



THIRTY - SECOND - ANNUAL  
INTERNATIONAL PITTSBURGH  
**COAL CONFERENCE**

University of Pittsburgh - Swanson School of Engineering

**ABSTRACTS BOOKLET**

**COAL - ENERGY, ENVIRONMENT AND  
SUSTAINABLE DEVELOPMENT**



October 5 - 8, 2015  
Pittsburgh, PA USA  
The David L. Lawrence Convention Center



Hosted By:  
University of Pittsburgh  
Swanson School of Engineering




## A NOTE TO THE READER

This Abstracts Booklet is prepared solely as a convenient reference for the Conference participants. Abstracts are arranged in a numerical order of the oral and poster sessions as published in the Final Conference Program. In order to facilitate the task for the reader to locate a specific abstract in a given session, each paper is given two numbers: the first designates the session number and the second represents the paper number in that session. For example, Paper No. 25-1 is the first paper to be presented in the Oral Session #25. Similarly, Paper No. P3-1 is the first paper to appear in the Poster Session #3.

It should be cautioned that this Abstracts Booklet is prepared based on the original abstracts that were submitted, unless the author noted an abstract change. The contents of the Booklet do not reflect late changes made by the authors for their presentations at the Conference. The reader should consult the Final Conference Program for any such changes. Furthermore, updated and detailed full manuscripts, published in the CD-ROM Conference Proceedings, will be sent to all registered participants following the Conference.

On behalf of the Thirty-Second Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation to Mrs. Heidi Peck, Mrs. Adrian Starke, Mrs. Patricia Park, and Mr. Rob Toplak for their lasting dedication and help to our Conference; and to Ms. Fabiana Arias, Mr. Omar Basha, Mr. Pedro Rosa and Mr. Yongtai Li for their invaluable help and assistance in preparing this Abstracts Booklet.

Thank you,

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

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

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## SESSION 1

### Clean Coal Demonstration and Commercial Projects -1 - DOE Demonstrations Overview, Financial Considerations & Polygeneration with EOR

#### Overview & Status Update of U.S. DOE Major Fossil Energy Carbon Capture & Geologic Storage Demonstration Projects

Thomas A. Sarkus, Nelson F. Rekos, Michael Knaggs, DOE/NETL, USA

This summary presentation will provide an overview of the U.S. Department of Energy's (DOE's) six major carbon capture & geologic storage demonstration projects, which carry a total estimated cost of approximately \$16.5 billion, including U.S. DOE's cost share of approximately \$1.7 billion (11%). The six major demonstration projects are:

- Petra Nova's Advanced Post-Combustion CO<sub>2</sub> Capture Project at NRG's W.A. Parish power plant in Thompsons, Texas. Total estimated cost \$1 billion; DOE share \$167 million (17%). Under construction; anticipated start-of-operations in early 2017; will capture and store 1.4 million metric tons of CO<sub>2</sub> per year in an enhanced oil recovery application.
  - Southern Company's Advanced Transport Integrated Gasification (TRIG)-Based Integrated Gasification Combined-Cycle (IGCC) Demonstration with CO<sub>2</sub> Capture in Kemper County, Mississippi. Total estimated cost \$6.4 billion; DOE share \$270 million (4%). Under construction; anticipated start-of-operations in mid-2016; will capture and store 3 million metric tons of CO<sub>2</sub> per year in enhanced oil recovery applications.
  - Summit Power Group's Texas Clean Energy Project, IGCC-Polygeneration with CCUS near Odessa, Texas. Total estimated cost \$3.5 billion; DOE share \$450 million (13%). Front-end engineering design (FEED) completed, working to achieve financial closure; anticipated start-of-operations early-2019; will capture and store 1.8 million metric tons of CO<sub>2</sub> per year in enhanced oil recovery applications.
  - Hydrogen Energy California Project, Advanced IGCC-Polygeneration with CCS near Bakersfield, California. Total estimated cost \$5 billion; DOE share \$408 million (8%). FEED completed, working to achieve financial closure; anticipated start-of-operations mid-2020; will capture and store 2.6 million metric tons of CO<sub>2</sub> per year in enhanced oil recovery applications.
  - Air Products & Chemicals Steam Methane Reforming with CO<sub>2</sub> Capture Project at a Valero Oil Refinery in Port Arthur, Texas. Total estimated cost \$431 million; DOE share \$284 million (66%). Operations started in December 2012; is capturing and storing 0.93 million metric tons of CO<sub>2</sub> per year in enhanced oil recovery applications.
  - Archer Daniels Midland (ADM) CO<sub>2</sub> Capture from Biofuel Plant in Decatur, Illinois. Total estimated cost \$208 million; DOE share \$141 million (68%). Under construction; anticipated start-of-operations in late-2015; will capture and store 0.9 million metric tons of CO<sub>2</sub> per year in a deep saline geologic formation.
- Several of these major demonstration projects will be covered in greater detail in separate presentations.

#### Considered Insights into Successful Financings of Clean Coal Demonstration and Commercial Projects with Governmental Financial Incentives

Martin Webler, DOE/NETL, USA

While the technical challenges of advancing clean coal technologies are great, the financing challenges for full-scale demonstration and deployment of these technologies are no less substantial. The U. S. Government has created a number of programs that are available to clean coal project developers to help offset the cost of these first-of-a-kind integrations of new technologies into power plant and other industrial plant designs. Clean coal technology deployment has faced and continues to face numerous challenges. From the shale gas revolution that promises abundant, inexpensive and less carbon-intensive energy; to present and forthcoming regulations; to the enticements offered in renewable energy production, clean coal is in heavy competition for scarce investment dollars. Federal government incentives for clean coal technology deployment exist to help bring investment risk down to levels acceptable for private investment. Under the Department of Energy, multiple grant programs were offered along with a loan guarantee program. The Department of the Treasury has implemented several federal income tax incentives such as those for gasification projects, advanced coal projects, and capture and storage of CO<sub>2</sub>; not to mention Bonus Depreciation and the Research & Experimentation tax credit, which are often applicable to clean coal projects. There are numerous examples of projects that made effective use of these grant and income tax incentives. By reminding readers about these incentive programs and relating some of their success stories, clean coal project developers and investors will gain knowledge of critical resources and insights into using them - - insights that could make the difference in their projects' ultimate success.

#### Financing Innovative Advanced Fossil Technology Deployment through the Title XVII Program

Andreas Marcotty, DOE/NETL, USA

The U.S. Department of Energy Loan Programs Office (LPO) administers \$24 billion dollars in loan authority to accelerate the deployment of innovative clean energy technologies through the Title XVII program. The Loan Programs Office (LPO) has issued the Advanced Fossil Energy Projects Solicitation, which makes up to \$8 billion in loan guarantees available to support innovative, advanced fossil energy projects in the U.S. that reduce, avoid, or sequester greenhouse gases. Eligible projects can utilize any fossil fuel and may come from across the spectrum of production and use, including resource development, energy generation, and end use. Fossil fuels currently account for more than 80 percent of U.S. energy production and are projected to remain a significant energy source in the future. As a result, President Obama's Climate Action Plan directed LPO to issue this solicitation to accelerate the commercialization of cleaner and more efficient fossil energy technology. This is an important part of the Administration's long-term plan to achieve a cleaner and more secure energy future as part of its "all-of-the-above" energy strategy.

#### Texas Clean Energy Project Update

Karl E. Mattes, Summit Power Group, USA

The Texas Clean Energy Project (TCEP or the Project) will be a first-of-its-kind integrated gasification combined cycle (IGCC) power plant sited in West Texas's Permian Basin, a hub of energy resource development and sequestration activity. TCEP will integrate for the first time proven gasification and carbon capture technologies to achieve a high carbon capture rate. The Project will capture approximately two million (2,000,000) tons of carbon dioxide annually for enhanced oil recovery (EOR) operations in the Permian Basin and ultimate geologic sequestration.

#### Clean Coal Power Initiative Update: Texas Clean Energy Project, 400 MW Integrated Gasification Combined Cycle Poly-Generation with 90 Percent Carbon Capture

Jason Lewis, DOE/NETL, USA

The Texas Clean Energy Project (TCEP) is a capstone commercial-scale clean coal demonstration incorporating decades of DOE-sponsored technology research and development (R&D) into coal gasification; environmental controls for criteria pollutants and mercury; high-hydrogen-capable combustion gas turbines; and carbon capture and storage (CCS). The facility will be among the cleanest commercial, solid-fuel power facilities in the world and will significantly surpass the emissions reduction targets for 2020 established under the Energy Policy Act of 2005 (EPAct 2005). The facility's emissions will be far below any limits previously permitted in Texas for a fossil-fuel plant, and will meet the EPA's 111(b) Rule for carbon dioxide (CO<sub>2</sub>) emissions. At about 90% carbon capture efficiency, the TCEP's CO<sub>2</sub> emissions on a pound per megawatt-hour (MWhr) basis will be only 20 to 25 percent that of a comparably-sized natural gas combined cycle (NGCC) power plant without CO<sub>2</sub> capture. The integrated gasification combined cycle (IGCC) project is being developed by Summit Texas Clean Energy LLC, a company of Summit Power Group, and will feature Siemens gasification technology and combined cycle power block, and Linde Rectisol® acid gas removal (AGR). The facility will generate a total of about 405 MWe, which will support internal loads and deliver about 200 MWe of the total to the electric grid. The facility is also designed to produce marketable products of urea fertilizer, CO<sub>2</sub>, and sulfuric acid. This presentation will provide background, a status update, and a government perspective on the TCEP.

## SESSION 2

### Coal Mining: Optimization of Mining Operations

#### Industrial Engineering and Productivity Management in Coal Mining and Utilization: A Study with Special Reference to India

Venkata Satya Surya Narayana, Rao Kambhampati, National Institute of Industrial Engineering, INDIA

Industrial engineering is system efficiency engineering and human effort engineering. Its objectives are productivity, employee comfort and health, and increased employee income. Consumers get more goods at less cost and shareholders get more profit due to increase in productivity. Industrial engineering is engineering based management activity of redesigning primarily engineering systems to make them more efficient and profitable. Compared to engineers who specialize in material related issues of their specialization, industrial engineers are concerned with human effort also and design the man-machine interaction from effectiveness and efficiency viewpoints. Industrial engineers also design various productivity devices that are attached to machines and equipment and also optimize processes using mathematics, statistics and operations research. They also focus on reducing production defects and rework. In coal related technologies, in the areas of coal mining and coal utilization in boilers for steam generation etc., industrial engineering was used and productivity improvements were obtained.

In this paper, an attempt is made to review the studies that reported theoretical issues related to application of industrial engineering and productivity management in coal mining and coal utilization through various combustion processes and case studies that reported process improvements in the area. An exploratory study is being done in coal mines related to Coal India Limited and thermal power plants of NTPC Limited and Maharashtra Generating Company to find out the productivity initiatives using industrial engineering and productivity management methods and techniques in the processes related to coal mining and coal utilization in boilers. The findings reported in the study would be useful to develop research agenda for future research in improving the coal mining and utilization technologies to make them more efficient and productive.

### **Indonesian Coal Production Forecasting Using Logistic Curve: Evaluation Based on Coal Basin**

Fadhila A Rosyid, Tsuyoshi Adachi, Akita University, JAPAN

Indonesia has nowadays grown up as an important coal producer in the world. It is ranked the first steam coal exporter in the world since 2009. The development of coal mining industry in Indonesia affect its contribution to total world carbon emission from the coal utilization. To deal with the energy policy and the environmental problem, forecast of coal production is important to formulate policy in energy sectors. However, because utilizations of coal are clearly distinguished by its quality which depends on the mine producing area, to disregard such a producing area it might mislead the policy. In this paper, the coal production forecasting in Indonesia is carried out using a logistic curve under Hubbert Peak Theory. In order to achieve better reality, the drawback of the logistic curve is resolved by forecasting the coal production per its coal basin instead of a country level. The forecasting is carried out in all the seven Indonesian economic coal basins; Ombilin, Bengkulu, Central Sumatera, and South Sumatera Basin in Sumatera Island, and also Tarakan, Kutai, and Barito Basin in Kalimantan Island. The peak production of Indonesian coal is predicted to be around 930 million tons in 2025. Kalimantan Island's coal basin will be depleted faster than Sumatera Island's coal basin. The depletion rate for coal in Kalimantan is predicted between 1.75 – 5.75%, while the depletion rate in Sumatera is estimated to be less than 1.88%.

### **SESSION 3**

#### **Gasification Technologies: Advanced Technologies**

### **Feasibility Analysis of Combined IGCC and Syngas Chemical Looping for Power Generation**

James C. Fisher, DOE/NETL; John E. Plunkett, Noblis, Inc., USA

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

The Ohio State University (OSU) has developed a chemical looping process based on an iron oxygen carrier. Traditional chemical looping utilizes an oxygen carrier to oxidize a fuel and hence reduce the oxygen carrier. The reduced oxygen carrier can then be exposed to steam to partially re-oxidize the carrier and produce high purity hydrogen. The carrier oxidation is then completed in a third reactor via exposure to hot air before being returned to the fuel reactor, thus completing the loop.

This work investigates the feasibility of potentially utilizing this chemical looping process in an integrated gasification combined cycle (IGCC) process. In the IGCC process, coal is gasified to produce synthesis gas. The synthesis gas is converted in the chemical looping fuel reactor to CO<sub>2</sub> and steam. In the syngas chemical looping (SCL) process steam reactor, the reduced oxygen carrier reduces steam to produce hydrogen fuel for the IGCC turbine section. One of the advantages of this technology is that the SCL technology replaces the water gas shift reactor and the downstream CO<sub>2</sub> separation process with a single process; process intensification is generally viewed as favorable in complex systems such as an IGCC plant.

This syngas CL concept has been modeled in ASPEN Plus, and results compared to NETL's Bituminous Baseline IGCC plant with a GE gasifier as a reference plant. The performance model was then sized and a cost analysis was completed using NETL's PSFM financial model to calculate a cost of electricity (COE). Performance parameters were varied, and associated COE's determined to understand the effects of key parameters on COE. These results, with a brief discussion on the model basis and construction, will be presented.

### **Optimization of a Novel CO Conversion Quench Reactor**

Philip Roessger, Konrad Uebel, Bernd Meyer, Institute of Process Engineering and Chemical Engineering, GERMANY

Products based on (coal) gasification, like methanol, SNG, or Fischer-Tropsch liquids have specific requirements to be met by the produced syngas. Typical requirements are e.g. a specific synthesis gas module and high H<sub>2</sub>/CO ratios. The raw gas H<sub>2</sub>/CO ratios out of (dry-fed) high-temperature gasifiers are considerably below 1, whereas required H<sub>2</sub>/CO ratios of products are equal or above 1. The necessary ratio normally is achieved by catalytic water-gas shift reaction (WGSR) in the raw gas treatment process.

A novel partial quenching concept was developed at the IEC to replace conventional full water quench chambers. The novel approach is designed to shift as much raw gas as possible to increase H<sub>2</sub>/CO ratio in order to minimize efforts in the subsequent catalytic WGSR. The homogeneous shift reaction is forced to proceed in the quench vessel in order to achieve a preferably high H<sub>2</sub>/CO ratio by adding steam to a highly controlled flow regime. The designated quench outlet temperature range of 1,173-1,300 K allows subsequent waste heat utilization to produce high and medium-pressure steam. This ensures self-supply with steam of the quench reactor and provides potential to increase the overall process efficiency.

The numerical setup was validated against gasification reactor measurements and simulation, respectively. It was pre-optimized from a numerical point of view in order to reduce computation time. For the design optimization procedure, including mesh manipulation, the generic MOGA-II algorithm with SOBOL sequence was used. Up to four geometric and process parameters like height to diameter (h/d) ratio or amount of steam were considered.

For evaluation, about 1,400 designs (= CFD simulations) were calculated. For the chosen syngas composition, results show a maximum H<sub>2</sub>/CO ratio and an increase compared to initial value at quench inlet. An optimized inner reactor h/d ratio was found for the designated design space without minimization of raw gas outlet temperature. By adding the minimization of raw gas outlet temperature as second target value a second setup was performed. A Pareto front, showing optimal designs, could be obtained.

### **SESSION 4**

#### **Combustion Technologies -Flue gas cleanup**

### **Pulsed Electron Beams Removal of NO<sub>x</sub> and SO<sub>x</sub> from Flue Gas**

Matthew F. Wolford, John D. Sethian, Matthew C. Myers, Frank Hegeler, John Giuliani, Tzvetelina B. Petrova, Brian T. Fisher, H. Douglas Ladouceur, Naval Research Laboratory, USA

Pulsed electron beams have been used to remove NO<sub>x</sub> and SO<sub>x</sub> in a surrogate flue gas mixture representative of effluent from a coal fired power plant. The electron beams are pulsed, using short bursts of energy, as opposed to continuous electron beams, on all the time, used at some pilot plant applications. The pulsed electron beam exposes the entire flue constituents as it moves through the stack and is more efficient in removal of the gas contaminants. It is also expected to have lower capital cost because the high voltage is only on for short durations. The total electrical cost is estimated to a few percent of plant power, based on small scale experiments and the projected efficiency of the electron beam system. The process used by the Naval Research Laboratory does not use reagents or catalysts which reduce capital costs and operating costs for additional emission control.

The Naval Research Laboratory has an ideal test bed, Electra, for pulsed electron beams used in flue gas scrubbing applications. Electra produces pulsed electron beams of 70 nanosecond to 1.5 microsecond pulses at up to five times per second and at voltages that range 200,000 to 600,000 volts, and currents from 20,000 to 100,000 amps. The voltage, integrated power, peak power, pulse length and electron beam size encompass the range of what is required for optimal NO<sub>x</sub> removal. Based on published results, the projected overall efficiency from, wall plug to electron beam energy deposited into the gas, is predicted to be greater than 65%.

The talk will focus on recent results of the Electra pulse power system in the application of removing emissions from a surrogate flue gas. Measurements at the minimum pulse electron beam energy required to remove various contaminants in the flue gas will be discussed. The talk will also discuss the dependence of the electron beam pulse width on removal efficiency. In addition the talk will include an explanation of the pulsed electron beam system, theoretical calculations for comparison to experiments in removing emission species, and discuss the advantages of a pulsed system.

### **Specification of NO<sub>x</sub> Emissions from Combustion of Lignites in a BFBC**

Jan Hrdlicka, Pavel Skopec, Jan Opatril, Czech Technical University in Prague, CZECH REPUBLIC

The paper is focused on discussion of experimental results of NO<sub>x</sub> emission measurement from combustion of two sorts of lignite coals in a bubbling fluidized bed

combustor. Tested fuels were central European lignites (Czech brown coal CBC and German young brown coal GYC) that have a significantly different content of fuel nitrogen. As the bed material was used the native ash of each sort of coal, therefore not expecting any special catalytic effect on the NO<sub>x</sub> formation. Experiments were performed in the pilot scale experimental BFB unit with power load capacity at approx. 350 kW. In the experiments were tested effects of several operational parameters of the fluidized bed combustor on NO<sub>x</sub> formation. To the studied parameters belong effect of nitrogen content in the fuel, effect of oxygen concentration in the bed, effect of bed temperature, effect of air staging and effect of fluidization velocity on the NO<sub>x</sub> formation. The ranges of the tested parameters were chosen to be typical to a normal full scale operation of a BFB. The temperature range was 790-850°C and the oxygen concentration in the bed from 4 to 8 vol. %. The effect of air staging was tested in secondary to primary air ratio 0.5 to 7 and the superficial fluidization velocities of the bubbling bed from 0.5 to 1.2 m/s, which was between the minimum fluidization velocity and the multiple of three. The experiments was carried out in such a way that one parameter was altered while the other were kept constant. From the measured concentrations of the NO<sub>x</sub> were evaluated N-NO conversion factors. Significantly different behaviour of the fuels was found. Although GYC has lower nitrogen content, it turns out to be more reactive and produces higher NO<sub>x</sub> emissions. The biggest correlation of NO<sub>x</sub> production for CBC was found for the effects of air staging and fluidization velocity. With increasing fluidization velocity and lowering the amount of secondary air increase the NO<sub>x</sub> emissions. The strongest effect on GYC's NO<sub>x</sub> productions has the oxygen concentration in the bed. With increasing oxygen concentration increases also the production of NO<sub>x</sub>. The N-NO conversion factor correlation with the oxygen concentration in the bed was found significantly weaker for both coals, however were found at values between 0.05 and 0.4 and it is generally higher for the GYC, even if it has a lower nitrogen content in the combustibles. This relation is not affected by varying the operation conditions.

