the future development of CBM/CMM in the country. The presentation will also highlight efforts by US government agencies such as the US Trade and Development Agency, the US Environmental Protection Agency, and the US Agency for International Development.

Opportunities for Methane Recovery and Use from Abandoned Underground Coal Mines

Michael Cote, Ruby Canyon Engineering; Felicia Ruiz, EPA, USA

The economic value of coal mine methane (CMM) can be extended well past underground coal mine abandonment. Abandoned mine methane (AMM) recovery and use projects, while smaller in size than CMM projects, have proven to be a stable, long-term source of methane for energy projects. Left uncontrolled, much of the AMM would reach the atmosphere via fugitive emission pathways, thus recovery and use projects can be important methane mitigation projects. Moreover, because of methane's higher global warming potential, carbon credits for AMM projects can become an important revenue stream (e.g., California Air Resources Board Compliance Offset Protocol Mine Methane Capture).

Currently, there are about 20 AMM projects operating in the U.S. at approximately 40 abandoned underground coal mines. These projects account for over 5 billion cubic feet (Bcf) of methane. Most beneficial use projects sell AMM to natural gas pipelines, while other projects generate electricity or use directly for boilers or heating. To foster additional AMM recovery and use projects, U.S. EPA's Coalbed Methane Outreach Program (CMOP) recently assessed and revised AMM opportunities at U.S. mines in a soon to be released update titled, *Abandoned Coal Mine Methane Opportunities Database*. CMOP estimates the potential to recover approximately 6 Bcf from an additional 80-100 currently abandoned coal mines in the U.S. In addition, continued coal industry restructuring and gassy mine closures could result in additional opportunity for AMM recovery. This presentation will focus on EPA's recent analysis and updated AMM data, assessment of recovery and use opportunities, and highlight several successful U.S. AMM recovery and use projects.

SESSION 37 Sustainability and Environment

Potential Remedial Options for a Site with Groundwater Adversely Affected by Coal Combustion Residuals

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Groundwater remediation at a site where coal combustion residuals (CCR) have been placed requires more than a cookie cutter approach because each site is different. Sites differ in the nature and amount of water quality degradation as well as important factors such as depth to water table, distance to water bodies and site boundaries, and the natural attenuation capacities of the soil and rock strata. Other site-specific aspects that should be considered include: geographic location, whether the relevant State or Federal CCR Rule is more stringent, whether CCR disposal is continuing or has ceased, the characteristics (physical, geochemical, hydrological, etc.) of the CCR material and disposal area, the local and regional geology, the nature (physical and geochemical) and hydrologic significance of the underlying strata, the nature of the CCR leachate (the documented contaminants of concern and their concentrations), groundwater flow rates, and whether groundwater contamination has reached or is approaching site boundaries or surface water bodies.

It is important that operators, consultants, and regulators all remain open to innovation, while remaining aware that site-specific aspects typically determine which remedial option(s) will be the most cost-effective. Although CCR leachates are typically much less toxic than leachates from hazardous waste sites, the tendency has been to consider only the most conservative approaches (excavation and removal and capping) to deal with it. In general, this is because the sites that have already taken remedial actions are responding to state regulations, such as North Carolina's, which required action before the Federal CCR Rule. However, operators in other states should not simply repeat what others have done. Techniques that have been proven to be effective in controlling contaminant release at hazardous waste sites can and should be considered at CCR sites. Granted, CCR leachate has some unusual characteristics (especially the typical levels of boron), but that simply means that these techniques may have to be adapted somewhat. Recognizing that the groundwater will remain contaminated for a very long time unless action is taken to reduce contaminant release from the CCR, this paper will first discuss potential options to control groundwater contamination at the CCR source. Then, we will suggest measures (other than the very expensive option of pumping and treating the contaminated groundwater) that should be considered to deal with groundwater that has already been contaminated. Experimental work will be necessary to modify approaches that have so far only been used at hazardous waste sites or to scale up approaches that

so far have only been proven to be effective in small-scale laboratory tests, but now is the time to proactively proceed with such research.

Sustainable Reuse of Lime Sludge from Water Utilities as an Environmental Sorbent in Power Utilities

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There are hundreds of water utilities across the U.S. that generate significant amounts of lime sludge as a result of the water lime softening process. Beneficial use of the lime softening sludge is a sustainable solution to the current landfill disposal practice and will eliminate the disposal cost and could potentially generate additional income for water utilities. A small fraction of the lime sludge is currently used for farmland application. However, this seasonal application may vary from location to location depending on the pH of the soil. This research evaluated the reuse of water treatment plant lime softening sludge as an effective environmental sorbent at power utilities. At an estimated disposal cost of about \$80 million, water utilities across the U.S. are currently generating about 4 million tons of lime sludge per year. While power utilities are using roughly the same amount of limestone per year for flue gas desulfurization (FGD).

Laboratory studies were performed on the effectiveness of lime sludge samples for sulfur dioxides (SO_x) removal and elemental mercury re-emission control. A comparative life cycle assessment (LCA) was also conducted to compare the total environmental impact of the current limestone mining and processing for FGD scrubbers to the environmental impact resulting from the reuse of the lime sludge generated at water treatment plants for FGD scrubbers. In order to highlight and quantify the environmental benefit of the lime sludge recycling in power plants, a third LCA case was included for the disposal of the lime sludge in landfills. Eight lime sludge samples were collected from sludge dewatering ponds at seven drinking water treatment plants in Illinois and Ohio. The collected samples were dried, ground, and sieved by standard methods to a particle size of less than 44 μm (a typical size for FGD applications). Lime sludge samples were characterized and tested for the capture of SO_x from a simulated flue gas and for control of mercury re-emission from a laboratory scrubber. Lime sludge sample characterization included measurement of surface area and pore size distribution from nitrogen isotherms, particle size distribution by laser scattering, trace metal analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), major and trace element analysis by X-ray fluorescence spectroscopy (XRF), and crystal structure and mineral composition by X-ray diffraction (XRD). The reactivity of the lime sludge samples were assessed and compared to the reactivity of selected limestone samples. Finally, the performance of the lime sludge and limestone samples were evaluated for mercury re-emission control.

Based on the LCA results, the total environmental impact of lime sludge reuse in power plants is about 2 orders of magnitude less than the traditional mining and processing of limestone for power plant use or than the lime sludge disposal by landfilling. This analysis clearly quantifies the environmental sustainability of lime sludge reuse as an environmental sorbent for flue gas clean up in coal-fired power plants. The results of the reactivity tests showed higher reactivity values for the lime sludge samples when compared with the limestone samples. This high reactivity may be attributed to the higher surface area of the lime sludge samples, in addition to the presence of residual unreacted lime (calcium oxide) in the samples. The lime sludge samples also showed superior performances for capturing SO_x and controlling mercury re-emission.

Hydrothermal Gasification Reaction of Phenol Water with Fe and Co Catalyst Supported on Carbon-Oxide Composite Carrier

Atsushi Ishihara, Yusuke Hirai, Tada-nori Hashimoto, Hiroyuki Nasu, Mie University, JAPAN

Waste water containing trace amount of organic compounds such as phenol generated in semiconductor factories and the chemical industry gives damages to the environment. However, conventional treatment of waste water using microorganisms by activated sludge process is significantly difficult to decompose aqueous aromatics, and combustion treatment is usually carried out using heavy fuel oil. However, this method has serious problems such as carbon dioxide emission and high cost of treatment. As an alternative, hydrothermal gasification reaction to produce fuel gases such as hydrogen and methane has been proposed.

Our laboratory has already reported that carbon supported nickel catalyst has high activity for hydrothermal gasification reaction. Therefore, in this study, a series of catalysts using iron and cobalt as a transition metal instead of nickel were prepared and investigated.

Reagents used for preparing the catalysts were aluminum tri-sec-butoxide, titanium(IV) isopropoxide, zirconium(IV) butoxide, polyethylene glycol (PEG) as a raw material of a carbon skeleton, Fe(NO₃)₃ · 9H₂O, Co(NO₃)₂ · 6H₂O, 2-butanol, 2-propanol and 1-butanol. Catalysts were prepared by the sol-gel method and calcination was carried out at 700 °C for 3 hours under argon or nitrogen atmosphere. As a notation of catalysts, Fe is iron, Co cobalt, C carbon, A alumina, T titania, Z zirconia, and the numbers in front of the alphabet represent wt% in the catalyst. 700-Ar and 700-N₂ represent the calcinations at 700 °C under argon atmosphere and nitrogen atmosphere, respectively.

The hydrothermal gasification reaction was carried out under the conditions of temperature 350 °C, pressure 20 MPa, LHSV 48 h⁻¹, reaction time 8 h, phenol water 2 g/L in a fixed bed flow reactor. Gaseous products were measured by GC-TCD, and liquid products were measured by GC-FID. For the characterization of catalysts, nitrogen adsorption and desorption, XRD, XRF, TG-DTA were performed.

From the results of the XRD measurement, peaks of iron metal were not confirmed in the alumina-supported catalysts and titania-supported catalyst, but peaks of Fe₃O₄ were observed. In contrast to this, in zirconia supported catalysts, peaks of iron metal were observed. From the results of nitrogen adsorption/desorption measurement of zirconia supported catalysts, surface areas and pore volumes before and after the reaction were very similar for most of catalysts, indicating that zirconia would be stable under the hydrothermal condition.

In the hydrothermal gasification of phenol water, 4Fe12Co63C21Z 700-N₂ catalyst showed the highest conversion. This catalyst has the largest surface area among all the catalysts, which may be related to the high conversion. The weight ratio of each element in the catalyst was calculated from the results of XRF and TG-DTA measurements. The amount of carbon in all the catalysts became smaller than those added as PEG in preparation, indicating that some amounts of carbon were released during calcination. As a result, catalysts containing a large amount of active metal were prepared by this method.

The activities of catalysts prepared using Fe and Co were much lower than those using nickel species reported before. Further, most of these Fe and Co catalysts did not produce methane and carbon dioxide, indicating that although phenol was decomposed on the catalyst surface, the reaction of water with decomposed species would be difficult to proceed.

Among the iron-based catalysts, only 16Fe63C21Z 700-N₂ produced hydrogen while the conversion of phenol was not so high. On the other hand, 16Fe63C21A 700-N₂ showed the higher conversion than 16Fe63C21Z 700-N₂ although it did not produce hydrogen. 16Fe63C21Z 700-N₂ showed iron metal in XRD, indicating that the formation of iron metal may be intrinsic for hydrogen production.

Vortex-Induced Vibration and Energy Harvesting of Two Staggered Circular Cylinders with Passive Turbulence Control

Lin Ding, Qianyun Ye, Li Zhang, Zhongqing Yang, Chongqing University, CHINA

The Vortex-Induced Vibration (VIV) and energy conversion of two staggered cylinders are investigated by using 2-D URANS simulations at Re=30000. The amplitude response, frequency response and energy efficiency of two cylinders are analyzed. The simulation results indicate that the amplitude ratio of upstream cylinder and downstream cylinder have symmetrical variation trend with the increase of the absolute value of S/D, and the maximum amplitude reaches 0.535D and 0.393D at S/D=0.8, respectively. The calculated oscillation frequencies of two cylinders are all smaller than the natural frequency of cylinder in water. There are four peaks of power conversion efficiency in the numerical simulations, which located at S/D=0.4, -0.4, 0.8, -0.8. The maximum efficiencies of the upstream cylinder and the downstream cylinder are 15.2% and 8.2% at S/D=0.8, means the optimum arrangement for energy harvesting is the case of S/D=0.8.

How to Overcome the Limitations Inherent in Sustainable Development

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Sustainable development is the ideology and practical strategy of the present and future socio-economic development in harmony with nature as the human environment. A wide range of policies and practical activities have been launched at a global, national and regional level in order to achieve sustainable development since its concept and implication emerged in 1987 by WCED. In 2015, United Nations adopted a set of sustainable development goals to be achieved over the next 15 years as a follow-up action plan of millennium development goals. However, it is true that sustainable development is not achieved as successfully as planned. This would mean that sustainable development includes limitations in its concept and implication. Nonetheless, it is quite rare to conduct a research on the limitations inherent in sustainable development.

In such a context, this paper aims at exploring how to overcome the limitations inherent in sustainable development. In order to achieve the objectives, this paper will first examine what is happening to nature since the industrial revolution in the 18th century, and followed by the emergence process of the concept and implication of sustainable development, the debates on the concept and implication of sustainable development in the 1990s, and the emergence of ecological modernization in the 2000s.

Based on the findings from the above reviews, this paper will draw the limitations inherent in the concept and implication of sustainable development and examine what and how to overcome the limitations.

Comparison of Different Modeling Approaches of Coal Pyrolysis for Improved Configurations in a CFD Framework for Entrained Flow Gasification

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Coal pyrolysis can account for a majority of the coal particle mass conversion during the gasification process, particular for high-pressure conditions in combination with fast particle heating rates. The focus of this work is a thorough analysis from analytic to advanced network models. The goal is to generate valid parameters for devolatilization rate, composition of the volatile matter, and energy and mass balances for a solid set of boundary conditions for CFD calculations. In literature different models are used to predict different aspects of the mentioned parameters. Light gas distributions of the pyrolysis content are estimated using simple analytical or averaging techniques. Tar and char fractions can be predicted using either a rough estimation of the proximate analysis or a more physical approach by using network models. All programs, incorporating a network model, are capable of predicting rate and transient behavior of volatilizing species without supporting experiments. They use a set of structural parameters and boundary conditions, for instance heating rates, of the given process as input but are founded in most cases on slow pyrolysis experiments for mostly bituminous and subbituminous coals. This has an influence on the overall results of those models. Furthermore light and heavy volatilizing component predictions need further inside for the use in CFD. For that reason the present work focuses on improved methods for a more reliable description of the pyrolysis process in a CFD framework, more precisely to bridge the gap between pyrolysis modeling, mostly based on network models, and the corresponding CFD model implementations. As a first step, major influencing parameters are identified, based on CFD results and in-house pyrolysis measurement by use of the PYMEQ test facility. The combination of detailed pyrolysis modeling and pyrolysis experiments leads finally to an improved workflow for the use in CFD.

Some Critical Improvements in Modeling the Kinetics of K₂CO₃-Catalyzed and Steam-Pressurized Gasification of Ash-Free Coal Char

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The intrinsic kinetics of coal char gasification has been extensively studied, generally using laboratory thermogravimetric analyzers (TGA). However, the external diffusion cannot be eliminated in this kind of apparatus, because the reactant gas is not allowed to flow through the sample bed with a fast speed. Moreover, the common kinetic models such as volumetric model (VM), shrinking core model (SCM) and random pore model (RPM) only consider the geometric transformations of coal char with burn-out. In this work, a specific vertically blown reactor (VBR) was developed to investigate the K₂CO₃-catalyzed gasification of coal char with pressurized steam. A differential reaction condition was also ensured to measure the intrinsic gasification rate. The limiting external diffusion was determined by altering superficial gas flow velocities (GFV). Based on the experimental data, we have further derived a new kinetic model in terms of an active site/intermediate mechanism of K₂CO₃-catalyzed steam gasification, which embraces external mass transfer. This model can wonderfully predict the sophisticated variations of gasification rate of all three main gases (CO₂, CO and H₂) with temperature, steam partial pressure, gas flow velocity and carbon conversion. The model can well quantify the external diffusion limitation to the intrinsic gasification rate.

Modeling of Cavity Growth in Underground Coal Gasification

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Coal is a combustible sedimentary rock which is composed primarily of carbon. Other elements are hydrogen, sulfur, oxygen and nitrogen. India is the third largest producer of coal and it mainly consists of non coking coal. In India, about 60% of the commercial needs and 70% of electricity needs are met by coal. Gasification is an effective method for the utilization of coal where the coal reacts with steam or/and carbon dioxide to give syngas (hydrogen, carbon monoxide and carbon dioxide). Underground coal gasification (UCG) is a method in which gasification takes place in-situ by injecting air or oxygen and steam to the coal seam directly and product is also collected directly from the seam. [1] This process eliminates the necessity of mining the coal and processing it through surface gasification. So, UCG offers the potential to use the energy stored in coal deposits particularly very deep mines that are uneconomic to mine by conventional methods. UCG is also used to utilize low rank coal in an effective way. In India, UCG has a good scope due to deep seated seams with high ash coals.