**Removal of Fine Particles from Flue Gas by Heterogeneous Condensation in WFGD System**

Hao Wu, Danping Pan, Yezheng Jiang, Linjun Yang, Southeast University, CHINA

A novel process is proposed to improve the removal of fine particles by heterogeneous condensation during limestone-gypsum desulfurization system from the flue gas. The supersaturation environment is achieved in the SO<sub>2</sub> absorption zone by means of flue gas humidification at the inlet of WFGD system, which is achieved by spraying water evaporation at inlet of electrostatic precipitator (ESP) and installing a low-low temperature heat exchanger at WFGD inlet. The numerical calculation results indicate that the supersaturation vapor environment can be obtained in the SO<sub>2</sub> absorption zone during this process. The fine particles in flue gas are activated in supersaturation vapor environment and act as nucleation centers to grow up to droplets, and the condensation grown droplets are then removed by the desulfurization liquid and a high-efficiency demister. The influences of the relative humidity and temperature of WFGD inlet flue gas on the removal of fine particles are investigated in this paper. The results show that inlet flue gas with high relative humidity can promote the removal of fine particles, the performance of the WFGD system for removal of fine particles can be significantly improved by this novel process, and the removal efficiency of WFGD system can be improved 40-50%.

**SESSION 5**

**U.S. EPA's Coalbed Methane Outreach Program (CMOP) Coal Mine Methane Conference Track: General -1**

**California Cap-and-Trade Panel Session #1:**

**Coal Mine Methane Destruction in the California Compliance Offset Market: Introduction to the California Compliance Offset Program**

David Antonioli, Verified Carbon Standard (VCS); Michael Coté, Ruby Canyon Engineering, USA

The Verified Carbon Standard (VCS) and Ruby Canyon Engineering propose to organize a series of discussions focusing on the California market for mine methane capture and destruction offsets under the State's cap-and-trade program for reducing greenhouse gas (GHG) emissions. We envision three separate panels, each addressing one of the following topics. With input from U.S. EPA Coalbed Methane Outreach Program, VCS will identify and recruit speakers for each of the panels.

1) Introduction to the California compliance offset program. This session will set the stage for the following two panels by outlining a number of key elements of the California cap-and-trade program including: the role of offsets in meeting the compliance requirements of the program; pertinent details of the Compliance Offset Protocol for Mine Methane Capture Projects; and the administrative infrastructure for verifying and facilitating the delivery of eligible offsets into the compliance program. Structure/Timing. This session will provide clear and concise information, with three main speakers (ARB, VCS as an Offset Project Registry, and Ruby Canyon Engineering as a verification body) addressing the thinking behind the cap-and-trade

program and the infrastructure that has been established to support it. After each speaker, the audience will be given a chance to ask questions. This session will require 60 minutes.

**U.S. Climate Action Plan: Strategy to Reduce Methane Emissions – Approach for the Coal Mines Sector**

Pamela Franklin, Environmental Protection Agency, USA

Methane is a short-lived climate pollutant, with an atmospheric lifespan of about 12 years. It is the second most prevalent manmade greenhouse gas after CO<sub>2</sub>, and is 28 times more effective at trapping heat in the atmosphere than CO<sub>2</sub>. Coal mines, and particularly underground coal mines, are among the largest sources of anthropogenic methane emissions accounting for 8 percent of global emissions. Within the United States, coal mine methane (CMM) emissions are expected to remain level in coming years, but worldwide CMM emissions have been growing and are expected to continue their upward trajectory through 2030. This will largely be driven by economic growth in emerging countries. Reducing CMM emissions has become an important domestic and international policy priority over the last 25 years. In addition to the environmental benefits of reducing greenhouse gas emissions, recovery and use of methane from coal mines enhances mine safety and presents enormous energy potential. The Environmental Protection Agency (EPA) is leading many of the U.S. Government's domestic and international climate initiatives, and with respect to coal mine methane EPA is committed to working with the U.S. and global coal industry stakeholders to foster greater CMM recovery and use. The Agency's work is carried out through two programs, the Coalbed Methane Outreach Program (CMOP) and the Global Methane Initiative (GMI). CMOP is a voluntary program whose mission is to promote the profitable recovery and use of CMM by working cooperatively with coal companies and related industries. Since its inception in 1994, CMOP has provided technical assistance to U.S. mines through pre-feasibility and feasibility studies evaluating the technical and economic merits of CMM and VAM projects, supporting policy analysis and development, and publishing tools to build the capacity of the coal industry and other stakeholders to implement CMM projects. The GMI, launched in 2004, is a voluntary, international effort of 42 countries and the European Commission to specifically target mine methane abatement, recovery, and use in five economic sectors, including coal mining. It promotes cost-effective, near-term methane recovery through partnerships between developed and developing countries, with participation from the private sector, development banks, and nongovernmental organizations. Both programs have been bolstered by the adoption of the U.S. Climate Action Plan, and in particular, the Strategy to Reduce Methane Emissions. This paper will further explore the role of CMOP in reducing domestic CMM emissions and the GMI in reducing international emissions, identify the critical project and policy tools used by both initiatives to achieve these goals, outline the role of the U.S. Climate Action Plan, and discuss the future roles for CMOP and GMI.

**SESSION 6  
Coal Science: General - 1**

**De-Sulfurization of Some Brazilian Power-Coals by Low Energy Ultrasonication**

Matheus S. Civeira, Luis F.O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North-West University, SOUTH AFRICA; Binoy K. Saikia, CSIR-North East Institute of Science & Technology, INDIA

In the present paper a report of an attempt of using low ultrasonic energy to clean some Brazilian coal samples in the presence of H<sub>2</sub>O<sub>2</sub> solutions is presented. All the forms of sulphur and mineral matter (ash) from the coal samples were removed by this process. The raw and ultrasonicated coal samples were characterized by chemical analysis, Fourier Transformation Infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), focused ion beam (FIB), high-resolution transmission electron microscope (HR-TEM) with selected area electron diffraction (SAED) and/or microbeam diffraction (MBD), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectrometer (EDS), and Thermogravimetry-Differential scanning calorimetric (TG-DSC) techniques to evaluate the clean-coal quality. The FT-IR spectroscopic analysis demonstrated the formation of oxidized sulphur species (S=O and -SO<sub>2</sub>) and their subsequent removals after ultrasonication. The XRD profiles supported the removal of some minerals from coals including their de-ashing. The TG-DSC profiles of the beneficiated coals revealed their improved quality for using in thermal plants with better combustion efficiency.

**Briquetting of Non- and Poor-Baking Hard Coals for its Usage in Smelting Reduction Processes under Consideration of Blending and Curing Effects**

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The production of stable briquettes from hard coal fines by briquetting with means of binder is a chance to make these hard coal fines feasible for feeding into smelting reduction processes like COREX® and FINEX®. In laboratory tests the several main influencing parameters, e. g. briquetting pressure and temperature as well as binder type and amount, were systematically varied and analyzed to find optimized values regarding the required briquettes quality. Therefore the special properties of each single coal have to be considered.

Besides the optimization of the central briquetting process it is possible and also necessary to further increase the strength and quality of the briquettes as well as their suitability for storage by using the post-processing method of "Curing" which means the post-hardening of film-type binder bonded briquettes by treating them in a drying cabinet at defined temperatures and over scheduled durations. The achieved effect is a hardening of the binding system which leads to increased crushing strengths but at the same time to an increasing brittleness which reduces the shatter strength of the briquettes. That is the reason why it is necessary to find the best curing conditions to increase the crushing strength by minimization of the embrittlement of the briquettes. Therefore systematic investigations by using different curing temperatures in a range between 100 °C and 180 °C and durations in the range between 15 minutes and 2 hours have been done. The briquettes were produced from typical COREX®/FINEX® hard coals from deposits in Australia and South Africa with the film-type binder polyvinyl alcohol and molasses in co-operation with calcium hydroxide. The tested coals show especially in combination with the polyvinyl alcohol a positive effect of the curing process by using a medium level temperature around 140 °C and maximal curing durations of about 1 hour.

But for some coals, which are relative hard and have an increased brittleness, curing can't increase the briquettes quality in the required range. This leads to the pre-processing method of blending of coals to use synergetic effects of a hard and brittle coal together with a more smooth coal as well as the properties of non-baking coal and poor-baking coal. Therefore also systematic investigations have been done which show that blending can help to increase the strengths and the quality of the briquettes.

The quality of the briquettes is determined by using typical mechanical strength tests like crushing strength, abrasion strength and shatter strength. Besides the strength of briquettes before and after curing the mechanical strength of the solid residue after carbonization is also tested and gives first information about the process behavior of the briquettes in a COREX®/FINEX® melter-gasifier. In addition to these macroscopic quality determinations the changes of the microscopic briquettes structure after briquetting, curing and also thermo-chemical exposure are investigated by spectroscopic methods to see modifications of the binding system which could be one reason for changes in the briquettes strengths.

#### **Manufacturing of Briquettes from Typical Highveld Coal Fines Using Various Binders**

Frans Waanders, Nthabiseng Modiri, John Bunt, Hein Neomagus, North-West University, SOUTH AFRICA

South Africa produces a large amount of coal fines, which occupy a vast amount of land, which poses enormous economic and environmental implications. To utilize agglomerated fine coal is becoming an important issue for use in operations such as gasification. From previous experience the binderless briquetting of inertinite-rich, high ash coal produced briquettes that were less water resistant and mechanically weaker compared to vitrinite-rich briquettes and thus the need arose to briquette inertinite-rich fine coal by using a suitable binder to reduce the briquetting pressing temperatures and pressures.

In this study, eleven binders such as 2 clays, bio char, cow dung, lignosulphonate, kraft lignosulphonate, paraffin, polyester resin, wax and two 2 South African coal tar pitches were mixed in a concentration of between 0 and 10 wt.% with the inertinite-rich, high ash coal. The cured (cured at 100 °C for 3 hours) and uncured, briquettes were compared to each other by means of compression strength, drop test and a water submersion test. It was found that the uncured bound briquettes and the binderless briquettes yielded a similar, 1.0 MPa, compressive strength. The binderless, cured briquette showed an average compressive strength of 5.0 MPa. The briquettes bound with the lignosulphonate and resin yielded the highest compressive strengths of 16 and 12 MPa respectively at a 7.5 wt. % binder concentration. All briquettes (with and without binder addition) retained their shape and size during drop tests and none of the briquettes proved to be water resistant; hence paraffin was used as a waterproofing agent after pressing and curing. Inertinite-rich coal briquetting with the use of a suitable binder shows promising results and substantiates further investigation for industrial application.

#### **The Influence of Lignin Sulfonate as a Binder for Fine Coal Pellets**

Christien A Strydom, T.S. Mthombo, J.R. Bunt, North-West University, SOUTH AFRICA

The microscopic constituents of coal are called macerals which are identified microscopically by their form and reflectivity and can be divided into vitrinite,

inertinite and exinite. The different macerals have the different utilization. Because of the immature technology of separation, the macerals isn't exploited effectively. Froth flotation is considered the most potential method to industrialize, but complicated surface properties of coal and little differences of the surface of macerals make flotation separation of macerals difficult. This paper focus on the study of methods for the separation and concentration of coal macerals, using a selective flocculation to strengthen the flotation separation process, thus improving the effect of maceral separation. The influence of the types and dosage of collectors and flocculants on flotation separation of macerals was explored. The mechanism of flocculation on the maceral flotation separation was revealed though tests like surface wettability, surface zeta potential, sedimentation etc. The results showed that selective flocculation can improve the effect of maceral flotation separation effectively. And the results of flotation separation were divergent when a different flocculant or collector was used. According to the differences of surface properties of vitrinite and inertinite, a suitable type and dosage of reagents was the key of maceral flotation separation. The floatability difference between vitrinite and inertinite can be magnified with the selective flocculation. The inertinite which has a stronger surface wettability, developed pore and electronegativity is more likely to be influenced by the cationic flocculant thereby reducing the floatability.

### **SESSION 7**

#### **Clean Coal Demonstration and Commercial Projects-2 - CCS Processes: Pre-Combustion, Post-Combustion & Oxy-Combustion**

##### **Polish Way of Managing Coal-Based Energy Sector alongside EU Policy**

Jan Antończyk, ENERGOPROJEKT-KATOWICE SA and AGH University of Science and Technology, POLAND

Polish energy sector has traditionally been based on coal. More than 80% of total electricity produced in the national power system is generated from hard coal and lignite. Poland is also the ninth biggest coal producer in the world. The future of Poland's coal-based power plants depends on global market fuel prices, economic efficiency of Polish coal mining, as well as EU regulations.

In line with conclusions of the climate and energy package agreed in October 2014, CO<sub>2</sub> emissions in EU should be reduced by 40% in comparison to 1990 level by 2030. This is the mid-point goal included in the Road Map 2050, aimed at reducing CO<sub>2</sub> emission by 50% by 2050. Polish government still has not supported radical declarations given in the Road Map 2050, as heavy economic consequences of such declarations would cause a severe threat for economic development. It seems probable that the agreement on indispensable offset connected with CO<sub>2</sub> reduction in countries with abundant coal resources still is not reachable. Without such agreement, however, decrease of CO<sub>2</sub> levels planned in Road Map 2050 will not be possible in some countries.

Currently total electrical power installed in Polish national power system is almost 40 GWe, therein ca 30 GWe in coal-fired power plants. The share of electricity generated from coal decreased from 97% in 1990 to approx. 84% in 2014, but at the same time production of electricity from coal slightly increased, from 132 TWh in 1990 to 134,5 TWh in 2014. Total generation of electricity counts for ca 160 TWh, while it is expected that demand in 2050 will reach 250 TWh. Ca 30% of power installed in Polish national power system is generated in coal units built in 60. And 70. This means that Poland needs both modernization of older power plants and new capacity.

As Polish indigenous resources of hard coal and lignite are an important energy safety stabilizer main investments in new capacities are basing on this source.

Several major projects are now in progress: two 900 MWe units in Opole Power Plant (hard coal), 1075 MWe unit in Koźmice Power Plant - the biggest unit of this typ in Europe (hard coal), 910 MWe unit in Jaworzno Power Plant (hard coal) and 450 MWe in Turów Power Plant (lignite).

All this supercritical units are basing on modern technologies (including carbon capture ready) enabling to follow environmental regulations.

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

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

The Kemper County IGCC plant is a lignite-fueled 2-on-1 Integrated Gasification Combined-Cycle (IGCC) facility incorporating the air-blown Transport Integrated Gasification (TRIG™) technology jointly developed by Southern Company; KBR; and the United States Department of Energy (DOE) at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. The plant is owned by Mississippi Power Company (MPC) and has a calculated nameplate capacity of 830 MW with a peak net output of 582 MW. Incorporating advanced emissions-control equipment, the facility is designed to produce marketable products of ammonia, sulfuric acid, and carbon dioxide. Over 65% of the carbon dioxide will be captured and used for enhanced oil recovery (EOR), making the Kemper facility's carbon emissions comparable to those of a natural gas-fired combined cycle power plant. The Kemper County project team is currently completing the last phase of construction for the plant and startup

commissioning activities are underway. The facility's Commercial Operation Date (COD) is set for the second quarter of 2016. This presentation will provide both background and a status update for the Kemper County IGCC project.

#### **Petra Nova Carbon Capture & Sequestration Project Construction Update**

Ted McMahon, DOE/NETL; Tony Armpriester, Petra Nova, USA

Petra Nova Parish Holdings, LLC, (Petra Nova) is currently overseeing design and construction a commercial-scale post-combustion carbon capture system (CCS) that will capture at least 90% of the carbon dioxide emissions from a 240 MW slipstream taken from Unit 8 at the coal-fired W.A. Parish Generating Station located southwest of Houston, Texas.

Petra Nova is a joint venture between NRG Energy and JX Nippon Oil and Gas Exploration, who are the Project Sponsors and Owners. The U.S Department of Energy is providing \$167 million in financial assistance to the project. Petra Nova has contracted with Mitsubishi Heavy Industries America (MHIA) and The Industrial Company (TIC) to provide engineering, procurement and construction services. MHIA is the carbon capture technology provider and TIC, a subsidiary of Kiewit, is responsible for the balance of plant (BOP) engineering and is the overall constructor of both the BOP and CCS facilities.

The project is designed such that the host power generation unit will not be derated because the power and thermal energy required to operate the carbon dioxide capture and compression system will be provided by a cogeneration plant comprised of a combustion turbine with a heat recovery boiler. Up to 5,265 tons per day, or approximately 1.6 million tons per year, of carbon dioxide will be captured and transported via a newly constructed 81-mile long pipeline to the West Ranch oil field where it will be used in enhanced oil recovery operations and ultimately sequestered. The Project is in the detailed engineering, procurement and construction phase and is scheduled for completion in the 4th quarter of 2016. The focus of this presentation will be to update the status and progress of construction activities of this first-of-a-kind, commercial scale, carbon dioxide capture and sequestration project

#### **Pre-, Post- and Oxy-Combustion Approaches to Mitigate CO<sub>2</sub> Emissions: Techno-Economic Comparison**

Giorgio Cucca, Francesca Ferrara, Alberto Pettinau, Sotacarbo S.p.A.; Giorgio Cau, Vittorio Tola, University of Cagliari, ITALY

Worldwide energy production requirements could not be fully satisfied by nuclear and renewables sources. Therefore a sustainable use of fossil fuels (coal in particular) will be required for several decades. In this scenario, carbon capture and storage (CCS) represents a key solution to control the global warming reducing carbon dioxide emissions. Currently, the integration between CCS technologies and power generation plants has not been demonstrated yet at commercial scale; therefore, technological risks, which enhance the already significant cost, represent the main near-term barrier to commercial diffusion of CCS. With the aim to comparing them and to estimate the current potential application of CCS technologies, this study reports a performance assessment of different coal-fired power generation technologies. In particular, different plant configurations including (i) integrated gasification combined cycle (IGCC) with pre-combustion capture, (ii) ultra-supercritical (USC) combustion with postcombustion capture and (iii) oxy-coal combustion (OCC) have been compared from both the technical and economic points of view. Each power generation technology has been analysed with reference to both the conventional configuration (without CO<sub>2</sub> capture and storage systems) and the more complex configuration with integrated CO<sub>2</sub> removal sections, considering a reference thermal input of 1000 MW. As for CO<sub>2</sub> storage, the sequestration in saline aquifers has been considered, being this technique characterized by the higher storage capacity in Italy. Performance assessment has been carried out by using simulation models implemented through commercial tools, such as Aspen Plus and Gate Cycle. On the other hand, the economic assessment has been performed through a detailed simulation model, properly developed by Sotacarbo for feasibility studies on CCS power generation plants. The model estimates the annual cash flow and the main typical indicators (such as net present value, internal rate of return, and cost of electricity) on the basis of plant performance and economic parameters. The integration between technical and economic simulation models allows a detailed feasibility assessment. Being the economic assessment strongly influenced by the fluctuation of several parameters (mainly the prices of both electrical energy and CO<sub>2</sub> allowances, governed by local and international markets), a sensitivity analysis has been carried out to estimate the impact of these parameters on plant economics. The analysis shows that USC plants are less expensive than IGCC in their basis configuration (without CCS), whereas the costs of the same power generation technologies equipped with CCS configurations are comparable. Moreover, in a short term future, oxy-fuel promises to become one of the most competitive technologies for a CO<sub>2</sub>-free power generation

#### **Advanced Supercritical Coal Generation with Carbon Capture & Storage: Location Comparisons in the Eastern Interconnect**

Joel Theis, DOE/NETL, USA

By 2025, the average age of coal generators in the Eastern Interconnect (EI) will be about 50 years, with about 120 GW aged 60 years or older. Coal-fired generation is projected to supply 30%-35% of electricity demand in the U.S. beyond 2040. This study compares operational and cost characteristics of advanced ultra super-critical pulverized coal (A-USCPC) in different locations in the Eastern Interconnection (EI) to assess whether there are significant advantages to locating a new A-USCPC plant with CCS capabilities in different areas of the EI. Break-even capital costs are determined for A-USCPC with CCS (A-USCPC/CCS) in each of the RTO systems at different mitigation levels. New A-USCPC generation are located in areas where existing coal plants are expected to retire and carbon storage has potential. The revenue flows to each plant from 2025 through 2030 are obtained from a production costing model and extrapolated for cash flow projections. Each RTO system is represented with sufficient wind to meet renewable resource standards (RPS) to simulate the A-USCPC/CCS units in a relatively high natural gas and renewable resource environment. Natural gas prices are included at the AEO 2015 Reference case forecasted level, and levels at which A-USCPC with CCS can be viable in each region. CO<sub>2</sub> mitigation for A-USCPC with CCS is assessed at different mitigation levels up to 90 percent. Findings suggest that, in order to maintain sufficient coal capacity, demand for natural gas and natural gas combined cycle (NGCC) generation will need to be balanced with tax credits for A-USCPC/CCS.