The product gas composition and heating value of UCG is influenced by many factors such as reaction kinetics, hydrodynamics of gases, heat and mass transfer between gas phase and solid phase, coal characteristics and geo-mechanical behavior of coal seams. It is difficult to visualize what is happening inside the coal seam while gasification takes place. Because of these complexities, there is a need to develop a model to predict the effects of physical and chemical parameters in UCG. Since the cavity growth, product composition and heating value depends on many factors, it is difficult to solve all equations using one single tool or model. So, it is better to divide the models into sub models, solve it separately and integrate them.^[2] In our work, we mainly include reaction kinetics and spalling in the model of UCG. When gasification takes place, the cavity grows in two directions from injection well; one vertically towards the overburden and other one horizontally towards production well.^[4] Our focus is to develop the model for the first part of cavity growth that is vertical growth with an assumption that the coal around the injection point gets consumed in the radial direction and so, the cavity is hemispherical in shape. We consider the cavity inside the coal seam as a packed bed reactor and for the simplification of equations, we account only for one dimension. This model can be used for predicting the product composition and calorific value of the product gas along the radial distance at different times. Pyrolysis, combustion, Boudouard reaction (carbon dioxide gasification), steam gasification, Methanation and water gas shift reaction are considered for modeling.^[3] Proximate and ultimate analysis is used to know the chemical composition of coal and char. The variation of product gas composition and density of coal and gas along the radius is obtained. Effects of thermo-mechanical spalling on the product gas composition are examined.

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SESSION 39
Coal Mining and Beneficiation

Blast Design in Accordance with the Safe Vibration Limits in the Coal Production Close to Settlements - A Case Study

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Mining and quarrying activities cause environmental vibration depending on the production technologies. Aboveground/underground structures and settlements may be found in close by mine pit where are carried out excavation works with blasting inevitably. These structures can be affected by environmental blast induced vibration. In this situation, Characterization of blast induced vibrations are so important to determine the effect of settlements which are closed the mines in terms of ensuring safety. Drilling and blasting method is used for the excavation of rock covering the coal seam (the overburden) due to the geomechanical strength of the formations in open pit coal mine where is located in Kutahya, Turkey. Production has been completed in most parts of this mine and the last part in the northwestern of permitted boundary of coal production is in close proximity to settlements. In this part, production planning has been carried out taking into some factors such as having an undisturbed natural land, being a last part which is produced the coal, being close to settlements. Especially, the vibrations can occur because of blasting in the northwest-west boundary of project area and these vibrations can be perceived in the settlement close to this area. The nearest village house is located at a distance 40 m to the bench slopes boundary of the planned excavation of rock covering the coal seam considering to permitted boundary. In consideration of the project boundary and settlements, it is necessary to characterize the vibration levels in order to determination of environmental impacts caused by excavation with blasting. This can only be possible with experimental blasting which is necessary to research about environmental impacts in the mining area. For this purpose, trial blasting operations were carried out in the areas determined previously and vibration measurements were taken from these blasting operations. A total of 37 vibration measurements were recorded from 10 trial blasting. Measurement results were analyzed and blasting design parameters such as drillhole length were determined. In the design phases, it were taken in consideration that the necessity of being a different and special of drilling-blasting operations which are applied close to village houses. The designed open pit coal mining project was changed so that not any environmental impact could occur in houses near the coal mine.

Influence of Gas Compressibility on an Accidental Methane/Air/Coal Dust Fire Scenario in a Coalmine Passage

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Coalmining keeps experiencing one the highest fatality and injury rates for employees among the industries dealing with flammable gases and explosive dust. To reduce such a high level or risks, novel preventive mining/fire safety strategies have recently been developed by Demir et al. [<http://dx.doi.org/10.1080/13647830.2017.1328129>], who has identified and scrutinized the keys stages of the premixed flame front evolution and quantified its major characteristics such as the flame shape and its propagation velocity, acceleration rate, run-up distance and flamegenerated velocity profile. However, that analysis adopted the approach of incompressible flows, which made it a little far from the practical reality. To fix this discrepancy, in the presented study, the effect of gas compression is incorporated into Demir's predictive scenario of methane/air/coal dust fire in a coalmining passage, for a twodimensional geometry. Among various mechanisms responsible for the flame acceleration such as combustion instability, turbulence, acoustics, and wall friction, acceleration due to a finger-shaped flamefront plays a dominant role in coalmines, because this mechanism is scale-invariant and, thereby, Reynolds-independent. This finger-flame acceleration is very powerful, promoting the flame speed by an order of magnitude. Starting with gaseous fuels, the formulation is then extended to gaseous-dusty flows, with combustible and inert dust as well as their mixture studied. Specifically, the effects of equivalence ratio on the flame evolution, as well as that of the size and concentration of the dust particles, are systematically investigated. It is shown that gas compression generally moderates flame acceleration, and its impact depends on various thermal-chemical parameters. While the effect of compression is minor (yielding 3-5% reduction) for lean and rich flames, thereby justifying the incompressible formulation in that case, it appears significant (up to the reduction of 22%) for near-stoichiometric methane-air combustion, and therefore should be accounted in a rigorous formulation. Furthermore, it is demonstrated that gas compression may control acceleration of slightly-reach flames.

SESSION 40
Value-Added Products from Coal - 2

Thin Films of Solution Processed Coal Nanoparticles for Electronic Devices

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Disordered carbon materials, both amorphous and with long-range order (such as reduced graphene oxide), have been used in a variety of applications, from conductive additives and contact materials to transistors and photovoltaics. In this work, we propose a flexible solution-based method of preparing thin films with tunable electrical properties from suspensions of ball-milled coals following centrifugation. The asprepared films retain the rich carbon chemistry of the starting coals with conductivities ranging over orders of magnitude, and thermal treatment of the resulting films further tunes the electrical conductivity in excess of 7 orders of magnitude. Optical absorption measurements demonstrate tunable optical gaps from 0 to 1.8 eV. Through low-temperature conductivity measurements and Raman spectroscopy, we demonstrate that variable range hopping controls the electrical properties in as-prepared and thermally treated films and that annealing increases the sp² content, localization length, and disorder. The measured hopping energies demonstrate electronic properties similar to amorphous carbon materials and reduced graphene oxide. Finally, Joule heating devices were fabricated from coal-based films, and temperatures as high as 285 °C with excellent stability are achieved, surpassing the performance of state-of-the-art thin metal-oxide Joule heaters. In preliminary results, we will show how film quality, homogeneity and controlled thickness can be improved by using tar as precursor leading to the fabrication of transparent conductive films with preserved electronic properties of thicker coal films.

Spectroscopic Diagnostics and Material Characterization for Wave Liquefaction™ Processing of Carbon Materials for the Production of Value-Added Chemicals and Feedstocks

Randy Vander Wal, Arupa-nanda Sengupta, Penn State University; George Skoptsov, James Strohm, H Quest Vanguard, Inc, USA

This talk presents optical spectroscopic diagnostics in H Quest Vanguard's microwave-plasma technology applied to coal and material characterization results from its application to H₂ generation from natural gas. Chemical analyses are also presented of CTL products.

1. Optical Diagnostics for CTL

H Quest Vanguard is developing broad-spectrum microwave plasma processes targeting conversion of hydrocarbon feedstocks such as coal and natural gas to value-added materials, chemicals and fuels. One initial deployment target is production of a *high-*

value coal-derived liquid chemical feedstock, roughly equivalent to coal tar. Coal tar, also known as high-temperature pyrolysis tar, is a valuable chemical and carbon product feedstock, supplies of which in North America are dwindling as coke ovens continue to close under heavy pressure from environmental regulations and from the continued reductions in blast furnace steelmaking capacities. Other promising targets for early deployment include production of high-value carbons, hydrogen, and added-value platform chemicals such as ethylene directly from methane and natural gas.