#### **SESSION 8**

#### **Coal Mining: Environmental Technologies for Mining**

#### **International Standards Development under ISO TC-82 Mining With A Focus On Equipment, Safety, Mine Reclamation, & Reserve Estimation**

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

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

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

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

Most significant is scope of work item number 3, which is designed to integrate the existing US (SEC Guide 7), Canadian (CN 43-101), and Australian (JORC) methods for determining mineral reserves. Future work is expected to include CMM/VAM and UCG. Current participating member nations include Germany, China, Finland, Iran, South Korea, Russian Federation, South Africa, Spain, Sweden, and the United Kingdom. The main focus of the paper will be to share and update the US TAG progress and to solicit expert participation.

#### **An Analysis of Scientific Investigations related to Reclamation of Coal Mines with Coal Combustion By-Products**

Kimery C. Vories, E-Ternion: Energy, Environment & Economy, USA

In the United States, the placement of Coal Combustion By-Products (CCBs) (i.e. fly ash, bottom ash, boiler slag, flue gas desulphurization (FGD) material, and fluidized bed combustion (FBC) material) in coal mines has been an area of significant controversy. The Federal and State governments, universities, National Energy Technology Laboratory (NETL), and industrial research organizations have taken an active role in encouraging and promoting technological advances, research, and technology transfer related to the use of CCBs at coal mines. CCBs have been placed at Surface Mining Control and Reclamation Act (SMCRA) permitted mines since 1977 for the purposes of: (1) a seal to contain acid forming materials and prevent the formation of acid mine drainage; (2) an agricultural supplement to create productive artificial soils on abandoned mine lands where native soils are not available; (3) a



flowable fill that seals and stabilizes abandoned underground mines to prevent subsidence and the production of acid mine drainage; (4) a construction material for dams, roads, or other earth like materials where such materials are needed as a compact and durable base; (5) an alkaline additive used to physically and chemically stabilize coal refuse during disposal; and (6) a non-toxic, earthlike fill material used to achieve approximate original contour for final pits and within the spoil area.

In 2003, Congress directed the U.S. Environmental Protection Agency (EPA) to commission an independent study of the health, safety, and environmental risks associated with the placement of CCBs in active and abandoned coal mines in all major U.S. coal basins. As a result, in September 2004, the National Research Council (NRC) established the Committee on Mine Placement of Coal Combustion Residues and charged it with conducting the study. In March 2006, the committee published its findings in a report titled "Managing Coal Combustion Residues in Mines." The NRC committee concluded that placing CCBs "in coal mines as part of the reclamation process is a viable management option as long as: (1) CCB placement is properly planned and carried out in a manner that avoids significant adverse environmental and health impacts; and (2) the regulatory process for issuing permits includes clear provisions for public involvement." The NRC committee further recommended that "enforceable Federal standards be established for the disposal of CCBs in minefills." On March 14, 2007, the Office of Surface Mining Reclamation and Enforcement (OSMRE) published an advance notice of proposed rulemaking (ANPRM) in response to the NRC report (72 FR 12026-12030). OSMRE requested comments on how it should implement the recommendations in the NRC report. Specifically OSMRE requested comments on how the regulations implementing Titles IV (abandoned mines) and V (active mines) of SMCRA to regulate the placement of CCBs should be revised. OSM received a wide variety of information and opinions from interested parties in response to this request.

This paper will examine the findings and provide an analysis of a wide range of scientific investigations that have evaluated the environmental impacts of this placement for the last three decades. It will also evaluate the findings of the National Resource Council (NRC) is their 2006 investigative report completed and evaluate its merits as potential evidence for or against the development of additional rulemaking either at the State or national level. It will make a recommendation on the necessary scientific and regulatory investigation that should be conducted by the Federal government prior to any additional Federal Rulemaking.

**SESSION 9**  
**Gasification Technologies: General-1**

**Pilot-Scale Demonstration of Advanced Hydrogen and CO<sub>2</sub> Separation Membrane Technology**

Joshua J. Stanislawski, Scott G. Tolbert, Tyler J. Curran, Michael L. Swanson, Energy & Environmental Research Center, University of North Dakota, USA

In order to facilitate the use of hydrogen in integrated gasification combined-cycle (IGCC) applications or as a transportation fuel, hydrogen-from-coal technologies that are capable of managing carbon will be needed. Many technologies are under development for the separation of hydrogen from coal-derived syngas, and among the most promising are hydrogen separation membranes. Studies indicate a significant IGCC plant efficiency increase can be realized if warm-gas cleanup and hydrogen separation membranes are used in place of conventional technologies. These membranes provide the potential to produce hydrogen while simultaneously separating CO<sub>2</sub> at system pressure. Membrane development to date at the Energy & Environmental Research Center (EERC) has taken place with small single-tube separators on coal-derived syngas to determine the impact of coal-derived impurities on membrane material. Gasification syngas typically has many impurities that, if not removed, will poison most hydrogen separation materials. In order to move this promising technology closer to commercialization, the EERC is installing pilot-scale warm-gas cleanup equipment that will enable demonstration of membranes at a 0.5-MWth scale. The EERC has partnered with Praxair, Inc., the U.S. Department of Energy, the University of Wyoming, and the State of North Dakota to test pilot-scale membranes for separating hydrogen and CO<sub>2</sub> from coal gasifier syngas streams. Membranes capable of separating 100 lb/day H<sub>2</sub> will be tested on a coal gasifier at the EERC's test facility. This will represent one of the largest demonstrations ever performed on hydrogen and CO<sub>2</sub> membrane separation technology using coal-derived syngas. Praxair will provide the pilot-scale membrane that will be tested on syngas produced in the EERC's pilot-scale transport reactor integrated gasification (TRIG) system. A fixed-bed water-gas shift catalyst will be used to maximize the hydrogen and CO<sub>2</sub> content in the syngas and minimize CO. The EERC's TRIG system operates at 120 psig; therefore, a compressor will be used to compress the syngas to up to 500 psig before separation in order to represent pressures observed in commercial gasification systems. The EERC will also employ fixed-bed desulfurization sorbents to remove sulfur to single-digit ppm levels while maintaining the syngas at elevated temperature. The overall goal of the project is to conduct a pilot-scale demonstration of coal-to-hydrogen production technology using warm-gas cleanup techniques and Praxair's hydrogen separation membrane. This presentation will review the

specifications for the warm-gas cleanup system and provide preliminary results from the membrane separation testing.

**Technologies to Mitigate Syngas Cooler Plugging and Fouling**

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

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

**Aspects of Chemical Quenching of Raw Gas From Entrained Flow Gasification**

Patrick Fertl, Rainer Reimert, Karlsruhe Institute of Technology, GERMANY

Entrained flow gasification at temperatures above 1200 °C produces a clean raw gas without organic contaminants while reducing the cold gas efficiency. The efficiency could be increased by applying direct quenching through endothermic reactions of an injected carbon based secondary fuel with H<sub>2</sub>O and CO<sub>2</sub> of the raw gas. Aim of this study is to determine a suitable secondary fuel, the governing chemical reactions and a reactor configuration for a technical application. The main process performance indicators considered are the cold gas efficiency of the gasification and the organic impurities of the produced raw gas. In principle, pyrolysed biomass, such as straw or wood derived char, is considered a suitable secondary fuel as it is reactive and rich in carbon. However, the nature of the original biomass and its pyrolysis conditions determine the char's gasification properties. CO<sub>2</sub> reactivity screening experiments of 6 chars showed that straw derived char is much less sensitive to the pyrolysis conditions than the tested wood chars, and, in general, straw char also reveals a higher reactivity. Both these findings are linked to the catalytic activity of the ash, especially to the surface bound potassium, which is a well known catalyst for carbon gasification. However, this becomes volatile when exposed to high temperature. To determine the gas composition and especially the production of organic compounds the kinetics of the secondary high temperature pyrolysis of a wood and a straw derived char were measured by drop tube reactor experiments. The pyrolysis reaction mechanism proposed by Shafizadeh was applied to evaluate the experimental results. The kinetic parameters of the pyrolysis reactions are in good agreement with literature values scarcely reported for the given conditions. However, it was found that the degradation reactions of the organic pyrolysis products of straw char are inhibited by volatile ash components, which resulted in an apparent negative activation energy near zero. The parameters found for the wood char degradation reaction are comparable to literature data. The obtained kinetic parameters for the Shafizadeh reaction mechanism and literature values for the H<sub>2</sub>O and CO<sub>2</sub> gasification reactions were applied to model and simulate an endothermic second stage (quench) gasifier. The gasifier model consists of an entrained flow injection part modeled as PFR and a subsequent conical, low density fluidized bed reactor treated as CSTR. The model accounts for mass and heat transfer between the two phases solid and gas as well as for heat exchange with the reactor wall, in addition to the chemical reactions. For the simulations the gasification conditions and the design parameters of the reactor configuration were varied. As a result of this parameter variation it can be concluded that the performance of the secondary quench gasification is mainly governed by the pyrolysis reactions releasing organic compounds as well as H<sub>2</sub> and CO from the biomass derived char. To keep the organic impurities at acceptable levels the ratio of secondary fuel feed to raw gas flow must be kept at a minimum and the secondary fuel needs to be kept at a defined particle size. The parameter significantly increasing the gasification rate and the cold gas efficiency is elevated pressure. Critical for the performance of the secondary gasification is an initially high raw gas temperature above 1300 °C. In the paper the experimental setup and the developed model will be presented as well as the obtained results will be discussed.

**Microwave-Assisted Steam Gasification of Low Rank Sub-Bituminous Coal**

Steam gasification of Powder River Basin (PRB) coal was conducted using both conventional convective heating and microwave-assisted heating in fixed-bed reactors. The microwave absorption was controlled and enhanced by mixing coal with magnetite ( $\text{Fe}_3\text{O}_4$ ) powder. Experiments results showed that microwave is an effective heating method for coal gasification due to release of volatiles, resulting in the increased electrical conductivity and higher microwave loss. In this study the effect of gasification temperature (600, 700, and 800°C), magnetite loading percentage (5, 20, and 40wt%) and steam flow rate (0.13, 0.19, and 0.26 ml/min) were studied. Different characterization tools such as dielectric measurements, TGA, BET and SEM/EDS were used to correlate coal properties with the improved gas production rate and syngas quality observed during gasification. The microwave absorption capability of PRB coal was investigated by measuring the dielectric properties at room temperature at a frequency range between 100MHz to 3 GHz. XRD analyses demonstrate that  $\text{Fe}_3\text{O}_4$  was partially reduced to FeO during gasification which could play a role in increasing the dielectric loss factor of coal. The activation energy decreased significantly from conventional thermal heating to microwave-assisted heating. Due to the endothermic reactions nature of steam coal gasification, typically high gasification temperatures of  $\geq 700^\circ\text{C}$  are required in conventional thermal gasifiers. However, with the microwave-assisted gasifiers, higher coal conversion was observed at 600°C compared to conventional ones. At low gasification temperature (600°C), the shift reaction became more significant under conventional heating compared to microwave-assisted heating.

### Sub-Liquidus Rheology of Coal Slags under Gasification Conditions

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An effective use of the world's fossil fuels is mandatory in terms of their limitation and the worldwide growing demand for energy. Besides natural gas, oil and low-carbon sources, coal will remain one pillar of energy supply in the foreseeable future, due to its low mining and transportation costs and of course the high global availability. Besides the combustion of coal in traditional steam-electric power stations with their limited efficiency and flexibility, the gasification technology is a promising way to convert coal into a chemical energy carrier like a synthetic gas. The combination of a steam cycle and a gasifier, known as Integrated Gasification Combined Cycle (IGCC) power plant, fulfils future requirements; as it is highly efficient and flexible. The gasification demands a fundamental knowledge of the thermophysical and -chemical processes during the conversion of the fuel. Especially the entrained flow gasifier requests an essential understanding of the physical properties of the non-converted residue. The high process temperatures up to 1400 °C will cause the ash to melt and flow downward the walls of the gasifier, where it forms a complex layer which contains solidified, partly-crystallized and liquid amounts depending on temperature and composition. The slag builds up a layer protecting the refractory material, but an efficient flow has to be ensured otherwise a blockage of the slag tap can lead to an unscheduled shutdown. The viscosity is consequently one of the most important parameters during the operation of an entrained flow gasifier. Whereas the flow of the fully molten slag can nowadays be well described based on the inner structure of the oxide melts, for example by way of the thermodynamic modelling, little is known about the flow behaviour of sub-liquidus melts. In this study the time dependence of rheological behaviors, including the viscosity, at decreasing temperatures was investigated. Existence of solid precipitation leads to an increase of viscosity. The raising amount of crystals in the melt strongly influences the flow behaviour and subsequently causes at a high fraction a change from Newtonian to non-Newtonian flow; this will lead to an obvious shear-thinning flow. To achieve a deeper understanding of the flow of supercooled slags a high-temperature viscometer was built up, which enables the viscosity measurements of slags under reducing atmosphere ( $\text{Ar}/\text{H}_2$  (4-Vol.-%)) at high temperatures (900 °C – 1600 °C). Isothermal measurements were conducted on German hard coals in the fully liquid and sub-liquidus melt using a concentric cylinder measuring apparatus. The results show the influence of time and supercooling degree on the viscosity as well as the flow behaviour of the slags. The presence and amount of crystals in the slag was determined by using thermodynamic equilibrium modelling and quenching experiments.

### SESSION 10 Combustion Technologies: Mercury Removal

#### Measurements of Fly Ash Optical Properties and the Effects of Powdered Activated Carbon Addition

Herek L. Clack, Tian Xia, James C. Hower, University of Kentucky, USA

Activated carbon injection (ACI) into the post-combustion flue gas is one of the most mature technologies for reducing mercury emissions from coal-fired power plants. Anecdotal evidence obtained during field tests of ACI have revealed that powdered activated carbon (PAC) emissions from electrostatic precipitators (ESPs) are evident

based on the visual appearance of filter media used in PM sampling at the ESP outlet. Recent published estimates of these emissions and their global climate forcing effect assume that PAC has optical properties equivalent to black carbon and is emitted in an unagglomerated form with fly ash. The present paper provides the first comparative measurements of optical scattering and absorption properties of varying mixtures of coal combustion fly ash and powdered activated carbon. Aerosols are produced by a fluidized bed containing several ESP-collected utility fly ashes mixed with 1-2% PAC to represent typical PAC injection for mercury emissions control. A photo-acoustic extinctionsampler samples a portion of the fluidized bed effluent and measures optical absorption and scattering coefficients. Results obtained for fly ashes alone, PAC alone, and fly ash-PAC admixtures provide important fundamental data, useful in assessing how the addition of PAC will influence optical properties of emitted PM from electric utilities employing activated carbon injection and assessments of any associated climate forcing effect.

### Dry Sorbent Injection with Hydrated Lime for Acid Gas Control to Achieve Regulatory Compliance while Burning Various Coals

Gerald Hunt, Lhoist North America, USA

Recent federal regulations such as Mercury Air Toxic Standards (MATS), Cross State Air Pollution Rule (CSAPR) and the Industrial Boiler MACT, mandate coal fired plants to further reduce acid gas ( $\text{SO}_3$ , HCl and  $\text{SO}_2$ ) and mercury emissions. These coal fired boilers are faced with a decision of converting to natural gas, shutting down or installing new air pollution control systems. Dry sorbent injection (DSI) is a mature technology has proven to be an attractive compliance option for acid gas control due to low capital cost and ease of retrofitting to existing plants. Additionally, Lhoist has engineered enhanced hydrated lime sorbents branded as Sorbocal® which offers an optimized calcium based solution via reduced sorbent usage as well as reduced fly ash disposal costs. Subsequently, these advancements provide an alternative solution for coal fired systems to achieve acid gas regulatory compliance in order to maintain affordable use of coal as a fuel. This paper will present multiple case studies where enhanced hydrated lime was successful in reducing acid gas emissions to comply with imminent federal regulations.

### Startup Lessons Learned from Dry Sorbent Injection and Activated Carbon Injection Systems

David Park, S. Glesmann, ADA Carbon Solutions; R. Chang, EPRI; M. Lund, Nol-Tec Systems, USA

The MATS rule and many state regulatory standards have driven the testing, design, procurement, installation, startup and now continuing operations of such equipment to control air toxics like mercury as well as acid gases, including HCl,  $\text{SO}_2$  and  $\text{SO}_3$ . Along with new applications of equipment comes challenges and learnings from initial installations, commissioning, operation and optimization. As material selection, coatings, control logic, and design features are revised to make the systems work better for coal-fired power plants, operators are learning ways to improve design and operation. Encompassing improvements from instrumentation and control logic to material selection to coatings to safe handling of materials and more, these systems can be operated in safe, reliable and effective manners to be dependable compliance systems.

The work reported in this paper is based on supplier knowledge and field experience, as well as survey results from power plant operators who have procured, installed, started up, operated and optimized Dry Sorbent Injection (DSI) and Activated Carbon Injection (ACI) systems. Operators each have their own site procedures and guidelines for handling new equipment and materials. The insights provided by their collective experiences can help those who are also looking to comply with stringent emissions standards. EPRI commissioned a report that provides details of these field experiences to reflect the current state-of-the-art of DSI and ACI compliance systems. This paper summarizes some of the key findings, stories from the field, and learnings that are useful for those seeking to improve their own system's effectiveness and reliability or reduce shakedown time and effort.

### SESSION 11 U.S. EPA's Coalbed Methane Outreach Program (CMOP) Coal Mine Methane Conference Track - General - 2

#### CMM Development in the U.S. – Where are the Sweet Spots?

James S. Marshall, Candice L. M. Tellio, Raymond C. Pilcher, Raven Ridge Resources Incorporated, USA

The success of coal mine methane (CMM) project development in the United States is dependent on several key factors, including the volume and rate of CMM that can be produced. Regional market conditions also have a significant impact on project success, and can include electricity sales prices, natural gas sales prices, cost of access to the regional and national grid, and simply the distance to access to the grid. In general, when compared to other regions of the world where gassy mining conditions

exist, electricity sales prices in the U.S. are very low, making it difficult to consider power generation and sales as a viable option. Natural gas sales prices also vary greatly across the U.S., along with access to the natural gas infrastructure, which limits CMM project opportunities.

The authors have identified mines in the U.S. that are faced with gassy mining conditions which may take advantage of economically viable opportunities to capture and use methane rather than venting it to the atmosphere. Through our analysis we have identified, classified and ranked these opportunities, incorporating factors that will determine their economic success. Factors considered are: regional energy market conditions, existence of infrastructure providing access to markets, and incentives provided through renewable and alternative portfolio standards. Other important considerations that are incorporated into the analysis are those related to the location of the project opportunities such as the BLM's Conflict Administration Zone designation in Wyoming, Enterprise Zone designations in many states, and costs associated with whether the project is located on Federal land versus private land.

### Where's the VAM Abatement Project Opportunity in the U.S.?

Michael M. Cote, Ronald C. Collings, Ruby Canyon Engineering, USA

In recent years, thermal oxidation technologies have been shown to operate effectively at bleeder shafts with methane concentrations averaging greater than 0.7 percent. However, only about 20 such shafts exist at U.S. underground coal mines. Methane abatement projects rely on greenhouse gas (GHG) emission reduction credits, (or carbon offset credits) for the sole revenue source. In April 2014, California's Air Resources Board approved a compliance offset protocol for mine methane capture projects that included VAM abatement as a project type. More importantly, VAM projects can now qualify for compliance-grade offset credits valued at about \$10.00/tonne CO<sub>2</sub>e. At this carbon price signal, VAM abatement projects located at mine ventilation shafts with methane concentrations averaging greater than 0.7 percent can be economically viable.

While only representing 10 percent of the underground coal mine shafts, the 20 high-concentration shafts represent approximately 30 percent of VAM emissions in the U.S. Should carbon offset prices reach \$15/tonne CO<sub>2</sub>e shafts with methane concentrations averaging as low as 0.4 percent could be economically viable. This would include about a dozen additional shafts and increase the VAM abatement potential to 40 percent of the total U.S. emissions, representing approximately 17 million tonnes CO<sub>2</sub>e emissions. The decision to extend California's cap-and-trade program from 2020 to 2030 is vital to the short-term deployment of VAM abatement projects. However, this decision is not expected until later in 2016. An important next step in evaluating the VAM abatement potential so that a strategic roll-out of projects can occur is to identify the 20-30 shafts with the most potential for further study. While one of the most important parameters, methane concentration is not the only technical barrier to VAM abatement projects. Shafts need to be evaluated for longevity, topographic setting, variation in VAM flow and concentration, access to power, and VAM air quality, among other things.

### California Cap-and-Trade Panel Session #2: Coal Mine Methane Projects, Carbon Offsets, and their Role in California Cap-and-Trade

Teresa Lang, Derik Broekhoff, Max DuBuisson, Climate Action Reserve, USA

With the adoption of the Mine Methane Capture (MMC) protocol by the California Air Resources Board (ARB) for use in California's regulatory cap-and-trade program last year, there has never been a better time to implement a new coal mine methane project for carbon offsets. Demand for carbon offsets is strong, supply is limited based on the protocols adopted to date, and MMC projects are shaping up to be a high volume, cost-effective opportunity. Reflecting on its role as an accredited Offset Project Registry in the California cap-and-trade program and author of an approved early action MMC methodology, the Climate Action Reserve will provide an update on the California cap-and-trade program and an overview of ARB's MMC Protocol. This presentation will provide guidance for each step in the process of developing a project. In particular, it will focus on the critical eligibility and monitoring requirements of the MMC Protocol, of which prospective project developers need to be aware prior to starting a project. Teresa Lang is a Senior Policy Manager at the Climate Action Reserve and manages the implementation of that protocol. (Time and space permitting, this presentation could be given as a solo presentation by Teresa Lang, OR Teresa Lang could provide an overview of the protocol and some background, and then facilitate a panel of project developers/verifiers with experience in developing projects under the compliance protocol, as well as the early action protocols, such as the Climate Action Reserve's Coal Mine Methane Protocol, which are transitioning projects over to the compliance protocols.)

## SESSION 12

### Coal Science: Rare Earth Elements -1

#### Uncertainties and Optimum Detection Modes for Rare Earth Analysis in Coal and Coal Ash using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Elliot Roth, Evan Granite, DOE/NETL; Tracy Bank, AECOM, USA

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a very powerful technique that can detect multiple elements at very low concentrations in a variety of matrixes. The advantages of low detection limits and multi-element analyses make ICP-MS an indispensable tool for rare earth elements (REEs) analysis in soils, sands, clays, ashes, coals and other solid and liquid matrixes. However, low concentrations of REEs and complicated matrixes of coals and coal ashes can induce a significant amount of error in the analysis if the digestion of the sample is incomplete and detection modes are not optimized. In this study standard reference materials of ash and coal were analyzed for REEs and other trace elements using ICP-MS with a lithium metaborate fusion digestion method. ICP-MS methods tested for optimum REE recovery included standard operating mode as well as advanced cell technologies including kinetic energy discrimination (KED) and dynamic reaction cell (DRC) mode. Each mode had advantages for certain rare earth elements indicating that using certain modes for specific REE may provide the most accurate method for analysis. The use of different modes for specific REEs is a relatively easy way to enhance the accuracy of REE measurements in coal and coal ash and may be a good technique for other complicated matrixes as well.

The instrument used in this study is a Perkin Elmer Nexion 300D ICPMS. The Nexion is designed with an internal cell that allows the user to apply gases which either chemically or physically react with a sample to minimize interferences with the analyte(s) of interest. In this study, KED mode uses ultra-high purity helium gas to physically collide with ions in a sample and minimize the concentration of interferences caused by high total dissolved solids. The result is fewer total ions reaching the detector, but the effect of removal is much greater for large diameter ions such as Na<sup>+</sup> and Cl<sup>-</sup>. Alternatively, DRC mode using ammonia removes molecular ions, such as <sup>35</sup>Cl<sup>16</sup>O<sup>-</sup>, that may overlap with metals of interest. For each complicated sample matrix, the exact conditions which optimize interference removal and maximize the signal for analytes of interest need to be experimentally determined.

#### Analytical Approaches for Determining REE in Coal and Coal Ash

Allan Kolker, Clint Scott, Nick Geboy, Ruth Wolf, Jamie McCord, U.S. Geological Survey, USA

Rare earth elements (REE) are essential in applications ranging from consumer electronics and transportation, to wind power generation, and military uses. Due to limited global supplies and growing demand, especially for heavy rare earths, alternatives to conventional carbonatite-hosted REE ores are sought. Among a range of possible sources, these alternatives include unusually REE-enriched coals [1, 2], and notably, coal ash, in which REE are preferentially retained during coal combustion [3]. In this paper we review the most widely used analytical approaches for determining REE concentrations in coal and coal ash, and consider the challenges to successful REE measurement in these materials. By far the most common approach for REE determination is by inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS offers advantages of high sensitivity needed to measure REE concentrations at the ppm or ppb range, coupled with the capacity to determine multiple elements in solution simultaneously. Digestion of solid samples is a critical step to ensure that REE in refractory trace phases such as monazite ((Ce,La,Th)PO<sub>4</sub>), and zircon (Zr[SiO<sub>4</sub>]), commonly present in sediments, including coal, are dissolved. For routine trace element analysis by ICP-MS in U.S. Geological Survey labs, coal samples are combusted at 525 °C and the residues are digested in a three-acid (HNO<sub>3</sub> + HCl + HF) mixture [4]. However, acid digestion, even if perchloric acid (HClO<sub>4</sub>) is added, may not fully break down acid-resistant REE-bearing trace phases. Alternatively, for REE, sinter digestion methods are used, in which the sample is mixed with sodium peroxide and sintered in a graphite crucible [5]. Using this approach, care must be taken to minimize REE-oxide isobaric interferences potentially introduced by sintering [6]. REE determination by neutron activation, in which samples are bombarded by neutrons, followed by gamma-ray counting, remains a viable alternative to ICP-MS [7]. This method is applicable to a range of sample materials, including solids, with no digestion required. Like ICP-MS, in neutron activation, multiple elements are determined simultaneously. Disadvantages include limited access to a neutron source to irradiate the samples, and residual radioactivity of samples following irradiation. Where high precision (1-2%) results are required, measurement of REE by isotope dilution remains an option. In this method, groups of REE (light, middle, and heavy) are pre-concentrated for analysis using ion exchange columns and then measured using a thermal ionization mass spectrometer. Determination of REE in coal by ion chromatography has also been shown [8]. Regardless of which analytical method is used, when sample REE abundances are normalized to chondrites, a smooth pattern should result with the exception of Eu, and in rare cases, Ce, each having dual oxidation states that may lead to REE fractionation. Group behavior of the other REE,

each having only a 3+ oxidation state, provides a powerful internal check of analytical results.

### **Synthesis of Layered Double Hydroxides Intercalated with Chelating Agents for Rare Earth Element Capture from Aqueous Streams**

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

Solid layer double hydroxides (LDHs) are promising adsorbents for heavy metal and rare earth element removal from aqueous streams. LDHs are layered materials that are built of positively charged brucite-like layers weakly bound with each other by exchangeable anions. LDHs are typically synthetically made and have positively charged layers that contain different bivalent cations (Mg, Mn, Zn, Cu, Ni, etc.) and trivalent cations (Al, Fe, Cr, etc.), but can also be formed in clay mineral silicates like kaolinite. These materials have been used in waste water treatment and in soil remediation to capture heavy metal ions. Additionally, these materials can be intercalated with different organic molecules to form organic-inorganic hybrid materials that can be used as sorbents. Specifically, LDHs can be intercalated with chelating anions in the interlayer space to enhance sorption properties of the materials. Studies on decontamination of aqueous media from U(VI), and sorption of Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> reported the use of inorganic hydrotalcite sorbents and LDHs. In this study a hydrotalcite material was synthesized and compared to a layered double hydroxide intercalated with ethylenediaminetetraacetic acid (EDTA). The materials were fully characterized using various characterization techniques including SEM, XRD, and BET. The material was then tested for extraction of rare earth elements from a synthetic ideal aqueous solution. Parameters such as the pH, and the LDH to water ratio were varied to see the effects on extraction efficiency for the materials. The rare earth element concentration was measured using ICP-MS.

### **Leaching of Uranium from Coal Using Samples from the Springbok Flats Coalfield: Acid Leaching**

Malumbazo Nandi, M. Ndhlalose, Council for Geoscience; N. J. Wagner, University of Johannesburg, SOUTH AFRICA

Springbok Flats Coalfield is known to be economically unviable due to the presence of uranium in coal. Five boreholes were drilled at various sites in the Springbok Coalfield to extensively understand the coal quality and to extract uranium from coal. Three out of five boreholes were observed to have low coal quality and two boreholes had good coal quality. A relationship was observed between the uranium and the ash content. The uranium content was observed to be low on borehole samples that had high ash content and high on borehole samples that has moderate amounts of both fixed carbon and volatile matter.

In all the samples that were sampled from the coal zones of the drilled boreholes; X-Ray Fluorescence (XRF) and Inductive coupled plasma mass spectrometry (ICP-MS) were used to quantify the amount of uranium in the coal samples. The uranium content detected in all the drilled boreholes varied from 199 ppm to 9 ppm. Coals with good coal quality and high uranium content were selected for the acid leaching experiments using sulphuric acid as a leaching medium. Temperature, time and pH were varied for the acid leaching experiments. An increase in temperature, time and low pH resulted in better uranium extracted from coal samples to the leachate medium. Samples that had high uranium extraction rates were further selected for optimization experiments. In the second acid leaching experiments, molarity of the leaching medium was included as a variation factor for the experiments. Both the leaching and the coal cake samples were analysed for uranium content. An increase in uranium in the leachate was observed with a decrease of uranium in the coal samples.

## **SESSION 13**

### **Clean Coal Demonstration and Commercial Projects: Industrial Processes**

#### **CO<sub>2</sub> Capture from Industrial Processes: Opportunities & Gaps**

V Pradeep Indrakanti, William Bender, John Huston, Sr., Leonardo Technologies Inc.; John Litynski, U.S. Department of Energy, USA

The purpose of the study was to identify specific industrial processes that could benefit from the application of advanced carbon capture technologies to reduce emissions of carbon dioxide (CO<sub>2</sub>). Coal and other solid hydrocarbons such as metallurgical coke, petroleum coke (petcoke) and rubber tires are used as fuels and reductants in several industrial processes. For example, around seventy percent of global steel production requires coal inputs. Four industrial processes were analyzed: iron and steel production, cement production, lime production, and ammonia production. Existing and advanced carbon capture technologies within the DOE research, development and demonstration (RD&D) portfolio were evaluated to identify potential applicability to each process. The application of these control technologies would permit the continued use of low-cost solid fuels and reductants (e.g., coal, petcoke, metallurgical coke, etc.) while limiting CO<sub>2</sub> emissions. The benefits and challenges associated with these applications are discussed.

According to the U.S. Environmental Protection Agency (EPA), the top four industrial processes emitted approximately 112 million metric tonnes (MT) of CO<sub>2</sub> in 2012 (this value accounts for process-CO<sub>2</sub> emissions alone and does not account for fuel-CO<sub>2</sub> emissions). Iron and steel production is the largest U.S. CO<sub>2</sub> emitting industry (54.3 MT CO<sub>2</sub>), followed by cement (35.1 MT CO<sub>2</sub>), lime production (13.3 MT CO<sub>2</sub>) and ammonia production (9.4 MT CO<sub>2</sub>). Industrial CO<sub>2</sub> capture may offer specific advantages compared to power plant CO<sub>2</sub> capture such as a more concentrated CO<sub>2</sub> stream and the potential to re-use CO<sub>2</sub> at the same facility. However, the wide variation in the characteristics of CO<sub>2</sub>-containing gas streams from industrial sources requires special design considerations often on a case-by-case basis. For example, the partial pressure of CO<sub>2</sub> varies from 2 to 70 psia, and the levels of impurities such as SO<sub>x</sub>, NO<sub>x</sub> and H<sub>2</sub>S vary from zero to hundreds of parts per million. Technologies that have been evaluated to capture CO<sub>2</sub> from industrial gas streams include solvent absorption, adsorption, and chemical looping. Results from the literature survey indicate that CO<sub>2</sub> capture has been demonstrated at both commercial and demonstration/pilot scales, with captured quantities varying from kilograms per day to thousands of metric tonnes per year. The captured CO<sub>2</sub>-rich stream has been used for several applications such as enhanced oil recovery (CO<sub>2</sub>-EOR), for industrial-grade liquid CO<sub>2</sub>, food-grade CO<sub>2</sub>, for enhanced urea/methanol production, and for process heating. Advanced capture technologies under development can lower the parasitic load of capture from industrial processes and reduce the total cost of production over conventional capture technologies.

Carbon capture from industrial sources presents several potential benefits. The addition of CO<sub>2</sub> removal may lead to the production of high-calorific value fuel gas which could be used for process heating or for generating auxiliary power. This is relevant for industrial gas streams such as coke oven gas. Advanced CO<sub>2</sub> capture technologies may also lead to the partial removal of air toxics, which may benefit industries subject to air permit requirements limiting the emissions of mercury and air toxics. Further, low-grade heat from industrial processes may be used to offset steam requirements for CO<sub>2</sub> capture. Finally, the captured CO<sub>2</sub> could be used to enhance production, or could be sold for CO<sub>2</sub>-EOR

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

Scott McDonald, Archer Daniels Midland Company, USA

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

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

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

IL-ICCS project has the following objectives:

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

- Develop and conduct an integrated communication, outreach, training, and education initiative.

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

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

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

Air Products and Chemicals, Inc. (APCI) has designed and constructed a state-of-the-art system to concentrate the carbon dioxide (CO<sub>2</sub>) from two steam methane reformer (SMR) process streams for delivery of the CO<sub>2</sub> via pipeline for sequestration by injection into the Hastings oil field (near Pearland, TX) as part of an enhanced oil recovery (EOR) project. APCI has retro-fitted their two SMRs, located in Port Arthur, TX, using Vacuum Swing Adsorption technology to separate the CO<sub>2</sub> from the process stream, followed by a drying process and compression. The CO<sub>2</sub> capture facility is designed to convert the initial stream containing 15% - 20% CO<sub>2</sub> to greater than 98% purity for delivery to the pipeline. The technology removes greater than 90% of the CO<sub>2</sub> from the process gas stream used in the world-class scale hydrogen production facility. Approximately 1 million tons per year are being delivered for sequestration and EOR, which results in additional domestic oil production.

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

#### **SESSION 14**

##### **Coal Mining: Gas Management in Mining Operations**

#### **Theory and Modelling of Explosion Scenarios in Coal Mines**

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

Explosions and fires are an important issue in the mining industry, because they may cause injuries and deaths as well as destruction of expensive mining equipment. Although mining fatalities have decreased by two orders of magnitude since the beginning of 1900th, the mining sector still has one of the highest fatality/injury rates, primarily caused by accidental gas and dust explosions. An unfortunate example of a fatal fire accident occurred in Soma, Turkey in 2014, which resulted in the deaths of over 300 miners. One of the major troubles is that the modern knowledgebase about dust explosions does not provide an acceptable level of risk assessments because the physics of the controlling mechanisms, associated with particle-air flames, have not been explored in depth. To reveal the inner mechanism of gas explosions, we work on prescribing the entire scenario of premixed flame front evolution within an accidental fire by means of novel theoretical and computational models. Specifically, we are developing a Dust and Gas Explosion Model (D-GEM) – a computational platform capable of quantifying the mining fire hazards, namely, a spontaneous ignition, the evolution of a flame front, and the possibility of a deflagration-to-detonation transition. A backbone for the platform is a fully-compressible, finite-volume Navier-Stokes code solving for the hydrodynamics and combustion equations in a homogeneously-gaseous, laminar environment. The development of a computational platform is accompanied by experiments on dusty-gaseous explosions as well as the comprehensive theoretical formulations, prescribing and quantifying the explosion and fire scenario. In this particular study, “finger” flame shape and “wall friction (Shelkin)” acceleration mechanisms are considered. Finger flame, which is one of the key stages of flame evolution, is scrutinized with the situation of a lean methane-air explosion. A transition from a globally-spherical front to a finger-shaped one occurs when a flame starts approaching the passage walls. This mechanism is Reynolds-independent and flame speed increases by an order of magnitude. While this acceleration is extremely strong, it terminates as soon as the flame touches the passage wall, followed by the “wall friction” scenario. In this mechanism, as a flame front propagates from a closed tube/channel end, the burning matter expands; it pushes a flow of the fresh fuel mixture; friction at the pipe walls makes the flow non-uniform, which bends the flame front, increases the flame propagation velocity and reduces flame acceleration. In this study, second, we implemented dusty-gaseous environment into “finger” flame shape and “wall friction” mechanisms by considering Seshadri formulation for the planar flame speed, with a uniform and non-uniform distribution of dust gradients. Specifically, linear, parabolic and hyperbolic spatial dust distribution gradients are incorporated into the flame acceleration mechanisms. As a result, by developing a

theoretical and computational platform (D-GEM), this study systematically investigates how the coal dust distributions affect fire evolution, the flame shape, and propagation velocity.

#### **Modelling of Gas and Ventilation Flow Characteristics at an Underground In-Seam Drilling Site**

Ting Ren, Zhongwei Wang, Jian Zhang, Frank Hungerford, University of Wollongong and Valley Longwall International Pty Ltd; Yuanping Cheng, China University of Mining and Technology, CHINA

Gas management has always been a challenging issue for mine operators, and this is becoming increasingly significant as the mining depth increases. Gas drainage sites or stubs are established to drill in-seam boreholes for pre-draining coal seam gas prior to gateroad development and longwall mining. The management of ventilation and gas emissions within the drainage site becomes a critical component of mine safety during gas drainage process. In this study, a three-dimensional (3D) computational fluid dynamics (CFD) model was developed based on an Australian in-seam drilling site to investigate the aerodynamics of seam gas (methane and carbon dioxide) emitting from the drilling site and boreholes during normal drilling, and in the case of a sudden gas inrush from the borehole. The model incorporates the major equipment within the drilling site and the common ventilation management practices (e.g., brattice and vent tube). Mesh independence studies were conducted to achieve a mesh independent solution. Initially, steady state calculations were conducted to analyze the effectiveness of different ventilation controls on gas removal, after which transient simulations were carried out to investigate the dynamic emission of gas from a borehole. Modeling results indicate that potential high risk zones can be formed if sufficient ventilation cannot be provided to the drainage site, particularly during a high gas inrush event from a borehole. The treatment of borehole discharges, the configuration of brattice as well as the layout of ventilation tubes all played important role in effective gas management. This study has demonstrated that CFD modeling technique can be a useful tool for the design of optimum ventilation/gas management in underground gas drainage site in coal mines, especially when abnormal gas emission is encountered during drainage operations.

#### **SESSION 15**

##### **Gasification Technologies: General - 2**

#### **Pilot Scale Studies on CO<sub>2</sub>-Enhanced Coal Gasification in a Circulating Fluidized Bed Reactor**

Aleksander Sobolewski, Andrzej Czaplicki, Tomasz Chmielniak, Marek Sciazko, Krzysztof Słowik, Institute for Chemical Processing of Coal, POLAND

Currently, concerns about the role of CO<sub>2</sub> in the greenhouse gas effect have led to several international agreements aimed at controlling carbon dioxide emissions. Substantial improvements in the processing of solid fuels are considered to be essential for achieving emission targets. Gasification is the primary conversion process used to produce hydrogen and carbon monoxide from carbonaceous materials. To date, CO<sub>2</sub> has never been considered as a co-gasifying agent to be fed into the gasification reactor.

The work presented herein discusses the results of experiments performed at 0.5 MW circulating fluidized bed gasification reactor working under pressure conditions. For the studies three coals, lignite (Belchatow), sub-bituminous (Janina) and sub-bituminous (Wieczorek), were selected. The samples were obtained from Polish mines, and prior to the experiments were dried, ground and sieved to particle sizes ranging from 0 to 3 mm.

The testing facility used for the study of solid fuels gasification was aimed at obtaining two basic products: char and process gas. The main components of the experimental rig are as follows: a circulating fluidized bed reactor, a system for raw material preparation, char separation from a hot process gas, and a combustion flare for process gas utilization.