Optical diagnostics are central to reaction characterization and hold particular value for species identification and temperature determination. Observed intensity ratios or spectra band shapes can yield temperature by Boltzmann analysis using spectral constants. Moreover, optical emission serves to identify reactive species and intermediates, albeit indirectly inferred by the observation of their electronically excited counterparts, e.g. CH* and OH* radicals. For example, the presence of key atomic or diatomic radicals can support postulates of electron impact dissociation, and radical mediated bond insertion or radical capping reactions and provide mechanistic insights from the temperatures associated with the different degrees of freedom – electronic, vibrational, such as from the C₂* (A²Δ-X²Π) Swan band emission.

2. Material Characterization for CH₄ to H₂

Hydrogen is envisioned as the energy carrier (fuel) of the future and is a crucial feedstock for various manufacturing industries. Presently 0.1 Gton is produced annually, 98% of this from reforming fossil fuels, for use in oil refineries, methanol and ammonia production. Steam reforming of methane (SMR), the present industrial practice produces 13.7 kg CO₂ (equiv.) / kg of net hydrogen and consumes 19.8 liters of water per kg of hydrogen. Thermo-catalytic decomposition of methane is an attractive alternative to conventional steam reforming because the process does not generate CO/CO₂ byproducts or consume water resources, so the need for water-gas-shift and CO₂ removal stages, along with stock desulfurization and steam generation are eliminated. The energy requirement for methane cracking process (37.8 kJ/mole of H₂) is less than that for steam reforming process (63.3 kJ/mole of H₂).

Microwave (MW) activated natural gas decomposition for H₂ generation produces no CO₂ and requires zero process water, in contrast to the present industrial process – steam reforming. Notably it opens a path for renewable energy storage by coupling electrical energy into chemical bond energy – with H₂ being particularly versatile as fuel or chemical precursor. Moreover, MW activated natural gas decomposition does not require a carbon as catalyst but rather produces carbon. Therein MW driven decomposition of methane achieves green hydrogen production and production of value-added carbon materials. Initial assessment of these carbon materials requires characterization by microscopic and spectroscopic techniques. Illustrative examples of carbon products by high-resolution transmission electron microscopy (HRTEM), Raman and X-ray diffraction will be shown. Complementary thermo-gravimetric analyses assess the oxidative reactivity of the carbon products. Optical diagnostics such as multi-wavelength pyrometry relate these material characteristics to reactor conditions and can be applied for process control.

3. Chemical Analyses

Microwave (MW) processing of carbon feedstocks for aromatic compounds and tars from biochars and coals does not produce CO₂ and requires zero process water, in contrast to the traditional process – via coke ovens. Aromatics and tars are valued chemicals and feedstocks for advanced composites – sought for light weighting transportation vehicles and accompanying energy savings. The MW process produces fast heating resulting in flash devolatilization and pyrolysis followed by fast quenching, preserving the primary pyrolysis products and volatiles' molecular structure. Within the MW generated Ar plasma the entrained carbon undergoes rapid pyrolysis. Multi-wavelength pyrometry of the carbon in the MW reaction zone yields a temperature of ~1200 K. Gas-chromatography mass spectrometry analyses of the process with coal as the hydrocarbon feedstock indicate *stabilization* of the aromatic pyrolysis products due to immediate quenching under inert atmosphere with hydrogenation or methylation in reactive atmospheres containing H₂ or CH₄ respectively. Optical emission spectroscopy identifies atomic and radical species participating in these reactions.

Mechanical Properties of Coal-Plastic Composites with Varying Filler and Coupling Agent Content

Ravinder K Garlapalli, Lakin Phillips, Keerti Kappagantula, Jason P. Trembly, Ohio University, USA

Plastic composites commonly used in outdoor applications, primarily wood-plastic composites, experience a myriad of issues stemming from their tendency to absorb water. Wood is a readily available and low cost filler material, but the issues associated with using wood as a filler require additional additives and make recycling difficult due to wood's low thermal stability. Coal is a readily available alternative filler material, which potentially alleviates issues associated with wood-plastic composites due to its limited water absorption and higher thermal stability. The objectives of this research are to demonstrate the tensile and flexural property behavior of coal-filled thermoplastic composites with varying coal (15-60% w/w) and coupling agent (0.5-3% w/w) content. The composite strength properties of coal-filled thermoplastic composites behaved similar to the wood-plastic composites with increases in filler content. With increase in coal content, the tensile strength decreased and elasticity modulus increased. The coal-plastic composites showed maximum flexural strength at 30% w/w filler content and

slightly decreased, similar behavior reported for wood-plastic composites. Further, surface group analysis of the composite materials is being performed to better understand the interactions between the filler and coupling agent.

Downhole Flexible-Fuel Gasification

Craig Pichach, CleanCarbon Energy Corporation; Donald W. Collins, Western Research Institute, USA

CleanCarbon Energy Corporation (CCEC) is developing an integrated CO₂ capture and low-cost Downhole Flexible-Fuel Gasification (DFFG) system technologies. CCEC leverages drilling technologies and knowhow, and geological expertise from in-situ steam assisted gravity drainage (SAGD) applied to cost-effectively produce and bring Canadian oil sands to market.

In partnership Western Research Institute (WRI) and incorporating a design from the Gas Technology Institute (GTI), CCEC has developed the patent pending Downhole Flexible Fuel Gasifier to enable economic gasification of wet coal and biomass. The technology potential is to lower the cost of gasification by thirty percent (30%) from current gasifier technology.

CCEC' approach entails drilling a well 2000-3000m deep that is then completed in a manner to ease injection of a biomass or coal slurry under supercritical conditions. Supercritical water gasification is used to convert biomass and coal to a hydrogen-rich gaseous product efficiently and cleanly. The produced syngas is returned to surface for conversion into a wide variety of products, including electricity generation.

Key advantages for the DFFG are: (1) in well water gas shift reaction increases hydrogen production; (2) no need to dewater fuel; (4) can handle low rank coals and biomass blend readily; (4) downhole wells reduces surface footprint, capital investment and operating expense; (5) clean stream of CO₂ provides carbon utilization commercial deployment opportunities; and (6) potential for ash to be used as carbon fiber precursor.

SESSION 41

Gasification Technologies: Co-Gasification

Kinetic Study on Co-Gasification of Coal-Biomass Blended Char in an Atmosphere Containing H₂O, CO₂, H₂, and CO: Inhibition and Competition

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Co-gasified coal and biomass offers several advantages including reduction of CO₂ emissions and decreased fossil fuel dependency. Due to the slow reaction rate, char gasification dominates solid fuel conversion. Hence, understanding the mechanisms of char gasification is essential for the design, optimization, and simulation of the gasifier. Several studies, such as [1,2], have investigated co-gasification of coal and biomass-blended char with pure CO₂ and H₂O over the past decade. In a real situation, however, gasification occurs in the presence of H₂ and CO as well as H₂O and CO₂. Therefore, the effects of H₂ and CO on char gasification need to be considered. Also the competition between CO₂ and H₂O for occupation of the active sites and the effect of existence of H₂ and CO on this competition in coal-biomass mixture gasification should be investigated. Some studies, such as [3,4], have considered the effects of H₂ and CO on char gasification, and some studies, such as [5-7], have investigated the effect of co-existence of CO₂ and H₂O on gasification of coal char or biomass char, however, there is no available literature on the gasification of char from a coal-biomass mixture in an atmosphere containing CO₂, H₂O, CO, and H₂. Therefore, this paper reports a study on the co-gasification of coal-biomass blended char with H₂O and CO₂ in the presence of H₂ and CO, at the atmospheric condition using a tube furnace and gas analyzer. In this study, various partial pressures of H₂O, CO₂, H₂, and CO were tested within a temperature range of 825°C –900°C. Chars were prepared from lignite coal, pine apple sawdust, and a mixture of these two with a mass ratio of 1:1. Random pore model was used to interpret the carbon conversion data. The experimental results showed that Langmuir–Hinshelwood (L–H) kinetic equation was applicable to describe the inhibition effect of H₂ on char–H₂O gasification and CO on char–CO₂ gasification. The inhibition effect was stronger in the mixture sample than in the pure samples and for each sample, the inhibition effect was stronger for co-gasification at lower temperature. The kinetic parameters in the L–H equation were obtained and expressed in an Arrhenius equation form to determine pre-exponential factor and activation energy. Using these L–H kinetic parameters, the competition between the char–H₂O and char–CO₂ reactions and the effect of existence of H₂ and CO on this competition was investigated for coal-biomass mixture chars. It was concluded that the char–H₂O and char–CO₂ reactions occurred on separate active sites for all samples whether H₂ and CO were present or not.