Coal after drying were delivered to the test facility in containers. The plant configuration and instrumentation enabled studying the gasification processes over a wide range of temperatures, using air, O<sub>2</sub>, CO<sub>2</sub>, and steam as gasification agents. Coal feed capacity to test rig is in the range from 100 to 200 kg/h.

The temperature and pressure distributions were measured throughout the system and gasifying agents and process gas flow rates were recorded for a mass balance evaluation. Coal and char mass flow rates were determined by averaging measured mass of the solids fed or received over the testing time.

The obtained results indicate that the more carbon dioxide is introduced the higher is the carbon monoxide content in the product gas. At the same time, the process temperature is decreasing correspondingly due to the increased participation of the Boudouard reaction in the process. Taking into account product gas yield and quality, it is more favorable to gasify the lignite coal in spite to other coals.

## Kinetic Studies for CO<sub>2</sub> Gasification of HOK Cokes Using Thermogravimetric Analyzers at High Pressures

Ziad Abosteif, Stefan Guhl, TU Bergakademie Freiberg, GERMANY

Many parameters can influence the gasification kinetics such as the gasification temperature, pressure, coal composition and particle size. Several models for the determination of reaction kinetics out of experimental data have been previously discussed. However, the precision of every model depends on the reaction parameters. In this study, the gasification of high quality Herdofenkoks (HOK) coke from a German power generation company in carbon dioxide atmospheres was investigated by using a thermogravimetric analyzer (TGA) from Rubotherm™.

The reaction step was held under isothermal conditions and only Boudouard reaction was considered in the evaluation. Temperatures from 800°C till 1000°C in 50K step were applied at 100 vol % and 50 vol % of carbon dioxide concentration. The total pressure was varied up to 10 bar.

Different kinetic models (volume model, grain model and random pore model) were applied to determine the activation energy, the pre-exponential factor and the order of reaction. The results of the different models were compared and discussed.

## In-situ Analysis and Mechanism Study of Char-Ash/Slag Transition in Pulverized Coal Gasification

Lu Ding, Guangsu Yu, East China University of Science and Technology, CHINA

Behaviors of char-ash/slag transition during char-CO<sub>2</sub> gasification of three different rank coals were studied by the combination of thermogravimetric analyzer(TGA) and an in-situ heating stage microscope. The effects of coal type and gasification temperature on the interactions of char-ash/slag were analyzed. The results show two reaction mechanisms in the char-ash /slag transition process, which relate to the reaction conditions and coal properties. Mechanism 1: char particles shrank along with carbon conversion when the reaction temperature was lower than the ash fusion temperature of coal. The accumulated ash might block some pore structure of semi-coke, which was unfavorable for the char-CO<sub>2</sub> reaction proceeding at a high carbon conversion. Mechanism 2: when the gasification reaction was conducted at high temperatures (above the ash fusion temperature of coal), the liquid film formed due to the ash melting with the shrinkage of char particles. In addition, the molten slag enclosing residual carbon at high carbon conversions was observed. These two mechanisms of char-ash/slag transition can well explain the variation of reactivity of coal char at different reaction temperatures. There is a threshold value of gasification conversion( $x=0.9$ ) during the char-ash/slag transition processes of YN lignite coal and SF bituminous coal, while the critical conversion do not appear in the gasification processes of ZY coal for the high ash fusion temperature. Results show that coal ranks, coal ash properties, and reaction conditions have great effects on the whole char-ash/slag transition process in pulverized coal gasification.

### SESSION 16

#### Combustion Technologies: Oxy-Combustion -1

## Chemical Looping Combustion by Using Iron-Based Oxygen Carrier in Moving Bed Reactor System for Hydrogen Generation

Ping-Chin Chiu, Chien-Hua Chen, Cheng-Hsien Shen, Jieh-Yn Sheu, Kuo-En Huang, Industrial Technology Research Institute, TAIWAN

Industrial Technology Research Institute (ITRI) was setup a 30 kW bench scale chemical looping reactor in 2013. ITRI 30 kW chemical looping system circulates Fe-based oxygen carrier with moving bed mode to yield CO<sub>2</sub> and H<sub>2</sub> from fuel reactor and hydrogen generator, respectively. The research of chemical looping in ITRI is consisted of development of iron-based oxygen carrier, reactor operation, and design of coal direct combustion system. Fe-based oxygen carrier for moving bed operation in ITRI system is prepared as spherical particle with 2.0 mm in diameter. A better performance recipe for preparation of Fe-based oxygen carrier was screened, and the cost was down to less than 3 USD/kg. The 30 kW system circulates oxygen carriers by using mechanical valves between reactors. CO<sub>2</sub> and H<sub>2</sub> concentrations were reached 95% and 90% in the effluent streams from fuel reactor and hydrogen generator, respectively. For consideration of system scaling up, oxygen carrier circulated by mechanical valves is unreliable for long-term operation and greatly increase capital and maintenance cost. Therefore, ITRI 30 kW chemical looping system is retrofitting by using non-mechanical valves to circulate oxygen carrier, including L-valve, U-valve and air injector. A 30 kW cold model system was tested for oxygen carriers circulation by non-mechanical valves, the circulating rate was stably controlled at 0.7-3.1 kg/min. The reactor system will be commissioned at the end of 2015 for fuel combustion and hydrogen generation

## Advanced Pressurized Oxy-Combustion: Towards Higher Plant Efficiency through Near-Zero Flue Gas Recycle and Boiler Designs

Adewale Adeosun, Fei Xia, Zhiwei Yang, Akshay Gopan, Benjamin M. Kumfer, Richard L. Axelbaum, Washington University in St Louis, USA

Oxy-combustion which involves burning coal in oxygen instead of air is a promising carbon capture and sequestration (CCS) technology for clean coal utilization. However, the loss of efficiency is high in comparison with plants with no CO<sub>2</sub> capture. Advanced oxy-coal combustion technology with high efficiency is therefore needed in order to deploy CCS on an industrial scale and to this end, an advanced oxy-combustion process called Staged, Pressurized Oxy-Combustion (SPOC) has been developed. SPOC eliminates the need for flue gas recirculation (FGR) through fuel-staging concept by utilizing oxygen as both the oxidizing and the diluting gas, avoiding the energy penalty associated with FGR. Temperature is extremely high when coal is burned in pure oxygen. This high temperature leads to dramatic increase in radiant heat flux on the boiler tubes as compared to combustion in air. SPOC addresses the concern over heat flux partly by fuel delivery in stages. Heat flux is also addressed by pressurization. Pressurization, hence low gas volume, creates high particle concentration. High particle concentration profile creates optically thick medium between the high temperature zone and the boiler tubes which allows the control of radiant heat transfer to the wall. SPOC burner and boiler are designed to achieve low mixing, ensuring distributed heat release which is important to manage heat transfer. Apart from saving energy associated with FGR and giving control of radiant heat transfer, SPOC concept can achieve higher plant efficiency by recovering latent heat of condensation in the flue gas moisture and thermal recovery from air separation units as a result of the elevated pressure.

Here in this work, the underlying concept of SPOC, results of the burner/boiler designs, optimization, radiative trapping mechanism unique to optically dense medium as well as the process modeling for a conceptual 550MWe supercritical power plant using SPOC boilers will be presented. The results of the boiler designs show that manageable heat flux from pressurized combustion in particle laden flow is achievable. The process modeling shows a gain of about 6 percentage points in net plant efficiency in SPOC process over atmospheric oxy-combustion. The increase in efficiency is a result of reduction in auxiliary loads, significant thermal energy recovery from direct contact column, heat integration from air separation unit compressors and intercoolers among others.

## A Standardized Method for the Characterization of Coal Ignition under Oxyfuel Conditions

Martin Schiemann, Anna Becker, Sebastian Heuer, Nikita Vorobiev, Viktor Scherer, Ruhr-University; Daniel Haxter, Anna Havekost, Johannes Mayer, E.ON Technologies GmbH, GERMANY

Oxyfuel combustion is known to change the combustion properties of solid fuels significantly. The high CO<sub>2</sub> concentrations in these atmospheres significantly change the thermo-physical properties of the gas phase, which in turn affects the reaction of the solid fuel, causing delayed ignition and changes in char burn out.

Ignitability is a very important parameter for coals which are foreseen for pulverized fuel combustion. Comparable and reproducible testing methods are needed when fuels have to be analyzed for their ignition properties. Typical research facilities for ignition measurements are drop tube reactors or wire mesh reactors, which are key elements in numerous publications. The results for Oxyfuel ignition tests typically show that ignition delay increases with higher CO<sub>2</sub> concentrations. However, currently there is no real standardized method available to characterize ignition under Oxyfuel conditions.

In the current work, a standardized method, originally developed by Zelkowski<sup>1</sup> to measure ignitability of pulverized coals under air-fired conditions, is adapted to Oxyfuel conditions (ignition in CO<sub>2</sub>/O<sub>2</sub> atmospheres). The experimental setup consists of a laboratory furnace, in which a small amount of pulverized coal is injected by pressurized air. The ignition delay is measured by a photo diode, which responds to the increasing light intensity caused by the ignition process. Under air fired conditions, a series of measurements is carried out for different furnace temperatures, which lead to variations in ignition delay. The coals are then compared based on the required temperature for an ignition delay time of 150 ms. In the current paper CO<sub>2</sub>/O<sub>2</sub> concentrations are varied. Typical coals with varying rank, which are utilized in power plants, are tested in the Zelkowski set-up. The results agree with the general tendencies known for the influence of oxygen concentration and coal rank.

The results of the standardized Zelkowski method are compared to ignition tests in a laminar drop tube reactor, which corresponds to the typical devices described in literature. As the results show, the Oxyfuel-adapted Zelkowski method bears good potential to act as a standard test for ignitability of pulverized coals with acceptable experimental effort.

<sup>1</sup> J. Zelkowski, S. Remke, J. Berkan Assessment of the ignition behaviour of pulverised coals by lab scale investigation 4th International Conference on Technologies and Combustion for a Clean

Environment, 07 - 10 Jul. 1997, Lisbon, Portugal

## An Experimental and Numerical Study of Volatile Combustion of Single Coal Particles in an Oxygen Enriched Atmosphere

Jan Köser, Robert Knappstein, Lukas G. Becker, Benjamin Böhm, Johannes Janicka, Andreas Dreizler, Technische Universität Darmstadt, GERMANY

For the reduction of CO<sub>2</sub> emission in coal combustion capture and storage of CO<sub>2</sub> is one option. Oxy-fuel combustion is a promising technology where N<sub>2</sub> is removed from the air first and combustion takes place in an atmosphere of O<sub>2</sub> and recycled CO<sub>2</sub>. In this environment the flammability limits are typically narrower than for combustion with air. With the changed characteristics of oxy-fuel environment models used in Computational Fluid Dynamics (CFD) simulations for air may not be applicable anymore. These models need to be inspected first, improved if needed and finally carefully validated to build trust in the simulations before using them as a design tool for future combustion systems. The combustion of a coal particle occurs in several stages: heating, devolatilization, ignition, volatile combustion, and char combustion which all need to be covered by a CFD simulation.

The aim of this work is to show a modeling strategy suitable for Large Eddy Simulation (LES) of volatile combustion phase of coal particles, by a comparison with a well-defined validation experiment and to study the effects of devolatilization, when particles cross a laminar flame front. For this purpose a flat flame burner was designed to provide oxygen/CO<sub>2</sub> environments at elevated temperatures for fundamental studies of the devolatilization, ignition, and volatile combustion processes of single coal particles as well as particle clouds. The coal particles were delivered by a carrier gas composed of the same mixture as the flat flame through a central pipe, providing a homogenous enclosed flat flame. Hence, the time was well defined when the particle starts interaction with the flame and hot flue gas. This allows studying ignition delay times more accurately compared to former designs where the particle was carried by cold non-combustible carrier gases which require additional time for mixing with the hot flue gas first.

In this work two types of coal with different percentage of volatiles were investigated in a hot atmosphere of N<sub>2</sub> and CO<sub>2</sub> with different levels of O<sub>2</sub> downstream of the flat flame front. The number of coal particles was varied for investigating single particle phenomena as well as the interaction of particles in a particle cloud. Coherent anti-Stokes Raman scattering (CARS) was applied for gas temperature measurements, as well as high speed particle imaging to visualize ignition delay times and the evolution of particle shape and diameter. High-speed laser induced fluorescence of OH was used to address the burning of the volatiles.

A LES has been performed to capture the transient behavior of the reacting flow caused by volatile gases of single particles or even particle clouds. For this, the academic three-dimensional finite volume code FASTEST has been used. Taking advantage of the laminar flame characteristics and the symmetries, the configuration has been treated as two-dimensional. The two-phase flow was computed by an Euler-Lagrange approach. Flamelet Generated Manifolds (FGM) have been coupled with coal devolatilization models. In this approach, the detailed chemical reaction processes were computed prior to the actual CFD simulation and then mapped onto a manifold which was spanned by a reduced set of control variables. These were the mixture fraction, a reaction progress variable, and the enthalpy. To account for devolatilizing gases, source terms have been included in the corresponding transport equations. A verification regarding the consistency of the table extraction of the thermo-chemical state has also been performed.

Numerical data of the reacting particles and the laminar flame are compared with experimental measurements with respect to the particles velocity and gas temperature. Special emphasis is put on the region in which volatiles combustion takes place. Further, the "path" of the volatiles through the manifold in the course of the reaction was analyzed.

## Coal Combustion Characteristics in a 1MWth Pilot-scale Circulating Fluidized Bed under Oxy-fuel Conditions with High Oxygen Concentration

Haoyu Li, Shiyuan Li, Qiangqing Ren, Jingzhang Liu, Chinese Academy of Sciences, CHINA

Oxy-fuel circulating fluidized bed (CFB) is a promising technology, which has a number of advantages that in some cases make it a better choice for CO<sub>2</sub> capture. Besides the advantages CFB have, the most remarkable feature of oxy-fuel CFB compared to oxy-fuel PC is that it can be operated at high O<sub>2</sub> concentration due to large cold solids from external heat exchanger allowing bed temperature control, which will substantially reduce unit size and manufacturing and operating costs. IET/CAS has operated a 0.1MWth oxy-fuel CFB at high O<sub>2</sub> concentration with recycle flue gas (RFG) since 2012, a lot of fundamental researches on oxy-CFB operating at high O<sub>2</sub> concentration have been done in that facility. To further study oxy-fuel CFB combustion, a 1MWth pilot-scale CFB test facility has been established at IET/CAS, which can be operated at air and oxy-fuel combustion mode with O<sub>2</sub> concentration between 21% and 50%.

This paper presents experimental results of two Chinese coals in a 1MWth pilot-scale CFB in air and oxy-fuel combustion with O<sub>2</sub> input concentration of 30%, 40% and 50%, at a bed temperature around 8500C. Air and oxy-fuel combustion with low O<sub>2</sub> concentration experiments were performed to provide a comparison for high O<sub>2</sub> concentration oxy-fuel combustion. The effect of atmosphere and O<sub>2</sub> staging on

combustion characteristics including temperature distribution profiles, combustion efficiency, gaseous pollutant emission and desulfurization efficiency were investigated. The results demonstrate that high O<sub>2</sub> concentration CFB combustion is stable and the transitions from air to the oxy-fuel firing mode and the reverse process are smooth, presenting little or no operational difficulty, CO<sub>2</sub> concentrations in flue gas can reach above 90% on a dry basis.

Under high O<sub>2</sub> concentration (50%) oxy-fuel combustion: (1) Temperature level in the bed is similar with other conditions, and the highest temperature in the combustor gets more close to the position where the secondary gas is introduced. (2) Combustion efficiency is higher with 50% O<sub>2</sub>/RFG > 40% O<sub>2</sub>/RFG > air > 30% O<sub>2</sub>/RFG. (3) Emission in mg/MJ unit such as NO is lower while N<sub>2</sub>O and SO<sub>2</sub> are higher than that in air, while these gaseous pollutant emissions are comparable to those of 30% and 40% O<sub>2</sub>/RFG conditions, when comparing to the differences between air and O<sub>2</sub>/RFG combustion. Furthermore, SO<sub>3</sub> emission seems to increase, but that needs further investigation. (4) Desulfurization efficiency of limestone is lower than that in air, but which is a little higher than that in O<sub>2</sub>/RFG at low O<sub>2</sub> concentration. O<sub>2</sub> staging combustion is a new and safe method for oxy-fuel combustion with high O<sub>2</sub> concentration by decreasing the O<sub>2</sub> concentration in the primary gas and increasing the O<sub>2</sub> concentration in the second gas, which also can provide an effective method to control combustion ratio and combustor temperature distribution at high O<sub>2</sub> concentration oxy-fuel combustion.

### SESSION 17

#### U.S. EPA's Coalbed Methane Outreach Program (CMOP) Coal Mine Methane Conference Track: General - 3

### Market for Carbon Offsets – Trading, Risks and the Current State of Play

John Battaglia, Evolution Markets, Inc., USA

Markets are quickly evolving for carbon reduction projects in North America. California has adopted a protocol for the reduction of methane at coal mining operations in the United States and the Canadian province of Quebec has recently proposed the same operations in Canada. Both sub-nation jurisdictions have designed carbon trading programs to meet stringent emission reductions targets presently defined for the year 2020, with more aggressive targets expected for 2050. In addition, Ontario has announced commitments to join in carbon trading expanding the market for carbon instruments by roughly 30%. The development of these new markets presents new revenue opportunities for the coal industry.

This presentation will outline the landscape for new environmental markets, including the policy driving the creation of new trading markets as well as commentary on existing markets. The presenter will illuminate the opportunity by describing the types of carbon products actively trading today, including pricing, liquidity and risks.

### Legal and Regulatory Developments Impacting Mine Methane Emissions and Projects in the U.S.

Collon Kennedy, Attorney at Law, USA

In 2013, methane accounted for 10 percent of all United States greenhouse gas (GHG) emissions from human activities. Coal mines face a range of legal and regulatory issues with respect to methane management and methane emissions. This paper will review the legal, policy and regulatory challenges that mine operators or project developers encounter today or could encounter in the future. Examples include the Federal "Tailoring" rule, the Bureau of Land Management's Waste Mine Methane Advanced Notice of Proposed Rulemaking, the Mandatory Greenhouse Gas Reporting Program, and various state regulatory programs and also relevant court cases.

### SESSION 18

#### Coal Science: Rare Earth Elements -2

### Deep Eutectic Solvents and Ionic Liquids for Extraction of Rare Earth Elements from Coal Ash

Elliot Roth, Evan Granite, DOE/NETL; Megan K. Macala, Tracy Bank, AECOM, USA

Deep eutectic solvents (DESs) are a relatively new class of ionic liquids (IL) that differ from traditional ionic liquids by mixing a hydrogen bond donor with a salt. One of the first deep eutectic solvents studied in depth was a 2:1 mixture of urea and choline chloride. An interesting property of this DES is its ability to dissolve metal oxides. The low volatility, inexpensive starting materials and ability to dissolve metal oxides could make deep eutectic solvents an interesting solvent for recovery of rare earth elements (REEs). Additionally, ionic liquids alone also have many interesting solvent properties and could provide a novel separation method for the recovery of REEs from many solid fossil fuel sources specifically coal ash. However, some ionic liquids are

potentially very expensive, and would need to be cycled many times for an economical extraction process.

This study reports preliminary data on the total amount of rare earth elements extracted from a sample of coal ash using a DES (choline chloride and urea) and an ionic liquid. Specifically, an ionic liquid with a reactive carboxylic group was synthesized and studied. The percentage of each REE extracted is reported and measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The viscosity and percentage of water, which are known to affect the kinetics of dissolution, will also be reported. Other parameters that are also important to consider are contact time, reactor configuration, extraction temperature, ratio of solvent to coal ash, stirring speed (mixing), pH, and the recovery of REEs from the solvent (regeneration of solvent), will also be discussed.

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#### **Contribution of the Rare Earth-Rich Tonstein to the Chemistry of Fire Clay (Eastern Kentucky) Coal-Derived Fly Ash**

James C. Hower, John G. Groppo, Rick Q. Honaker, Cortland Eble, Kentucky Geological Survey, USA

Three locations of the Fire Clay coal were investigated. In all three cases, the coal and rock partings were sampled and analyzed individually. In one of the latter settings, we also were able to sample the fly ash resulting from the burn of the coal. The coal profiles represent three distinct occurrences of the rare earth-rich tonstein: (1) the tonstein not present with any other rock partings, (2) the tonstein underlain by an illitic clay parting, and (3) the tonstein is not present but the coal has a high-REE concentration. Of the first two settings, the tonstein comprises about 10% of the total thickness of the coal + parting profile and contributes about 20-35% of the total rare earth elements + Yttrium (REY). For mines with preparation plants, the latter amount of REY represents material largely not shipped to power plant. For mines shipping run of mine coal and/or shipping coal from the type (3) setting, the resulting coal combustion fly ash might have 1400-1600 ppm REY. In contrast, power plants burning coal with lesser amounts of entrained REY-rich partings, the fly ash REY is about 800-900 ppm.

#### **Rare Earth Occurrences in Coal and their Association with Tonsteins, Diapirs, and Igneous Activity**

H.T.Andersen, Digitus International; Rex Bryan, Thomas Gray, Dave Richers, Tetra Tech, Inc., USA

Rare earth elements (REE) are often found to be associated with coals and coal waste products in numerous coal basins across the United States. The source of the REE can be somewhat enigmatic. Recent work in both eastern and western coal basins suggest that both regional ash falls and localized diapiric or other intrusive activity can account for some REE occurrences. Data from the Appalachian basin of eastern Kentucky, southwestern and central Pennsylvania, and the Raton basin of south-central Colorado suggests that igneous activity has played an important role in introducing REE material into these coal basins. In some instances, the occurrence of REE is associated with stratigraphic layers that should be predictable and widespread, possibly allowing for careful mine management to segregate the coals and waste materials as a possible source of REE materials. Presented will be empirical data derived both from the literature and from recent field studies showing the correlation of REE in coals with such igneous features.

#### **Characterization of Rare Earth Elements in Canadian Oil Sand Process Streams**

Elliot Roth, Evan Granite, DOE/NETL; Tracy Bank, AECOM, USA

The concentration of rare earth elements in an Canadian oil sand ore and six oil sand waste streams were examined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The results indicated that the rare earth elements (REEs) are largely concentrated in the TSRU tailings, similar to typical froth floatation tailings, with a total rare earth concentration of 1380 ppm (1380 µg/g). This is a 13.5 fold increase in concentration compared to the oil sand ore itself, and an 8 fold increase compared to average Clarke value of sedimentary rocks. Not surprisingly the process water used for extracting the oil from oil sands and the water fraction associated with the different waste streams had very low values of REEs that were near or below the detection limits of the instrument. The highest total concentration of REEs in the water fraction of the samples tested was from the mature fine tailings with a total rare earth concentration of ~ 7 ppb (7 µg/kg). These results give insights into the possibility of

recovering rare earth elements from REE concentrated waste streams generated from oil sand processing.

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

#### **Application Progress of ECUST OMB Gasification Process**

Guangsu Yu, Zhijie Zhou, Xueli Chen, Zhenghua Dai, Yifei Wang, Haifeng Liu, Fuchen Wang, Xin Gong, East China University of Science and Technology, CHINA

Coal-Water Slurry (CWS) gasification technology of Opposed Multi-Burner(OMB) is a typical entrained-flow gasification technology, which is suitable for large-scale. OMB gasification technology is applied widely in China. There are 16 users (40 gasifiers) in commercial operation. In addition, there are about 30 users (more than 60 gasifiers) in design or construction phase. The total capacity is over 130 thousand tons coal per day. The products include methanol, ammonia, oil, acetic acid, olefin, hydrogen and so on.

In 2014, the largest hydrogen production plant in China adopted OMB CWS gasification. In June of 2014, a new project with largest single capacity (2500TPD) of OMB gasifier in Inner Mongolia has start-up, and this plant is in stable operation state. Due to robust feeding system and other improvements of OMB CWS gasification, the projects in operation show very high operating stability and reliability. For all OMB gasification plant which passed the performance test, carbon conversion are all near 99%, which shows OMB gasification process is highly efficient.

#### **China's 600 Mwe CFB Boiler - Some Issues in the Development and its Operation**

Leming Cheng, Zhongyang Luo, Mengxiang Fang, Qinhui Wang, Mingjiang Ni, Kefa Cen, Zhejiang University; Li Nie, Qi Zhou, Dongfang Boiler Group Co. Ltd., CHINA

Circulating fluidized bed (CFB) combustion technology is rapidly developed due to its fuel flexibility and low pollutant emission especially in China. The world's first 600 MWe supercritical CFB boiler has been passed its 168 hours operation smoothly with full load on April 14, 2014 in Baima Power Generation Plant at Sichuan Province in China, and put into commercial operation successfully. It is a remarkable milestone in the development of the circulating fluidized bed technology in the world.

Some key issues were studied during its development including the solids particle mixing in dense bed, bed material balance and its overturn condition between a breeches-leg, gas-solids flow distribution among different cyclones, heat transfer and heat flux distributions on waterwall and suspended heat transfer walls in the furnace. These aspects are important in developing a large size supercritical CFB boiler. This article reports the main research status on those aspects and the operation of the 600 MWe supercritical CFB boiler. The successful and smooth operation of the boiler verified these important considerations in the design and research results

#### **Advances in Flameless Oxy-Combustion Technology**

Peter Reineck, ITEA S.p.A., UNITED KINGDOM; Massimo Malavasi, ITEA S.p.A., ITALY

Flameless Pressurized Oxycombustion (FPO) is a technology that burns fuels using industrial oxygen instead of air: as a result, the mass and volume of flue gas are reduced by ~ 85%, with the advantages of less heat lost in flue gas and cost of flue gas scrubbing reduced considerably versus other known combustion processes. Combustion takes place in an atmosphere of CO<sub>2</sub> and water vapour. To maintain this atmosphere, a portion of flue gas is recirculated, and at least 25% water is added with the fuel.

FPO outperforms competitors with complete oxidation (six-nine conversion) of low ranking coal and other brown fuels. NO<sub>x</sub> is close to zero; any organic nitrogen is converted to elemental nitrogen (N<sub>2</sub>). The flue gas is primarily CO<sub>2</sub>. Total organic content (TOC) at combustor exit is hundreds of times lower than for traditional combustion processes, with dioxin and furans close to zero.

FPO can process fuels with up to 40% incombustible content as well as high levels of heavy metals. There is no fly ash: all non-combustibles are converted into totally inert vitrified slag which is drained from the combustor bottom. This vitreous slag has zero residual carbon and contains all minerals and heavy metals. The FPO plant is highly automated, compact and efficient: 96% of introduced heat (LHV) is recovered. It accepts up to 65% water content in fuel, and is rangeable from 10% to 100% of capacity rate in less than 4 hours.

The advantages of FPO technology will be discussed, including processing coals with high incombustible content and high melting point ashes, and CO<sub>2</sub> capture. Recent advances which will be discussed include processing high levels of heavy metals, chlorine and sodium; incorporation of turbo-expander; rangeability of combustor and boiler, and FGD and volatile heavy metal capture.



**CCS Flameless Pressurized Oxy-Combustion: Emphasis on “large scale pilot” facility, as the key step for process & equipment validation, before demo projects launching, and the new opportunity “ready for CCS” introduction**

Massimo Malavasi, ITEA S.p.a., ITALY

Indeed the crowding of CCS DEMO project cancellations at FID step call for a review of development strategy of innovative technologies, in a capital intensive industrial segment, as Power is. Capex-Opex huge increase (multiples) vs original theoretical estimates, and uncertain carbon reduction scenario (timing, entity) for economics, are the apparent issues on new technologies industrial exploitation. In addition, the promises of tuning the transition via retrofitable technologies are not materializing. More specifically, about new technology engineering side issues, it is apparent OEM are caught unprepared to provide performing new solutions supported by required guarantees, thus impacting both efficiency and capital. Moreover, higher capital spending put additional pressure on engineering bodies. In order to have a bankable (zero-risk) initiative, they are assigned the dominant goal of zero-risk, running at capacity since button pushing, thus multiplying redundancies and hot back-up solutions.

ITEA Spa, which pioneered Flameless Pressurized Oxy-Combustion at its 5 MWh pilot since 2003, it have been cooperating, since 2006, with ENEL and MIT for coal firing CCS application development, and for 350 MWe DEMO unit detailed engineering study.

FPOC looks the sole case of engineered favorable performance result (2012) not far from theoretical projections. However, engineering study results, though positive, pictured a situation qualitatively corresponding to the story of the above described DEMO cases. Therefore, engineering study teachings are adding the opportunity/necessity of more ambitious technical targets, to be addressed in cooperation with OEMs, to be added to the next development step represented by the 50 MWh large pilot initiative at Sulcis (Sardinia), thus increasing development cost, to be accomplished before any DEMO initiative.

Finally, just to respond to the uncertain regulation scenario, some FPOC fundamental performance (efficiency, flexibility) have been reviewed. They are giving ground to the alternative “ready for CCS” FPOC set up, here pictured with the support of engineering figures elaborated from the engineering study. Ready-for-CCS promises to be competitive with traditional SCPC technologies, and easily, and progressively, retrofitted to CCS set up with simplified CO<sub>2</sub> compression section modules.

**Design of a Commercial-Scale Oxy-Coal Supercritical CO<sub>2</sub> Power Cycle**

Nathan T. Weiland, Walter W. Shelton, DOE/NETL; Charles W. White, Noblis, Inc., USA

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

Power cycles utilizing supercritical carbon dioxide (SCO<sub>2</sub>) have been receiving increased attention as a potential means to improve power plant efficiency as compared to conventional steam power cycles. In addition to improved efficiency, the high density of SCO<sub>2</sub> relative to steam (at equivalent turbine inlet temperature and pressure) suggests that SCO<sub>2</sub> power cycles may allow for a much smaller plant footprint, as well as a reduction in capital costs.

NETL has been investigating the SCO<sub>2</sub> recompression Brayton cycle for application to commercial scale power plants with CO<sub>2</sub> capture. The recompression Brayton cycle has the potential to achieve over 50% cycle efficiency, in large part due the recuperation of heat from the SCO<sub>2</sub> turbine exhaust, which effectively preheats the CO<sub>2</sub> entering the heat source. Prior work at NETL has investigated several options for powering closed (indirect) SCO<sub>2</sub> power cycles with fossil-fueled heat sources. The research has indicated that PC circulating fluidized bed (CFB) boilers that have been modified with enhanced combustion air preheating would be well-suited for use in SCO<sub>2</sub> cycles. Such CFB boilers could be operated as either air-fired or oxy-fired units to enable CO<sub>2</sub> capture in the plant's exhaust gas.

This paper investigates several options for integrating an oxy-fired CFB boiler into the SCO<sub>2</sub> recompression Brayton cycle to maximize overall plant efficiency. In particular, this work investigates the possibility of utilizing the low-quality heat from the combustor exhaust to reduce or eliminate the SCO<sub>2</sub> bypass flow around the low temperature recuperator. In addition, integration options with the air separation unit and other plant equipment are also explored with the goal of further increasing cycle and plant efficiency. Finally, the effect of these design choices on the capital cost of the overall power plant is also discussed.

**SESSION 21**

**Gasification Technologies: Biomass co-gasification**

**Synergy and Inhibition during Co-Gasification of Biomass-Coal Blends**

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With the clean coal power initiative of the US government, technologies such as co-gasification of coal-biomass blends are being investigated because they present numerous advantages: lower emissions of CO<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub>, better H<sub>2</sub>/CO ratios, and lower feedstock costs. The inorganic matter present in biomass catalyzes the gasification of coal improving the overall process efficiency. Catalysis in biomass gasification is usually attributed to the alkali and alkaline earth metals inherently present in biomass. Especially potassium is known to mobilize and transfer from one biomass feedstock to another. Therefore, co-feeding potassium rich feedstock such as switchgrass with a potassium deficient coal is expected to promote the gasification of coal. Potassium added to coals in various forms (through biomass, as K<sub>2</sub>CO<sub>3</sub>, KOH etc.) is known to be deactivated by the mineral matter in coal forming catalytically inactive compounds such as potassium aluminosilicates. Due to these complicating interactions of the catalyst in biomass with the mineral matter in coal, observations regarding the synergy and inhibition effects during co-gasification are largely feedstock dependent.

In this context, the objective of this study is to examine the synergistic and inhibition effects during co-gasification of switchgrass with either low-grade lignite (Texas Lignite) coal or bituminous coal (Illinois # 6). Switchgrass is rich in potassium and silica while the coals contain much lower potassium and a large amount of silica. The effect of addition of switchgrass in the form of char or ash to coal char has been explored. In some cases, the pine char or pine ash were added to the coal chars to test co-gasification of a calcium rich biomass containing negligible silica with coals. Results showed that potassium added to lignite, irrespective of the source, was scavenged by the silica in lignite. In case of bituminous coals, significant synergistic effect is observed.

**Poison Resistant Water-Gas-Shift Catalyst for Coal and Biomass Co-Gasification**

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

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

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

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

This presentation is an update of our work: 1) investigating the effects of catalyst poisons (now including selenium) on the performance of our new low temperature, poison-resistant, sour WGS catalyst, 2) our catalyst synthesis scale up efforts and catalyst pellet testing, and 3) upcoming testing at the Power Systems Development Facility (PSDF) in Wilsonville, AL. The PSDF is part of DOE's National Carbon Capture Center and is operated by Southern Company, located at their Wilsonville, AL power plant. Field testing using real coal and coal/biomass derived syngas is key to convincing customers of the activity, durability and cost effectiveness of our new sour WGS catalyst.

Simon Roussanaly, David Berstad, Rahul Anantharaman, Petter Nekså, Jana Jakobsen, SINTEF Energy Research, NORWAY

CO<sub>2</sub> capture conditions vary greatly between large point sources within power generation and industries [1]. The CO<sub>2</sub> concentration ranges from roughly 1% for diluted off-gas from aluminium smelters, up to 80–90% for dried oxy-fuel flue gas. The differences become even more distinct when considering the CO<sub>2</sub> partial pressure as this varies by 3–4 orders of magnitude, from approximately 1 kPa to 2 MPa. The higher range can be found in shifted syngas compositions from coal gasifiers. With high CO<sub>2</sub> partial pressure high energy and cost efficiency for CO<sub>2</sub> capture processes can be achieved.

This work presents a high-efficiency low-temperature CO<sub>2</sub> capture unit for integrated gasification combined cycle (IGCC) power plants [2]. The capture process is based on partial condensation and phase separation of liquid CO<sub>2</sub> from non-condensables. The shifted syngas assumed in this work consists close to 40 % CO<sub>2</sub>, while the remainder is mainly made up by hydrogen.

Different process designs are possible for the low-temperature CO<sub>2</sub> capture unit. The baseline design generates high-pressure supercritical CO<sub>2</sub> for pipeline transport. The syngas feed is first dehydrated and compressed to specified separation pressure and subsequently cooled to separation temperature in a heat exchanger network. After the first separation stage the liquid CO<sub>2</sub> is further purified in a secondary flash separator and subsequently pumped and heated to transport state. The hydrogen-rich non-condensable fuel product is heated and expanded to the combustor feed state. Auxiliary refrigeration for the capture unit can be provided by vapour-compression cascade refrigeration units.

The design and performance of heat exchangers has been verified through simulations of geometric multi-stream plate-fin heat exchanger models. The assumed performance of compressors and expanders has also been shown to be achievable with state-of-the-art technology. This indicates that all process components may be available within a relatively short time frame. The low-temperature capture unit should therefore provide a relatively low-risk technology option for pre-combustion CO<sub>2</sub> capture.

In addition to producing high-pressure supercritical CO<sub>2</sub> for pipeline transport (base case), the process can be modified to producing liquid CO<sub>2</sub> for ship or tanked transport (around 8 bar) by extracting the liquid product directly from the secondary separation unit [3]. In an early phase of CCS deployment where seaborne bulk transport of liquid CO<sub>2</sub> from source to sink may be required due to lagging pipeline infrastructure, the low-temperature capture unit can provide a flexible solution, including a real option for future modification to production of high-pressure CO<sub>2</sub> for pipeline transport.

The net specific power requirement for the base case has been estimated to 273 kJ/kgCO<sub>2</sub> at 85% CO<sub>2</sub> capture ratio, while the net specific power requirement is estimated to 317 kJ/kgCO<sub>2</sub> the system delivering cold liquid at around 8 bar for ship transport [2-3]. Based on the electricity output and the plant costs, the cost of electricity (LCOE) of the two processes has been evaluated and benchmarked to Selexol process as the reference case [3]. The evaluation shows that the cost of electricity with the base case low-temperature CO<sub>2</sub> capture is 9% less expensive than the reference plant with Selexol CO<sub>2</sub> capture. When looking directly at the cost of capturing CO<sub>2</sub>, the low-temperature concept for pipeline transport, with a cost of only 22 €/tCO<sub>2,avoided</sub>, is 35% more cost-efficient than the Selexol process.

For the capture process producing liquid CO<sub>2</sub> for ship transport, the cost of electricity with low-temperature CO<sub>2</sub> capture and internal CO<sub>2</sub> liquefaction is 11% less expensive than the reference plant with Selexol CO<sub>2</sub> capture and liquefaction by ammonia cycles commonly used in the literature [10, 11]. The CO<sub>2</sub> avoidance costs of the concept delivering cold liquid CO<sub>2</sub> is evaluated to 23 €/tCO<sub>2,avoided</sub> and is therefore 37% more cost-efficient than the Selexol process (38 €/tCO<sub>2,avoided</sub>). This is primarily due to the already existing cost advantage of the process in the case of a pipeline export, and the extremely energy- and cost-efficient low-temperature internal liquefaction for ship transport compared to liquefaction by ammonia cycles.

Acknowledgements: This publication has been produced with support from the BIGCCS Centre, performed under the Norwegian research program Centres for Environment-friendly Energy Research (FME) and Gassnova. The authors acknowledge the following partners for their contributions: Gassco, Shell, Statoil, TOTAL, GDF SUEZ and the Research Council of Norway (193816/S60).

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#### Emissions Control by Monitoring Total Excess Air and O<sub>2</sub>

Dario DiMaggio, Kurz Instruments, Inc., USA

Monitoring total excess air is an emerging concept and important process, but it has largely been ignored or properly analyzed. Most coal-burning facilities, especially outside the U.S., pay little attention to excess air or Oxygen – the predominant ideology is to push as much air as possible through the system to ensure everything is burned. Excess air in the combustion process is any additional air flow above the stoichiometric air-to-fuel ratio for theoretical complete combustion. Coal-fired boilers should operate with about 10-20% excess combustion air to prevent the formation of dangerous carbon monoxide and unburned hydrocarbons in the flue gas.

To control gas emissions and decrease Nitrous Oxides (NO<sub>x</sub>), many sites attempt to control emissions by installing expensive SCR before upgrading to low NO<sub>x</sub> burners, installing stage gas recirculation, or attempting to monitor excess air. This is based on the misconception that the flue gas composition coming out of the boiler should match the gas composition coming out of the stack. However, the correct amount of excess air in a coal-fired plant can be determined by continuously monitoring and analyzing the Oxygen (O<sub>2</sub>) or Carbon Dioxide (CO) concentrations in the exhaust flue gas. Too much air increases NO<sub>x</sub> and lowers CO<sub>2</sub>, while too little air increases CO<sub>2</sub> readings and lowers NO<sub>x</sub> emissions. Total and accurate monitoring of the excess air throughout the entire combustion cycle is necessary in order to achieve, maintain, and control the delicate balance between CO and NO<sub>x</sub> emission and boiler efficiency.

It is finally possible to achieve continuous and accurate monitoring of O<sub>2</sub>, CO<sub>2</sub>, and other gases across a coal-fired facility to obtain a system-wide snapshot of total Oxygen content – from the primary air inlet to the stack. These total excess air monitoring systems are relatively inexpensive. Installing multiple excess air monitoring devices throughout all combustion stages will provide a key detection function in keeping a balance for a continuous optimal percentage of Oxygen flowing throughout the process. The output data can be used to control combustion air dampers in order to maintain uniform Oxygen percentages, and indicate potential drafts or leaks that can affect emissions.