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Gasification Reactivity of Coal Char in gasification Syngas at High Temperature

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The gasification reaction is the key step in coal gasification process. And the kinetic study of coal char gasification in the gasification syngas (H₂O, CO₂, H₂ and CO) at high temperature is limited. The inhibition effect of H₂ and CO and a suitable reaction model both need to be studied. The coal char gasification reactivity in gasification syngas was carried out in a fixed-bed tube reactor at atmospheric pressure. The effects of reaction temperature, raw gas composition and coal amount on gaseous products composition and carbon conversion were studied. The experimental results indicate that CO flow rate increases significantly while H₂ flow rate increases a little in the gaseous products. CO₂ flow rate only decreases in the condition of high temperature, high gasification agent concentration and high coal amount. The results reveal that CO₂ gasification reaction rate is much slower than other reaction, and the inhibition effect on CO₂ gasification reaction is significant. The concentration of effected gas (CO+H₂) in the gaseous products was able to increase through the reaction between syngas and coal char and its largest increase was 3.3 percentage points in the experimental conditions. The inhibition effect of CO and H₂ and the competitive effect between H₂O and CO₂ were obvious. The coal char reaction rate in gasification syngas was only 49% and 69% of it in pure gasification agent (CO₂ and H₂O) at 1100 °C and 1300 °C respectively. Because the inhibition effect is very significant, the effect of temperature on gasification reactivity in the gasification syngas is more significant than it in pure gasification agent in the experimental temperature range. The coal reaction rate in 1300 °C is much higher than it in 1100 °C in syngas. The effect of gas diffusion in pores on the gasification reaction rate was obvious in the syngas. The random pore model is suitable for the experimental conditions. However, the volume reaction model and core shrinking model are poor in fitting of data as they ignore the gas diffusion in pores.

SESSION 42 Coal Bed and Shale Gas - 2

Catalytic Combustion of Low Concentration Methane over Supported Bimetallic Cu-Ni Catalysts

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Low concentration methane is widely existed in coal mine ventilation. It's difficult to use due to low and fluctuated concentration of methane. Most of low concentration methane was directly emitted, and cause resources waste and environmental pollution. Catalytic combustion is one of promising way to utilize it. The key of catalytic combustion is to seek efficient catalyst, which can make catalytic combustion of methane more efficiently. For single metal catalysts, the catalytic activity is decreasing as the single phase metal reacting with the carrier at high temperature. In this paper, bimetallic catalyst Cu-Ni/γ-Al₂O₃ has been studied in catalytic combustion of low-concentration methane.

The characteristics of Cu-Ni/γ-Al₂O₃ catalyst in catalytic combustion of low concentration methane were studied experimentally. Both the conversion and the characteristic reaction temperature of the low concentration methane in reaction temperature from 400°C to 650°C and inlet methane concentration from 1% to 3% were investigated. The effects of the ratio of the catalytic metal concentration and calcination temperature on the catalytic activity of methane were discussed. Meanwhile kinetic model was established to analyze activation energy. The catalytic activities of single metal catalyst and bimetallic catalyst were compared.

The results show that when quality ratio of Cu and Ni is 2:1, the catalyst has the highest activity. What's more, the catalytic activity of bimetallic catalyst Cu-Ni/γ-Al₂O₃ is higher than both that of single metal catalyst Cu/γ-Al₂O₃ and Ni/γ-Al₂O₃. In the presence of bimetallic catalyst Cu-Ni/γ-Al₂O₃, the ignition temperature (T₁₀) is decreased from 480°C (for Ni/γ-Al₂O₃) and 450°C (for Cu/γ-Al₂O₃) to 430°C. And the characteristic temperature (T₉₀) has been reduced. The stability of bimetallic catalysts Cu-Ni/γ-Al₂O₃ is similar to the stability of single metal catalysts Cu/γ-Al₂O₃ or Ni/γ-Al₂O₃. The catalyst calcined at 600 °C shows the highest catalytic activity among catalyst calcined at 550 °C~700 °C. The reason is that the catalyst calcined at low

temperature is not steady enough at high temperature while the catalyst calcined at high temperature will interact with carrier for its higher acidity which is get from the high temperature calcination. According to the model established from the experimental data, the activation energy of bimetallic catalyst Cu-Ni/γ-Al₂O₃ (84.39 kJ/mol) is lower than that of single metal catalyst Cu/γ-Al₂O₃ or Ni/γ-Al₂O₃. The reason is that the structure of active sites is changed due to the interaction between Cu and Ni. The pre-exponential factor of the bimetallic catalyst is lower than that of the single metal catalyst, which is related to the number of the active sites.

POSTER SESSION 1 Gasification Technologies

Characterization of Solid Products of Co-Gasification of Coal and Bio-oil

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Biomass pyrolysis liquid (or bio-oil) is difficult for direct utilization due to its high water content and low heating value. One possible way for bio-oil utilization is to prepare coal/bio-oil slurry. This slurry provides higher heating value and can be considered as a partial green fuel since biomass was carbon neutral. The slurry could be used to substitute the commercial coal/water slurry for production of syngas through gasification. The present study provides characteristics of solid products from gasification, which reflects the interactions of bio-oil and coal during gasification. Char and soot were obtained from the pilot-scale entrained flow gasification of bio-oil, sunflower oil, coal/bio-oil slurry, coal/water slurry and coal/sunflower oil slurry at the same conditions. Results show that char and soot obtained from coal/bio-oil slurry gasification contain alkali and alkaline metals which come from bio-oil. The carbon content of solid residuals produce by the gasification of coal/bio-oil slurry is the lowest in comparison with other coal slurries in the present study, which implies that coal/bio-oil slurry is easier to be gasified under the same gasification conditions.

Characterization of the Flowability of Biomass-Coal Blended Powders

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Co-gasification of coal with biomass has been considered as a new research focus of clean coal technology, as well as a novel utilization technology of biomass energy [1]. However, the processing and handling problems related to biomass-coal blended powders, such as arching and blocking phenomena in feeding and pneumatic conveying systems, have severely hampered the widespread applications of the co-gasification technology [2, 3]. Most of the published investigations have been focused on thermo-chemical conversions of biomass-coal blends due to the economic and environmental goal, but little attentions have been paid to the flowability properties of biomass-coal blended powders, and the fundamental understanding of the underlying mechanisms which cause those above-mentioned annoying problems is still lacking [4].