#### Investigation of Temperature Uniformity during High Oxygen Concentration Combustion in 1MWt Circulating Fluidized Bed

Jingzhang Liu, Shiyuan Li, Qiangqiang Ren, Haoyu Li, Wei Li, Institute of Engineering Thermophysics, Chinese Academy of Sciences, CHINA

Oxyfuel combustion technology is a promising technology to reduce carbon dioxide emissions. As one of oxy-combustion technologies, a novel oxycoal combustion with high-oxygen concentration (~50 vol.%) in circulating fluidized bed has been developed in the worldwide recently. However, in this regime, high-oxygen coal char burning can raise local region temperature and destroy in-boiler temperature uniformity, excepting its high calorific value release for maintaining continue combustion. Keeping temperature uniformity under safety restrict in boiler is essential to dense coal particles high-oxygen combustion especially in a large scale circulating fluidized bed. This work numerically investigates combustion temperature uniformity for oxygen-staged combustion with high-oxygen concentration in 1MWt circulating fluidized bed boiler. Total oxygen partial pressure ratio is 50vol.% and another remained part of recycled flue gas is 50vol.% in boiler and different partial pressure ratios of oxygen in primary stream are about 21vol.%, 25vol.%, 29vol.%, separately. Effects of oxygen-staged combustion on in-boiler temperature uniformity are discussed in detail, which focus on dense coal burning chemical reaction mechanism, including pyrolysis and devolatilization, volatiles release and combustion, char oxidation and gasification especially with carbon dioxide and gas water. Volatile matter releases and combustion regions have been discussed to improve char burning and high calorific value release, which affect local region temperature in boiler. As a primary thermal source for varying in-boiler temperature uniformity, coal char kinetic reactions and burning rates also have been compared in different oxy-staged combustion methods. Present model and methodology, i.e., dense discrete phase model-two flow model-kinetic theory of granular flow (DDPM-TFM-KTGF), have been employed to investigate this high-oxygen dense coal particles oxy-staged combustion by modified physical parameters and improved chemical reaction mechanism. The results showed that in-boiler temperature uniformity was nearly achieved by low oxygen partial pressure ratio in primary stream with oxy-staged combustion. High-oxygen partial pressure ratio in dense region brought coal combustion enhancement and burning temperature improvement in bottom local region. Reducing oxygen concentration in primary stream and raising oxygen concentration in secondary stream generated that local temperature in the lower part of boiler decreased and that in the upper increased. Improved oxy-staged combustion obtained in-boiler temperature uniformity and promoted better controlling coal char chemistry and burning rates. Temperature uniformity in boiler can effectively improve intense turbulent combustion stability and safety for high-oxygen oxyfuel combustion in large scale circulating fluidized bed.

## Examination of Changing Char Reactivity with Isothermal Oxy-Combustion Conversion by a Simplified Atomistic Simulation

Haihui Xin, Deming Wang, China University of Mining and Technology; Chang'an Wang, Xi'an Jiatong University, CHINA; Jonathan P. Mathews, Penn State, USA

Oxy-combustion is of interest due to lower emission via energy conversion efficiency gains. The combustion process is highly influenced by the char reactivity and its transformations in the chemical controlled regime. However, there are challenges in rationalizing these transformations based on experimental and modeling approaches. Atomistic simulations may provide a means to explore these transformations with a level of control not available via experimental approaches. Our earlier work has enabled construction of chars in an highly automated strategy capturing structural features observed from experimental approaches: notably the structural distributions of graphene molecule size, orientation, stacking, order, and the pore size distribution in large-scale atomistic representations (~100 x 100 x 100Å char volume and >41,000 atoms) with low computational cost (via Fringe3D and VOL3D scripts). Here a large-scale 84% micro-and 16% mesoporous hydrocarbon char was evaluated for isothermal reactivity changes during conversion by a simplified an inexpensive simulation approach. While maintaining a rigid char structure (to reduce computational expense), oxygen (>18,000 molecules) diffused via molecular dynamics (the desired oxygen penetration being observed at ~1000 °C for 150 fs) in a series of iterations controlled by an in-house created script within Materials Studio. Reactive edge carbon atoms <3.5Å from an oxygen molecule are deleted while retaining the oxygen molecule. Carbon atoms in ring fragments formally connected to an atom deleted in previous iterations were deleted if < 6Å to clean up highly reactive structures. The automated process captures the transformations specifically the atoms deleted with each interaction, their location, changes in frequency of reactive and unreactive carbons, an estimation of the overall volume change (minimum size box), and envelope density estimations. The pore size distribution and helium densities transformations spanning 20 of the 47 stages were evaluated using the Poreblazer script. Visualization approaches (movies, and novel graphics) aided in analysis of the rate change during conversion. The reaction rate slowly increased reaching a maximum at ~30% of the conversion, there was almost linear slow decline until ~90% conversion. The char size remained constant for ~30% of the conversion before shrinking core behavior was observed with two stages of a slow then more rapid decline in axis lengths. The envelope density estimation (mass / box volume) was relatively unchanged (~0.82 g/cm<sup>3</sup>) for the first ~10% conversion after there was a more rapid transition until the 35% conversion stage before a less rapid transformation occurred. Helium density was relatively constant for the first ~10% of conversion (~1.9 g/cm<sup>3</sup>) after which the decline rate was relatively constant reaching ~1.6 g/cm<sup>3</sup> after 90% conversion. Porosity was also constant until the ~10% conversion had been reached (0.6), after porosity increased reaching 0.9 at 95% conversion. The mesoporosity also remained relatively constant (~15%) until 30% conversion after which it increased rapidly to around 85% conversion increasing to 80% of the volume. Total surface area was steady with small losses in carbon number, peaking at 30% conversion rate consistent with the highest reaction rate observed. Surface area then declined as mesoporosity increased. Thus, char was changing in density and then volume reduction (shrinking core) concurrently. If continued work is able to elucidate the applicable parameters that capture experimental observations, this simulation approach offers the potential to improve reactivity models. Simulations exploring combustion, gasification etc. may also be explored utilizing these approaches with unprecedented access to explore the transformation occurring at low computational cost. Multiple improvements in the approach complexity are possible.

### SESSION 23

U.S. EPA's Coalbed Methane Outreach Program (CMOP) Coal Mine Methane Conference Track: General - 4

## Gob Gas Production during Mining of Blue Creek Coal Seam, Alabama, and Production Analysis of Ventholes

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Longwall mining of coal seams affects a large area of overburden by deforming it and creating stress-relief fractures, as well as bedding plane separations, as the mining face progresses. Stress-relief fractures and bedding plane separations are recognized as major pathways for gas migration from gas-bearing strata into sealed and active areas of the mines. In order for strata gas not to enter and inundate the ventilation system of a mine, gob gas ventholes (GGVs), can be used for methane control. While performances of these ventholes vary depending on the design, operation and gas sources present in the strata, they can produce high-quality gas.

The aim of this paper is to analyze performances of GGVs drilled to control methane emissions from the Pratt group of coals into a longwall mine operating in the Mary Lee/Blue Creek coal seam of the Upper Pottsville Formation in the Black Warrior Basin, Alabama. During the course of the study, Pratt coal's reservoir properties, estimated for the same date as the start of mining by using production history matching

of coalbed methane (CBM) wells in the same area, were integrated with production data of the GGVs, and were analyzed by using material balance techniques.

The study showed that the GGVs are highly effective in capturing strata gas from stress-relief fractures and bedding plane separations, and they are shown to be more effective than conventional CBM wells in capturing strata gas for methane control purposes.

Production performances of GGVs show a strong apparent correlation between mining rate and methane production rates. This signifies the importance of mining rate on dynamic subsidence and associated methane release from gassy strata, as well as the enhancement of hydraulic conductivity around gob gas boreholes to capture it more effectively. Volumetric gas in-place assessment was performed to estimate drainage area of each GGV, as well as changes in formation pressures and in-place gas contents. These calculations showed that the radii of drainage varied between 362 m and 455 m for GGVs. These numbers indicate that strata deformations in terms of stress-relief fracturing and bedding plane separations exceed panel widths and are slightly overlapping between GGVs and suggests approximate wellbore spacings.

Material balance analyses indicated that the initial pressure of the Pratt coals, which was around 648 KPa when longwall mining started, decreased to approximately 150 KPa as the result of strata fracturing and production of released gas. These analyses showed that approximately 70% of the initial gas-in-place within the area of influence of the GGVs was captured during a period of one year. The study further showed how efficient GGVs were in extracting a high volume of methane, which otherwise could have migrated into active workings, from the Pratt coals within a short period of time (~1 year) compared to traditional CBM wells, owing to fracturing of the formation by longwall mining. In addition, an approximate linear relationship between the amounts of gas production per unit decrease in pressure, which can be used for coal mine methane production design in this area, was observed.

## PA Coal Mine Methane Recovery

Steven E. Winberg, Battelle, USA

The release of methane gas to the atmosphere is a major component of Greenhouse Gas emissions. Methane gas is a fossil fuel and energy source, commonly known as natural gas, which occurs in various geologic formations in Pennsylvania, including coal formations. When coal is mined and processed for use, substantial amounts of methane gas are released. Coal bed methane (CBM) is methane contained within coal formations and may be extracted by gas exploration methods or released as part of coal mining operations.

According to data reported to EPA from 2011-2013 approximately 90-93% of the methane gas released during the mining of coal in Pennsylvania occurs from mining in longwall underground mines. The five large longwall underground coal mines now operating in Pennsylvania extract approximately 50% of the 60 million tons of coal mined each year within Pennsylvania. These high amounts of longwall mine production and the fact that the longwall mines recover coal from greater depths than other mines make longwall mining the predominant current source of coal mine methane release and an important contributor to Greenhouse Gas emissions. In recent years several mines have begun to capture and utilize methane gas within longwall underground mines, resulting in a reduction of methane Greenhouse Gas emissions.

Coal mine methane (CMM), the methane within the coal that can be vented or recovered prior to mining the coal, during mining, and immediately after mining as some gas escapes to the surface through post-mining vents or boreholes. Methane gas that remains sequestered within an abandoned underground coal mine does not contribute to Greenhouse Gas emissions, but could be and sometimes is recovered by subsequent gas exploration operations.

This paper evaluates the cost of capturing methane from boreholes for both longwall and non-longwall mines in Pennsylvania.

## Lessons Learned in Developing Mine Methane Capture Projects across the U.S.

Tom Vessels, Vessels Coal Gas, Inc., USA

Vessels Coal Gas, Inc. (Vessels) has been worked on qualifying energy from waste mine methane for the high value carbon and energy markets since 2007. Vessels has developed and is expanding projects for capturing mine methane in the Rocky Mountains and Northern Appalachia. The largest project is in Colorado, and the longest running project is in Pennsylvania. Vessels received awards in recognition for environmental excellence in both states.

The Colorado Project at the OXBOW MINING LLC Elk Creek Mine in October 2012. In 2013 Vessels received the Conservation Achievement Award from the Conservation Center in Colorado. As of February 28, 2014 the project had been issued 35,454 Climate Reserve Tons from combusting almost 100,000,000 cubic feet of venting waste mine methane. From then through February of 2015 around 300,000 unverified offsets have generated through thermal oxidation (combustion) in an enclosed flare. Since December 2013 electricity production has been approximately seventy (70) Mega Watt Hours per day.

Vessels received the 2011 Pennsylvania Governor's Award For Environmental Excellence for their project in Cambria County. Vessels currently operates a coal mine methane recovery facility on Bethlehem Energy Mine 33. Pipeline injection of mine gas emissions came on-line in May of 2008. Electrical generation began in December

2010. As of October 31, 2014 the plant has sold around 470,000 mcf of natural gas product into the Peoples Natural Gas local distribution company pipeline. The plant produced over 209,000 Verified Carbon Units (VCUs) using the VCS methodology, and generated 14,000,000 kilowatt hours (kWh) of electricity and 14,000 Renewable Energy Credits (REC's).

This presentation will emphasize the importance of access to carbon markets and impact of the California Air Resource Board's Cap and Trade System on Mine Methane Capture. It will cover the stages of project development from conception, initial discussions, and initial designs to operations and include a discussion of the technical issues to resolve in local environments and the policy and political hurdles encountered. And finally the unexpected benefits of the projects will be discussed.

### **CMM Recovery & Utilization Amidst Low Gas Prices & Abundant Shale Gas**

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

The Appalachian Basin has been a historic cost effective source of abundant energy for America for the past 150 years. It is rich with Carbon in all of its phases starting with solid coal, then natural gas, and within the last 5 yrs shale gas along with its rich natural gas liquids. The over abundance of shale gas has resulted in low gas prices of \$2.00 - \$2.50 / MCF. The over abundance has also caused high basis costs and high firm transportation costs leaving low net back revenues for the producer.

This paper will describe various methods to overcome the current Technical and Financial Challenges currently facing CMM Recovery in the USA. Drilling Techniques will be described and evaluated to select the most cost effective drilling. Production & Gathering pipeline methods will also be described. Gas Processing alternatives will be described and evaluated as gas quality of CMM is typically lower than 1,000 Btu due to the mixture of non-calorific gases such as carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) etc. We will describe efficient non-cryogenic unique gas separation technologies to reject the non-calorific gas from CMM in order to make pipeline quality natural gas.

Utilization of the CMM is critical to the financial justification of a CMM project. The most obvious utilization would be to make pipeline quality natural gas and sell into a close proximity pipe. Though there are plenty of gas pipelines in Appalachia, we may not be close enough to be feasible. Therefore consideration will be given to Power Generation, Liquid Natural Gas (LNG), and Gas-to-Liquids (GTL) fuels such as diesel. As the product value goes up so do the costs. This paper will attempt to show the economic break points of each option.

Greenhouse Gas (GHG) offsets is another opportunity for CMM recovery financials to be enhanced. Currently some offset registries do not recognize CMM recovery to pipeline natural gas as being eligible and actually encourage flaring or combusting the CMM and recovering no energy at all. CMM to pipeline actually displaces a like amount of energy that would have come from some other part of the world thus reducing the GHG footprint even further. Therefore this issue should be re-addressed by the particular registries.

The paper will conclude with an in-depth analysis of the Coal and Gas reserves in the USA and the best utilization of each. This should be a serious objective of both Government and Industry leaders alike. Just because we have a temporary abundance of natural gas, that doesn't mean that we should throw it away and burn it in a fire for electricity with low thermodynamic efficiency. Lastly, a brief review of what America should be doing with its new found wealth of natural gas, from a globally experienced scientist's point of view.

### **Overview of Global CMM and CBM Activity**

Jonathan Kelafant, Advanced Resources International, Inc., USA

Interest in coalmine methane (CMM) and coalbed methane (CBM) has been eclipsed over the last 10 years or so by the tremendous interest in shale gas, both domestically and internationally. However, CMM/CBM activity is far from dormant as new projects are coming on line in a number of countries including Botswana, India and Turkey. The growth of CMM/CBM in these and other countries is due to a number of factors including limited conventional gas resources, high energy costs, and expanding coal production.

This paper will review the current status of CMM/CBM activity in a number of countries; discuss the technologies being used to develop the resources, and provide an overview of the economic and market conditions that are driving the growth of development in these countries.

### **SESSION 24 Coal Science: General - 2**

#### **Fullerene Functionalized Fullerenes Aggregates on Surface Soils and River Sediments from Santa Catarina Coal Mining Area**

Matheus S. Civeira, Luis F.O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North-West University, SOUTH AFRICA

In this research, a new and useful analytical approach is proposed for the analysis of seven fullerenes (C<sub>60</sub>, C<sub>70</sub>, Nmethylfulleropyrrolidine, [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester, [6,6]-thienyl C<sub>61</sub> butyric acid methyl ester, C<sub>60</sub> pyrrolidine tris-acid ethyl ester and [6,6]-phenyl C<sub>71</sub> butyric acid methyl ester fullerenes) in soils and sediments around coal mining and coal power plant.

The present procedure combines an ultrasound-assisted solvent extraction (UAE) with toluene followed by liquid chromatography (LC), using a pyrenylpropyl group bonded silica based column, coupled to a high-resolution mass spectrometer (HRMS) using atmospheric pressure photoionisation (APPI) in negative ion mode.

The analytical performance for fullerene separation of the pyrenylpropyl group bonded silica column was compared to the C<sub>18</sub> column. For the ultra-trace analysis of fullerenes in complex environmental samples, the use of the APPI source and the use of the electrospray ionisation (ESI) source were compared.

By the presented method for the analysis of fullerenes in complex matrices, a series of advantages, in terms of sensitivity and specificity, have been demonstrated. The method limits of detection (MLOD) and the method limits of quantification (MLOQ) in soils and sediments ranged from 0.022 to 0.39 pg/g and from 0.072 to 1.3 pg/g, correspondingly.

Recoveries were between 68 and 106%. The analytical method was applied in order to assess the occurrence of selected fullerenes in 45 soils of Santa Catalina State, Brazil and 15 sediments from the Tubarão River, presenting different pressures of contamination: a coal-combustion power plant, car exhaust, and coal mining industry and wastewater effluents. C<sub>60</sub> and C<sub>70</sub> fullerenes have been detected at concentrations ranging from the MLOD to 0.150 ng/g. None of the functionalised fullerenes were detected in any of the samples.

Coal and others combustion processes, in particular car exhaust, were identified as the main source of fullerenes. However, the potential degradation of residual concentrations of engineered fullerenes to more stable forms, such as C<sub>60</sub> and C<sub>70</sub>, should also be considered.

### **Nature and Origin of the Variation in Coke Strength after Reaction in Heat-Recovery Coke Making Technology**

Mhlwazi Solomon Nyathi, Richard Kruse, ArcelorMittal USA; Maria Mastalerz, Indiana Geological Survey, USA

Blast furnace raw material variations and specifications necessitate efforts to identify and control factors that determine the quality of coke. Coke quality is expressed, in part, by its mechanical strength at high temperature, commonly known as coke strength after reaction (CSR). Coke CSR determines the reactivity of coke towards oxidizing gases and the extent of its degradation within the blast furnace. The metallurgical coke characteristics that influence its quality are surface area, carbon forms, and chemistry. These parameters, in turn, are influenced by coal blend properties, and coking conditions. By-product coke making technology has been and continues to be the main method of metallurgical coke production. The use of non-recovery/heat-recovery coke-making technology offers new possibilities for coke makers. The literature shows that most of the knowledge about the development of coke properties is based on work done on the traditional by-product coke-making technology. This study investigates the nature and origin of the variation in CSR obtained in different regions of the heat-recovery oven chamber.

In this work, coke fingers collected from three different zones (bottom center, top center, and top right) of a commercial heat-recovery oven were studied. Coke fingers were collected intact and studied incrementally, starting from tar line to cauliflower end. Coke samples were investigated using the coke strength after reaction (CSR) test, gas adsorption techniques, optical microscopy, and X-ray diffraction analyses. The results show that the CSR trend in the bottom center region of the oven is unidirectional, increasing from tarline to cauliflower end, whilst a curving CSR trend is observed in coke collected from top center and top right regions of the oven. The highest CSR value was found in the bottom center region, a characteristic attributed to limited swelling, which inhibits porosity development in this region. It was found that, while the CSR trend along the coke finger is influenced by both the porous structure and carbon matrix, variations in CSR are better explained by porosity-related properties, particularly pores in the mesopore range (2-50 nm pore diameter). Swelling patterns in different zones of the oven appear to have a significant role in the determination of mesopore volume. For cokes with high surface area available for solution-loss, contrary to expectations, a weak relationship was found between CSR and carbon matrix development, as expressed by crystallite height and percentage of less-reactive carbon forms.

### **Mössbauer and Other Spectroscopic Analyses of North-East Indian Coals and Tailings Products**

Frans Waanders, North-West University, SOUTH AFRICA; Binoy K Saikia, CSIR-North East Institute of Science & Technology, INDIA

Coal is considered as one of the potential candidates to supplement the need for energy in the North-East region of India, which is rich in various natural resources, including a large coal reserve. These coals are low in ash, have a high heating value, are high in volatile matter and tar yield during carbonization and can be classified as sub-bituminous to bituminous. Moreover, the coals of this region contain high organic sulphur which is different from coals around the world where sulphur occurs in

inorganic forms and can be removed to a substantial amount by physical, chemical, radiological and biological methods. The NER coals generally contain 2-8% sulphur, where 75-90% is organically bound, while the rest is in inorganic form such as sulphates and pyritic sulphur and hence desulphurization of such coals cannot be achieved completely.

The dumping of mine tailings and other reject materials (referred to as overburden, OB) generated from opencast coal mines is considered as a major contributor to the ecological and environmental degradation as the OB materials also contain elevated concentrations of trace metals. Due to the presence of the high amounts of sulphur (2-12%), the mine OB of the North-East collieries results in highly acidic conditions to prevail where pH values range between 2.0 and 3.0.