The flowability is the ability of a powder to flow under specified conditions. It is a complex characteristic of a given powder, which is not only an inherent property of the powder but also is highly dependent on its physical properties, such as particle size, particle shape, moisture content and surface roughness of particle material, etc [5-7]. Characterisation of powder flowability has great importance in the consistent operating of powder handling processes and the reliable designing of equipment involved, especially for those mixtures of binary particles whose flowability has not been fully understood. There are a quantity of characterization parameters to evaluate powder flowability, such as angle of repose, Hausner ratio, compressibility index, Carr flowability index and flow function, etc [8-10]. At present, researches on powder flowability are mainly focused on food and pharmaceutical powders, and there are less investigations on the flowability of pulverized coal, as well as biomass powders [11-13]. Furthermore, the researches on flowability of biomass-coal blended powders are basically rarely reported. Qian et al. [14] investigated the differences between biomass powder and pulverized coal, and found that the flowability of biomass-coal blended powders is more complicated than that of pulverized coal. They also found that the pulverized coal particles move faster than biomass powder, as the mass fraction of biomass powder increases, the mean velocity of the particles of blends decreases and the flow stability of the blends decreases. Cui et al. [15] thought that the flow of biomass particles is significantly different from that of smooth spherical particles due to the complex physical properties of biomass, which is worthy of further research. Guo et al. [10, 16, 17] carried out a series of research on the flowability of biomass-coal blended powders and found that needle-shape particles of biomass powders can improve the flowability of viscous pulverized coal in a certain range. They also found that the factors affecting the flowability of the blends are length-width ratio and surface roughness of biomass particles. Guo et al. [18] studied the on the flow properties of the blended particles of rice straw and coal, their research mainly focused on the effects of particle size and mass fraction of biomass powders in the blends. Zulfiqar et al. [4] investigated flow properties of Australian coal and biomass as well as their blends systematically, they found that the flow properties of the coal-biomass blends were dependent upon the

form of biomass, the blends of sawdust and coal could reduce the possibility of flow stoppage, while the blends of woodchips and coal were more susceptible to flow stoppage. It is now commonly accepted that compared with pulverized coal, biomass particles are different in shape, density and material properties, and the flowability of biomass-coal blended powder has its certain particularity. However, the flowability of biomass-coal blended powders plays an important role for reliable dense-phase pneumatic conveying in the co-gasification process, which may not only affects the composition of the synthesis gas, but also the long-period, continuous and stable operation of the gasifier. Therefore, a series of experiments are still needed to characterize the flowability of biomass-coal blended powders, which has important guiding significance for ensuring the stable flow and continuous controllable feeding of biomass-coal blended powders.

In this paper, three kinds of biomass including rice husk, rice straw, and soybean stalk, a kind of typical Chinese pulverized coals (bituminous coal) were chosen as the experimental materials to prepare the biomass-coal blended powders. The flowability parameters were measured experimentally with a powder comprehensive characteristics analyzer. The effects of biomass species, biomass mass fraction and biomass particle diameter on the flowability of the blended powders were analyzed. The research of this paper would provide essential data for the proper design of processing and handling equipment involved in co-gasification process of coal with biomass.

Study on Co-Pyrolysis Impact on Co-Gasification Reactivity of Biomass and Coal Blended Char and Synergy Behavior During Co-Gasification

Xia Liu, Juntao Wei, Yifei Wang, Guangsuo Yu, East China University of Science and Technology, CHINA

In this work, isothermal gasification experiments of coal char, rice straw char and their blended chars with/without undergoing co-pyrolysis were carried out using a thermogravimetric analyzer (TGA). Moreover, physicochemical evolution during coal-biomass co-pyrolysis and coal char-biomass char co-gasification was quantitatively investigated in order to evaluate co-pyrolysis impact on co-gasification reactivity of biomass and coal blended char and synergy behavior during co-gasification. Gasification reactivity comparison between co-pyrolyzed chars and the corresponding blended chars without undergoing co-pyrolysis (i.e. coal char-biomass char mixtures) showed that co-pyrolysis process had inhibition effect on reactivity of subsequent co-gasification. The results of relative reactivity quantifying the co-pyrolysis impact on co-gasification reactivity indicated that the inhibition effect was weakened with increasing gasification temperature and rice straw proportion, which was mainly attributed to weakened promotion effect of co-pyrolysis on order degree and active K transformation of co-pyrolyzed chars with increasing rice straw proportion. Additionally, comparison between experimental and calculated co-gasification reactivity of coal char-biomass char mixtures indicated that synergy behavior during co-gasification was presented as inhibiting effect in initial co-gasification and was converted to synergistic effect at a characteristic conversion, which decreased with increasing rice straw char proportion and decreasing gasification temperature. Active calcium transformation was enhanced in whole process of coal char-biomass char co-gasification and active potassium transformation was obviously inhibited in mid-late co-gasification. Hence, synergy behavior on co-gasification reactivity of coal char-biomass char mixture was synthetically determined by the enhancement of Ca deactivation and the strengthening of K catalysis.

POSTER SESSION 2 Combustion Technologies

Formation Characteristics of Aerosol Particle in Wet Ammonia Desulfurization Process

Jingjing Bao, Licheng Sun, Guo Xie, Jiguo Tang, Sichuan University, CHINA

The environmental pollution caused by energy consumption is a globe issue. A large number of pollutants are generated from fossil fuel combustion, which is the primary source of SO₂ and particles in atmosphere. In order to control SO₂ emission, various flue gas desulfurization (FGD) techniques have been developed and widely applied. In recent years, ammonia-based wet flue gas desulfurization process using ammonia as absorbent has drawn increasing attention as it results in the production of ammonium sulfate without generating any other polluting by-products. However, there are a large number of aerosols generated in ammonia-based WFGD process. Since these aerosol particles are mainly in the submicron range, they cannot be removed by scrubbing action of desulfurization liquid. These aerosol particles can easily escape from WFGD system and enter the atmosphere, which may cause the formation of secondary pollutants by the reactions between aerosol particles and chemical matter in atmosphere. Therefore, it is necessary and urgent to solve the aerosol emission problem during ammonia-based WFGD.

Based on the previous researches, it is suggested that the main components of aerosol particles generated in ammonia-based WFGD process are (NH₄)₂SO₃, NH₄HSO₃, (NH₄)₂SO₄ and NH₄HSO₄, etc. These aerosol particles could be generated by two

possible mechanisms. First, gas-phase reaction between SO₂, H₂O, and gaseous NH₃ volatilizing from desulfurization solution is an important way for the formation of aerosol particles. The submicron particles account for a very large proportion of the aerosol particles generated from this way. The gas-phase reactions are related to the concentration of NH₃ and SO₂ in the flue gas. The concentration of gaseous NH₃ is depended on the concentration of aqueous ammonia (namely the pH value of desulfurization liquid) and the temperature of desulfurization liquid. A higher pH value and temperature of desulfurization liquid is beneficial to the volatilization of gaseous NH₃, leading to the enhancement of NH₃ concentration in flue gas. Correspondingly, aerosol particles generated from the gas-phase reactions enhance significantly. Second, some aerosol particles result from the evaporation and entrainment of desulfurization solution droplets, which is influenced by the temperature of inlet flue gas and desulfurization liquid, and superficial gas velocity, etc. These aerosol particles are mostly larger particles in the micron range.

In this work, a comparative research for the formation characteristic of aerosol particles in ammonia-acid method, ammonia-ammonium sulfate method and ammonia-ammonium sulfite method desulfurization process was carried out. The results reveal that a large amount of aerosol particles generated in the three WFGD processes. The formation of aerosol particles is the most significant for ammonia-acid method, and the ammonia-ammonium sulfite method takes second place. The least formation of aerosol particles is found while using ammonium sulfate as desulfurizer. The formation of aerosol particles increases with liquid-to-gas ratio, pH value and temperature of desulfurization liquid. The enhancement of SO₂ concentration in the inlet flue gas is beneficial to the generation of aerosol particles at a lower pH value of desulfurization liquid. However, the contrary happens for a higher pH value. A small amount of SO₃ in the inlet flue gas would lead to the formation of a large number of aerosol particles. The optimum operating conditions found are as follows: temperature of desulfurization liquid 50℃, mass concentration of desulfurizing agent 10%, liquid-to-gas ratio 10~15L/Nm³, pH value of aqueous ammonia, ammonium sulfate and ammonium sulfite 11, 7.0 and 8.0.

POSTER SESSION 3 Clean Coal and Gas to Fuels

Mesoporous ZSM-5 Supported Ni-Mo Catalysts for Hydrodenitrogenation of N-heterocyclic Compounds

Juan Liu, Wenying Li, Xiang Gao, Zhongyang Luo, Taiyuan University of Technology, CHINA

Deep hydrodenitrogenation (HDN) has become one of the most essential subjects for the clean utilization of coal-based liquid fuels. Mesoporous ZSM-5 with high surface area was hydrothermally synthesized as support of Ni-Mo catalysts by incipient wet impregnation method in order to induce bifunctional properties. The HDN activity of prepared catalysts was examined in a fixed bed continuous flow reactor under different conditions. Quinolone and carbazole were used as model basic and nonbasic nitrogen compounds, respectively, and the objective products were preferred to be cycloalkanes and hydroaromatics, which are considered as ideal components for high performance jet fuel. Previously, the catalysts were characterized by XRD, BET, SEM, XPS, NH₃-TPD and IR spectroscopy of absorbed pyridine. An impressive HDN activity was achieved at the optimum condition due to the improved dispersion of MoS₂ active phase and increased mass transfer of reactants.

Modular Reactors and Process Intensification for Gas-To-Liquid Applications

Fabiana Arias Pinto, Omar M. Basha, Badie Morsi, University of Pittsburgh, USA

Microchannel reactors (MCRs) exemplify significant miniaturization of the physical dimensions and process intensification when compared with conventional industrial reactors, allowing for linear scaleup, flexible manipulations, and substantial capital cost reductions. MCRs have promising applications in Gas-to-Liquid (GTL) technologies, such as the Fischer-Tropsch (F-T) synthesis, particularly for monetizing small onshore and offshore gas fields, which is economically unfeasible with other conventional industrial F-T technologies. Even though MCRs were proposed for commercial implementations and demonstration plans have already been built, adequate literature publications on the use of MCRs in F-T synthesis is scanty and to the best of our knowledge many details concerning the hydrodynamics, mass transfer, heat transfer, and reactor performance are not available.

The overall objective of this study is to investigate the performance and the flow distribution of a MCR, using one-dimensional (1-D) and Computational Fluid Dynamics (CFD) models. A MCR consisting of 50 channels, each packed with 100-micron cobalt catalyst, operating under the low temperature F-T synthesis (500 K and 25 bar) was used to study the reactor performance. The inlet flow distribution was investigated using another CFD model with air at 298 K and 1.01325 bar. A 50-channel MCR was used in this investigation. The modeling results led to the following conclusions:

1. The 1-D model systematically predicted steeper hydrocarbon flow rate profiles when compared with those of the CFD model, however, both models converge to the same values at the channel outlet.
2. For one channel of the MCR, both the 1-D and CFD models indicated that increasing the H₂/CO ratio in the feed increased CO conversion, C₅₊ yield, pressure drop, F-T reaction rate, and the heat transfer requirements. Increasing the inlet syngas velocity decreased CO conversion and increased the pressure drop. Also, increasing temperature, increased the F-T reaction rate, CO conversion and the C₅₊ yield, and decreased the pressure drop. Furthermore, under the conditions investigated, the F-T process in the MCR used was kinetically-controlled.
3. The CFD model used to investigate the flow distribution in the MCR showed that using a flow distributor resulted in a homogenous flow distribution and eliminated the strong gas recirculation.

Stable Supported and Non-Supported Catalysts for Methanol Synthesis from Carbon Dioxide

Mauro Mureddu, Francesca Ferrara, Sotacarbo S.p.A; Elisabetta Rombi, Università di Cagliari; Alberto Pettinau, So-tacarbo S.p.A, ITALY

Because of the continuous increase in the global energy demand, due to growth of population and industrial development, the concentration of CO₂ in the atmosphere has reached approximately 400 ppm in 2016; this is considered the main cause of global warming and climate change. The recent strategic policies to stabilize and reduce CO₂ emissions are promoting research in the field of carbon capture, storage and, more recently, utilization technologies. One of the feasible and attractive strategies is the utilization of waste CO₂ (together with hydrogen from renewable sources) as reactant to produce methanol, since it can be directly used as a fuel additive or a clean fuel, and can be converted to high-octane gasoline or other chemicals (e.g. olefins).

In this scenario, Sotacarbo, within the "Centre of Excellence on Clean Energy" research project (funded by the Regional Government of Sardinia), is developing technologies and catalysts for the synthesis of methanol by catalytic hydrogenation of captured carbon dioxide. This work presents a general overview of the research, with a description of the experimental equipment and the results of the characterization of several kinds of catalysts together with the catalytic performance in terms of conversion and selectivity. In particular, different copper and zinc oxide based catalysts, both supported and non-supported, have been synthesized by different methods. Supported ones have been synthesized as nanopowders by a sol-gel self-combustion method and, to improve the structural-morphological properties, mesostructured SBA-15 silica has been used as the support. To this aim, composite catalysts differing as to their active phase loading and mass ratios, have been prepared through a novel impregnation-sol-gel self-combustion combined strategy. The confinement of the active phase in the SBA-15 structure could enhance its ability to interact with CO₂ and H₂. Moreover, the effect of the ZrO₂ promoter has been evaluated on the final CO₂ conversion performance. Catalysts have been characterized by XRD, TEM, CHN/S analysis and N₂ physisorption in order to correlate the textural and microstructural properties with their performance as CO₂ hydrogenation catalysts. Their activity in methanol synthesis has been determined in a high-pressure automatic bench-scale reactor under realistic conditions (250°C, 30 bar, gas feed: 75% H₂/25% CO₂, by volume) and compared with that of a Cu/ZnO-based commercial catalyst. Both series of prepared catalysts showed good results concerning CO₂ conversion and methanol selectivity. Furthermore, the only liquid products obtained during the reaction are methanol and water, and only a small amount of CO as gaseous product has been detected. These findings reveal that the prepared catalysts partially inhibit the Reverse Water Gas Shift reaction if compared to the commercial one. Additionally, both supported and non-supported catalysts do not show any deactivation during 50 h on-stream.

POSTER SESSION 4 Carbon Management

Continuously Looping Physical Solvent CO₂ Capture Test Facility at NETL

Omar M. Basha, ORISE/U.S. DOE/NETL; Isaac Gam-wo, David Hopkinson, Nicholas Siefert, NETL, USA, Badie Morsi, University of Pittsburgh, USA

Due to the high partial pressure of CO₂ at Integrated Gasification Combined Cycle (IGCC) facilities, the use of physical solvents for CO₂ capture offers the potential for enhanced process operation and superior techno-economic performance compared to chemical solvents. For example, physical solvents have a significantly lower energy penalty associated with removing CO₂ and H₂S [1], and physical solvents also allow for a significant amount of CO₂ to be flashed at higher pressures, thus reducing CO₂ compression costs [2].

Although there are a number of physical solvents which can potentially be used for CO₂ capture from IGCC processes (such as Selexol®, Rectisol®, Purisol® etc.), these solvents vary widely in a number of aspects that affect process performance and economics. Typically, these commercially-available solvents are operated at below room temperature because, at elevated temperatures, these solvents suffer from a

combination of high vapor pressure, high corrosivity, and/or low CO₂/H₂ selectivity [3]. Due to these limitations, these solvent operate below room temperature, and hence they can't be regenerated thermally using waste heat or low grade heat at a power plant. Therefore, there is a need for the development, characterization and assessment of novel physical solvents that can overcome these issues and that can be regenerated using waste heat.

However, there is a distinct lack of experimentally measured values of mass, momentum and heat transfer parameters as a function of industrially relevant, independent design and operational parameters, which significantly hinders the ability to predict the behavior and performance of novel solvent both within an absorption unit and the overall process. Moreover, there is very little prior research addressing commonly occurring phenomena, such as foaming, misting or aerosol formation, which affect the column performance.

To address these issues, a continuously-looping, pre-combustion CO₂ capture test facility is being designed to be built at the National Energy Technology Lab in Pittsburgh, PA. The facility will be used to identify and characterize novel CO₂ capture solvents, with the aim of quantifying solvent performance in terms of solvent stability, CO₂/H₂ selectivity, energy requirements, pressure drop, effect of solvent hydrophobicity and ease of solvent separation. The measured data will be used to improve the prediction abilities of process modeling tools such as AspenPlus by developing empirical correlations and design criteria with the aim of enhancing confidence in such tools for the techno-economic assessment of different solvents. Furthermore, the measured data will be used to help develop Computational Fluid Dynamics (CFD) sub-models and validate CFD simulations of gas-liquid absorption columns through comparison to experimental data measured under relevant industrial conditions.

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Oxygen Enrichment in Ultra-Supercritical Coal-Fired Plants for CO₂-Free Power Generation: A Techno-Economic Assessment

Alessandro Orsini, Alberto Pettinau, Francesca Ferrara, Andrea Porcu, Sotacarbo S.p.A; Vittorio Tola, Giorgio Cau, University of Cagliari, ITALY

Carbon Capture, Utilization and Storage (CCUS) technologies must play a key role for the mitigation of global warming. In general, CO₂ capture technologies can be classified into three main approaches: (1) pre-combustion, (2) post-combustion, (3) oxy-fuel combustion. The main issues that limit the commercial diffusion of CO₂ capture technologies are related to the high capital and operating costs and mostly to the very high energy penalties. At now, post-combustion CO₂ capture technologies by chemical absorption with liquid solvents (amines) are well known and near ready for commercial application, but needs a further optimization to reduce the energy penalties mainly related to solvent thermal regeneration. On the other hand, the industrial-scale experience in oxy-fuel is still not enough to assure the safety of the investment in such a technology. The main drawback for the large-scale deployment of oxy-combustion is the high energy consumption for pure O₂ production in the air separation unit (ASU), which causes a high energy penalty.

A solution which is becoming more and more interesting, in particular for short-term applications, is the so-called partial oxy-combustion, which is a compromise between post- and oxy-combustion approaches. The concept is very easy: being CO₂ partial pressure one of the key parameters which affect the chemical absorption process, primary fuel can be burned in an oxygen-enriched environment in order to reduce the dilution of flue gas by nitrogen, thus improving CO₂ concentration. The ASU for oxygen separation is smaller (which means a lower impact in terms of capital cost and energy penalty) than the same equipment required by oxy-combustion and a flue gas recirculation requires just minor modifications on conventional boilers; in parallel, thanks to the less dilution by nitrogen, the volume of flue gas to be treated is significantly lower and CO₂ partial pressure is higher than conventional post-combustion processes.

This work aims to assess, from both the technical and economic points of view, the performance of partial oxy-combustion power plants (compared with conventional air-blown ultrasupercritical plant with post-combustion capture and full oxy-combustion plants) in order to evaluate in which conditions the technology could be feasible for commercial applications. In particular, the effects of oxygen concentration in the oxidant agent from 21% (conventional post-combustion) to 95% (full oxy-fuel) have been assessed by using a simulation model implemented with Aspen Plus commercial tool and a detailed economic model developed for feasibility studies of power generation plants.

Effect of Apparent Viscosity on the Fluidization and Separation Characteristics in an Air Dense Medium Fluidized Bed

Xueshuai Zhu, Lubin Wei, China University of Mining & Technology, Ping Feng, State Key Laboratory of Multiphase Complex Systems, CHINA

In dry coal beneficiation with air dense medium fluidized bed, the moisture of dense medium would affect the apparent viscosity of fluidized medium, and then change the coal separation performance. In the present work, the apparent viscosity of gas-solid dispersion was measured by using the falling spheres method, and the effect of apparent on fluidization and separation characteristics has been investigated. Results show that the rheology of gas-solid dispersion can be described by Bingham plastic model, and it can be expressed by $\mu_e = \mu + \tau_0 d_0 / 3v_r$. As the increase of moisture in the dense medium, the apparent viscosity of gas-solid dispersion increases. This leads to a larger initial fluidization velocity and possible deviation in separation process, in which case the higher separation efficiency cannot be achieved.

Metallurgical Coal of the United States: GIS Files of Modern and Historical Mining Locations and Geochemical, Rheological, and Petrological Data from Modern Samples

Michael Trippi, Leslie Ruppert, U.S. Geological Survey; Cortland F. Eble, Kentucky Geological Survey; James C. Hower, University of Kentucky, USA

Metallurgical, or coking, coal has been produced in the United States for nearly 200 years. In 2015, the U.S. exported a total of 46,006,859 short tons of metallurgical coal, down about 34 percent from its 2012 peak of 69,875,978 (Energy Information Administration, 2017). Falling coking coal prices from 2012-2015 forced some producers to close mines and (or) go into bankruptcy. A recent upswing in coking coal prices since late 2016 has allowed some companies to reopen mines (Loh, 2017), but others may need to make large capital reinvestments to restart mines that have been closed for several years (Mordant, 2016).

Appalachian, Illinois, and Arkoma basin coking coals are Pennsylvanian in age. New Mexico, Colorado, Utah, Wyoming, Montana, Washington, and Alaska coking coals range from Early Cretaceous through Eocene. The most productive coking coals in the U.S. are found in the Appalachian basin, especially in Pennsylvania, West Virginia, Virginia, Kentucky, and Alabama. Arkansas currently also produces coking coal which is exported to Asia. Other U.S. States (Ohio, Tennessee, Illinois, Oklahoma, New Mexico, Colorado, Utah, Wyoming, Montana, Washington, and Alaska) have produced coking coal in the past, but do not currently produce.

The U.S. Geological Survey (USGS) is preparing an Open-File Report of U.S. coking coal. The report includes maps of coking coal occurrences and mines of both historical and current importance, the history of coking coal mining for these occurrences, and a summary of coal rank, stratigraphy, age, geochemistry, and other coking characteristics of these coals. Geographic Information System (GIS) data files showing coking coal occurrences and mines will be available on the USGS website for download and use by the general public. Coking coal locations from previously published maps were digitized to create these GIS files. GIS files are in shapefile format, with attached metadata describing data sources and processing steps in the creation of shapefiles.

To provide characterization of recently produced coking coals, fifteen new coking coal samples, including seven from Alabama and one from Kentucky (all collected by the Kentucky Geological Survey), three from Oklahoma (collected by the Oklahoma Geological Survey), and three from Arkansas (collected by the Arkansas Geological Survey) were analyzed for geochemistry (including proximate and ultimate analyses; calorific values; major-, minor-, and trace-element abundances; and sulfur forms), rheology (free swelling indices, Arnu-Audibert dilatation, and Geiseler plastometer analyses), and organic petrography. Additional analytical data for 13 Pennsylvania coking coal samples, 55 West Virginia samples, 6 Virginia samples, and one Kentucky sample (all from anonymous coal mining companies) also are included in the report.

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Influence of Gas Compressibility on an Accidental Methane/Air/Coal Dust Fire Scenario in a Coalmine Passage

Elizabeth Ridgeway, Sinan Demir, V'yacheslav Akker-man, West Virginia University, USA

Coalmining keeps experiencing one the highest fatality and injury rates for employees among the industries dealing with flammable gases and explosive dust. To reduce such a high level of risks, novel preventive mining/fire safety strategies have recently been developed by Demir et al. [<http://dx.doi.org/10.1080/13647830.2017.1328129>], who has identified and scrutinized the keys stages of the premixed flame front evolution and quantified its major characteristics such as the flame shape and its propagation velocity, acceleration rate, run-up distance and flamegenerated velocity profile. However, that analysis adopted the approach of incompressible flows, which made it a little far from the practical reality. To fix this discrepancy, in the presented study, the effect of gas compression is incorporated into Demir's predictive scenario of methane/air/coal dust fire in a coalmining passage, for a twodimensional geometry. Among various mechanisms responsible for the flame acceleration such as combustion instability, turbulence, acoustics, and wall friction, acceleration due to a finger-shaped flamefront plays a dominant role in coalmines, because this mechanism is scale-invariant and, thereby, Reynolds-independent. This finger-flame acceleration is very powerful, promoting the flame speed by an order of magnitude. Starting with gaseous fuels, the formulation is then extended to gaseous-dusty flows, with combustible and inert dust as well as their mixture studied. Specifically, the effects of equivalence ratio on the flame evolution, as well as that of the size and concentration of the dust particles, are systematically investigated. It is shown that gas compression generally moderates flame acceleration, and its impact depends on various thermal-chemical parameters. While the effect of compression is minor (yielding 3-5% reduction) for lean and rich flames, thereby justifying the incompressible formulation in that case, it appears significant (up to the reduction of 22%) for near-stoichiometric methane-air combustion, and therefore should be accounted in a rigorous formulation. Furthermore, it is demonstrated that gas compression may control acceleration of slightly-reach flames.

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