Proximate and ultimate analyses, Mössbauer spectroscopy, SEM and HR-TEM analyses of the coal and tailings samples yielded a better insight into CV-values, carbon types present and the types of sulphur minerals present with Mössbauer spectroscopy detecting mainly pyritic sulphur, iron sulphate and in some instances hematite. From the SEM analyses Ti, Zr and Cd were observed and HR-TEM typical pyrite crystals to be present. This initial report forms part of a detailed research project currently underway.

## SESSION 25

### Clean Coal Demonstration and Commercial Projects: Clean Coal & Coal/Biomass-to-Liquid Fuels Processes

#### Overview & Status Update of U.S. DOD/DOE Joint Greenhouse Gas Emissions Reductions Research & Development Leading to Cost-Effective Coal-to-Liquids (CTL) Based Jet Fuel Production

John M. Rockey, Thomas A. Sarkus, DOE/NETL; Robert Allen, AFRL/RQTF, USA

This summary presentation will provide an overview of the U. S. Department of Defense's (DOD) and the U. S. Department of Energy's (DOE) joint Coal and Biomass to Liquid Fuels projects. These seven projects were awarded in September 2014, and carry a total estimated cost of \$25.7 million, including U.S. DOD/DOE's cost share of \$ 20 million (78%). Most of the funding comes from the U.S. Air Force (\$17.3 million) while the remaining (\$2.7 million) funding comes from DOE's Office of Fossil Energy. The 7 projects are:

- RTI International's Breakthrough Hybrid CTL Process Integrating Advanced Technologies for Coal Gasification, Natural Gas Partial Oxidation, Warm Gas Cleanup, and Syngas-to-Jet Fuel. Total estimated cost \$ 5.5 million; DOD/DOE share \$4.4 million (80%). The indirect liquefaction project plans to demonstrate that the jet-fuel intermediate produced at the 1 bbl/day pilot plant is suitable for upgrading to jet fuel using commercial refinery processes, and to establish a clear commercialization path within the next 5-15 years.
- Altex Technologies Corporation's Green-House-Gas-Reduced Coal-and-Biomass-to-Liquid-Based Jet Fuel (GHGR-CBTL) Process. Total estimated cost \$3.68 million; DOD share \$2.83 million (77%). This project combines aspects of direct and indirect liquefaction technologies at the 1 bbl/day scale to produce 200 gallons of JP-8 to be tested for compliance with military jet fuel specifications.
- Battelle's Direct CTL for Jet Fuel Using Biomass-derived Solvents. Total estimated cost \$3.76 million; DOD share \$2.95 million (78.4%). This project will demonstrate a hybrid, direct coal-to-liquids jet fuel process using novel biomass derived solvents as a hydrogen source. The 1 bbl/day scale testing will generate 500 gallons of jet fuel for characterization for suitability as JP-8 without requiring blending in petroleum-derived JP-8.
- Southern Research Institute's Indirect Liquefaction of Coal-Biomass Mixtures for Production of Jet Fuel with High Productivity and Selectivity. Total estimated cost \$3.78 million; DOD share \$3 million (80%). This project uses process intensification approaches in auto thermal reforming of syngas and recycled FT tail gases and a hybrid Fischer-Tropsch (FT) catalyst/heat transfer system with a target of at least 85% of liquids with at least 60% jet fuel selectivity. Tests are planned at the NCCC operating on PRB coal/wood pellet blends containing up to 45% biomass.
- Ceramtec's Greenhouse Gas Emissions Reductions Research and Development Leading to Cost-Competitive Coal-to-Liquids (CTL) Based Jet Fuel Production. Total estimated cost \$6 million; DOD share \$4.5 million (75%). This indirect gasification project uses a Molten Salt Gasifier operated on coal water slurry and biomass, and novel desulfurization and FT reactor systems at the 1 bbl/day scale. An analysis of the cost structure of a commercial sized plant with all required equipment to generate jet fuel will be conducted.
- Princeton University's Design/Cost Study and Commercialization Analysis for Synthetic Jet Fuel Production at a Mississippi site from Lignite and Woody Biomass with CO<sub>2</sub> Capture and Storage via EOR. Total estimated cost \$1.6 million; DOE share \$1.17 million (73%). The project will develop a design based on a TRIGTM gasifier in an oxygen blown scenario sufficient for a Class 3 cost estimate to evaluate cost competitiveness for converting syngas via FT to the primary product being jet fuel.

- Lummus Technology's Feasibility Study for Conversion of Wabash River Unit 1 – IGCC to a CTL Plant. Total estimated cost \$1.37 million; DOE share \$1.09 million (80%). The project will develop a feasibility study for potential conversion of Wabash River Unit 1 to a coal-to-jet fuel plant producing jet fuel in compliance with EISA 2007 requirements.

Several of these projects will be covered in greater detail in separate presentations to follow.

#### Design/Cost Study & Commercialization Analysis for Synthetic Jet Fuel Production at a Mississippi Site from Lignite and Woody Biomass with CO<sub>2</sub> Capture & Storage via Enhanced Oil Recovery

Eric D. Larson, Tom Kreutz, Hans Meerman, Robert H. Williams, Princeton University; Steven Baxley, Southern Company Services, USA; Chris Grieg, University of Queensland, AUSTRALIA

A commercial-scale facility is being designed to convert a co-feed of Mississippi lignite and woody biomass into synthetic Fischer-Tropsch jet fuel certified for 50/50 blending with conventional jet fuel. Coproducts include refinery-grade naphtha and grid electricity. The capture and storage of byproduct CO<sub>2</sub> and the use of sustainably-produced biomass will result in lifecycle greenhouse gas (GHG) emissions for the jet fuel that are lower than for petroleum-derived jet fuel. The CO<sub>2</sub> will be used for enhanced oil recovery. This first-of-a-kind (FOAK) plant will be located at the site of Mississippi Power Company's Plant Sweatt generating station slated for retirement. The site is a few miles south of Meridian, MS, and 30 miles south of the Kemper County IGCC plant. The two year study began in October 2014, and completion of the basic plant design is expected by October 2015, followed by development of PFDs, equipment lists, and other design documentation to support detailed estimates of capital and operating costs and an assessment of the project's feasibility.

The design will include an oxygen-blown KBR transport gasifier (TRIGTM) co-processing 25% biomass with lignite. The TRIGTM technology has operated successfully at pilot scale with up to 30% biomass co-feeding at the Southern Company's Power Systems Development Facility. The raw syngas will be cleaned, water-gas shifted to achieve H<sub>2</sub>:CO = 2, and subjected to Rectisol™ for acid gas removal. Captured sulfur will be made into saleable sulfuric acid onsite, and captured CO<sub>2</sub> will be compressed for sale into a pipeline network connecting to oil fields. The Fischer-Tropsch synthesis island will utilize tubular fixed-bed, low-temperature synthesis reactors and a syncrude upgrading system designed by Emerging Fuels Technology (EFT). Purge gas from the FT Island will be used to fuel a gas turbine combined cycle to meet onsite power needs and export some to the grid. A waste-heat recovery steam cycle will complete the design of the power island.

Process design and optimisation work at Princeton is being supported by KBR, EFT, and other key technology providers, and the Antares Group is providing input on biomass supply. WorleyParsons is providing engineering and cost estimating services. The final cost estimate will take into consideration the early stage of this design study and the FOAK nature of the plant. A set of principles for project design are helping to guide design decisions. Key among these is limiting expected total capital required to about \$2 billion, so as to improve chances for financing the project. The current expectation is that the facility will have a capacity of about 2000 barrels per day of liquids and about 50 MW of net electricity exports. It is unlikely that the FOAK facility will produce cost-competitive jet fuel without subsidy, but the primary objective of the FOAK plant is to demonstrate technical feasibility of a scalable concept and to identify opportunities for future cost reductions and performance improvements. The financial viability of the project and strategies for scale-up commercialization will be analyzed rigorously under various scenarios to judge the extent to which cost-competitiveness with conventional petroleum-derived jet fuel can be realized. A detailed public design report will be available to project developers and other relevant decision makers.

Primary funding for this design study is being provided by the Major Projects Division of the National Energy Technology Laboratory. The Southern Company and the University of Queensland are providing cost-sharing.

#### Direct Coal-to-Liquids (CTL) for Jet Fuel using Biomass-Derived Solvents

Satya P. Chauhan, Dan Garbark, Herman Benecke, Nick Conkle, Rachid Taha, Battelle; Jason T. Lewis, DOE/NETL, USA

Battelle, under a cost-shared program supported by the U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL) and the Ohio Development Services Agency (ODSA), is demonstrating a hybrid, direct coal-to-liquids (CTL) process for producing a syncrude from coal using a bio-based coal solvent, and a method for conversion of the syncrude into jet fuel. The project objectives are to demonstrate a straightforward path to near-term commercial production of jet fuel from coal using biomass-derived coal solvents. The Battelle process will offer a significant reduction in capital and operating costs and a substantial reduction in GHG emissions, without requiring carbon capture and storage (CCS) at the coal liquefaction site. The results of the project will be the advancement of all key steps of the hybrid coal/biomass- to-jet fuel process to the technology readiness level (TRL) of 5. The project objectives will be accomplished over a 2-year, 7-task R&D effort. The three major Subsystems of the process – biomass to coal solvent conversion, coal

dissolution and demineralization to produce a syncrude, and hydrogenation/hydrotreatment of the syncrude to jet fuel – are being developed and tested in batch/lab-scale, continuous bench-scale and then at pre-pilot scale. The project objectives will be achieved over two phases. Phases 1 and 2 are each 12 months long. In Phase 1, which is nearing completion, all major process steps will be explored and refined at continuous bench-scale, including: (1) biomass conversion to high hydrogen-donor coal solvent; (2) coal dissolution in biomass-derived solvent without molecular H<sub>2</sub>, to produce a syncrude; and (3) two-stage catalytic hydrogenation/hydrotreating of syncrude to jet fuel and other distillates. In Phase 2, these same process steps will be scaled-up to continuous, pre-pilot scale, allowing realistic estimates of process economics and GHG emissions reduction, thus defining the path for widespread process commercialization in a short time period. The process is expected to meet the requirements for limiting greenhouse gas (GHG) emissions under Section 526 of Energy Independence and Security Act of 2007 (EISA 2007) without requiring CCS, as well as to help meet the requirements of secure jet fuel supply without requiring blending with petroleum-based JP-8/JP-A.

This paper will cover the key results to date, which are quite encouraging. The initial testing has shown that several biomass-derived coal solvents are comparable to tetralin in dissolving coal. A couple of syncrudes prepared under this program are currently being tested in lab-scale hydrogenation/hydrotreatment system.

**SESSION 27**  
**Gasification Technologies: Modeling - 1**

**Analysis of Sub Models for CFD Simulation of Industrial Coal-Water Slurry  
Entrained Flow Gasifier**

Andreas Richter, Bernd Meyer, TU Bergakademie Freiberg, GERMANY; Yu Zhang,  
Jian Xu, Yong Yang, Synfuels China Technology Co., Ltd., CHINA

A comprehensive CFD model was developed for the simulation of a 900 t/d industrial single burner coal-water slurry entrained flow gasifier. The coal-water slurry gasification process comprises several sub processes, including water evaporation, devolatilization, gas reactions and char reactions. The CFD model is based on the Eulerian-Lagrangian method, so the gas phase is simulated by an Eulerian approach, while coal-water slurry droplets are tracked by a Lagrangian method. In the presented CFD model, the Eddy Dissipation Concept is used to describe the turbulence-chemistry interaction in the gas-phase of the gasifier. The proposed CFD model was carefully validated using literature data for lab-scale reactors, and the final model for industrial scale reactors was approved by process design data for a 900 t/d coal-water slurry gasifier currently operated at a demonstration plant for indirect coal liquefaction, located in Inner Mongolia. In this work, a sensitivity analysis of several models was performed. This comprises the turbulence modeling, the chemical mechanism for gas-phase reactions, and the sub-models for evaporation, pyrolysis, and char conversion. The final impact of these models on the main gas species compositions and temperature will be discussed.

**Low Cost, High-H<sub>2</sub> Syngas Production for Power, Hydrogen, and Liquid Fuels**

Wei Yan, Arunabha Basu, Joseph Masin, S. James Zhou, Razima Souleimanova,  
Timothy Tamale, Naomi Klinghoffer, Howard S. Meyer, Gas Technology Institute,  
USA.

For coal gasification technology to penetrate the commercial market, technical solutions are required that can reduce the capital investment by at least 30%. GTI is determining the technical and economic feasibility of a system approach for producing high hydrogen syngas via a hybrid coal gasification and natural gas partial oxidation (POX) process coupled with advanced downstream treating processes for multi-contaminant removal and for H<sub>2</sub>/CO<sub>2</sub> separation. This system could have the potential to reduce the total plant cost (TPC) of the gasification plant by over 40% and the cost of finished products by 25% and provide a path to be ready for first-of-a-kind commercially relevant demonstration by 2030.

Gasification is used to convert a solid organic feedstock into a gaseous form, referred to as syngas. With gasification-based technologies, pollutants can be captured and then disposed of or converted to useful products more easily than combustion-based technologies. In the DOE's vision for clean power using gasification, steam is added to syngas in a water-gas shift reactor to convert the CO to CO<sub>2</sub> and to produce additional H<sub>2</sub>. The H<sub>2</sub> and CO<sub>2</sub> are separated – the H<sub>2</sub> is combusted to make power or sold as a chemical and the CO<sub>2</sub> is captured and sequestered, converted to useful product, or used for enhanced oil recovery. Alternatively, the water-gas shift unit can adjust the H<sub>2</sub>/CO ratio as required to prepare the syngas for a catalytic conversion to liquid fuels. These liquid fuel plants can produce diesel, gasoline, or alcohol while capturing CO<sub>2</sub>.

This paper will describe the ultimate embodiment of GTI's technology system where coal and natural gas, with >50% of the total energy from coal, are first converted to syngas in the Aerojet Rocketdyne gasification reactor and a PO<sub>x</sub> reactor, respectively. The combined syngas goes through a series of conventional processing steps, such as water gas shift and temperature conditioning, prior to GTI's contaminant removal process. GTI's Integrated Multi-Contaminant Removal Process (SR2) uses co-current

static mixing reactors to scrub heavy metals, ammonia, and chlorides from the syngas, and to convert hydrogen sulfide in the syngas to liquid elemental sulfur plus water by reacting the H<sub>2</sub>S with added sulfur dioxide in the presence of a solvent and homogeneous catalyst. In the power and chemical hydrogen cases, GTI's developmental hydrogen membrane, a thin, hydrogen-permeable, metal layer deposited on a high specific surface-area, porous, hollow fiber, would be used for hydrogen/CO<sub>2</sub> separation downstream of the SR2 unit. The retentate carbon dioxide rich stream is produced at near the feed gas pressure, thereby minimizing downstream compression for sequestration or EOR use.

The paper will also present the results of three techno-economic assessments for the production of high-purity hydrogen, power, and liquid fuels utilizing this system. The costs of the finished products were sensitive to the relative cost of coal and natural gas. Even with natural gas costing 2.3 times that of coal on an energy basis, the study estimated that the hybrid system could produce electricity, chemical-grade hydrogen, and Fischer-Tropsch liquid fuels at costs 25-30% less than conventional gasification systems. The TPC for the hybrid system is about 40% less than a conventional IGCC system and can approach the cost of a natural gas combined cycle plant with carbon capture. Hydrogen and liquid fuel hybrid plants will have 30-35% lower TPC. These lower capital investments reduce the risk of employing gasification technology.

**Development and Application of a New Structure Based Viscosity Model for  
Oxide Melts Relevant to Fuel Slags**

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and Climate Research (IEK-2), Forschungszentrum Jülich GmbH; Klaus Hack, GTT  
Technologies, GERMANY

The IGCC power plants allow a high efficiency and a good opportunity to control the CO<sub>2</sub> emissions produced from the use of fossil fuels such as coal. The core of an IGCC power plant is the gasifier, in which slag viscosity as a function of temperature and composition plays a significant role in determining the optimum operating conditions due to the fact that many processes during the gasification are related to the slag viscosity, such as the particle sticking (or droplet sticking), slag flow and slag tapping. However, most of the previous viscosity models are only valid in a limited range of temperatures and compositions resulting from the lack of an effective description of the structural dependence of the viscosity. In this study a structure based model has been developed for the fully liquid system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-MgO-Na<sub>2</sub>O-K<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub> and its subsystems in the Newtonian range, based on the thermodynamic modified associate species model. To obtain an effective structural dependence of the viscosity, it is linked to the associate species distribution and the connectivity of associate species. With this principle, both the temperature- and composition-induced structural changes of oxide melts can be described with a set of monomeric associate species in combination with the critical clusters induced by the self- and inter-polymerizations. With the new model, one of the challenges of the viscosity behavior in SiO<sub>2</sub>-based binary systems, the so called lubricant effect, is well described. The viscosity behavior when substituting one network modifier for another at constant SiO<sub>2</sub> contents is also well described. Moreover, the Al<sub>2</sub>O<sub>3</sub>-induced viscosity maximum is described, in which the position and magnitude of the viscosity maximum as a function of temperature and composition (charge compensation effect) are properly predicted. The new model is self-consistent and gives a reliable prediction over the whole range of compositions and a broad range of temperatures using only one set of model parameters, which all have a clear physico-chemical meaning. In addition, the iso-viscosity lines and 3-dimensional viscosity surfaces are generated and further applied to determine the effects of coal ash fluxing and blending.

**Performance Analysis of Power Generation and Synthetic Natural Gas (SNG)  
Production from Coal Gasification with Integrated versus Non-Integrated  
Configuration**

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Research, Atomic Energy Council, TAIWAN; Ting Wang, University of New Orleans,  
USA

Taiwan is an isolated island with a dense population and limited natural resources. In 2013, 97.58% of the energy produced in Taiwan relied on foreign imports. The status of energy demand in Taiwan, by primary energy statistics, consists of 47.60% crude oil, 30.15% coal, 11.97% natural gas, 8.42% nuclear, and 1.86% others, respectively. The portfolio of electricity generation consists of coal (48.06%), gas (27.55%), oil (2.35%), nuclear (16.5%), pumped hydro (1.26%), and renewables (4.28%). It could be expected that the power generated from fossil fuel plants will be increased to cover the imminent shortage of electricity supply in Taiwan due to the pending retirement of three nuclear power plants.

Due to the relatively higher price of liquefied natural gas (LNG) compared to that of coal, the capacity factor of NGCC (natural gas combined cycle) units is substantially lower compared to the counterpart of coal-fired plants in Taiwan. Hence, it would be beneficial to convert coal to synthetic natural gas (SNG) so as to fuel the NGCC units, provided that the SNG price is lower than that of LNG. If SNG is employed in Taiwan, the idled NGCC capacity could be activated. Then, electricity generation can be increased without adding new investments for NG powered units. This would help stabilize the price of electricity by softening the impact of high LNG price.

The objective of this study is to investigate the performance and the pros and cons between integrated and non-integrated SNG plants. Considering the complexity of building an integrated, once-through SNG power plant and the uncertainty of the long-term SNG market in Taiwan, the concept of utilizing a non-integrated approach to produce SNG and power has become attractive for the best interests of various stakeholders (in spite of the lower overall plant efficiency of the non-integrated approach). In Taiwan, there are several other reasons that drive the consideration of pursuing non-integrated systems. First, the long-term need of SNG in Taiwan is not certain. It is risky for investors to make a decision when the future market conditions of SNG are uncertain. Second, making SNG is not the specialty of the government-owned utility company, which prefers to have the flexibility of purchasing either LNG or SNG, whichever is cheaper, under contractual terms, rather than build and operate integrated SNG plants. Third, it is more attractive to the investors to build the gasification plant separately from the SNG plant because the syngas market is broader. The fourth reason is related to Taiwan's future carbon policy. The current trend in Taiwan's carbon policy involves imposing regulations on coal-fired power plants such that the total CO<sub>2</sub> emissions would be on the same level as NG-fired power plants. However, these regulations would likely not be placed on other industrial plants for a foreseeable future. In this scenario, the non-integrated approach will be evaluated by the policy as three independent plants, and only the combined power plant will be subjected to the power plant carbon regulations. By using coal-derived syngas as the fuel, the power plant can easily meet the emissions criteria of a NG-fired power plant. The non-integrated configuration includes three separated systems: a syngas plant, a SNG plant, and a combined cycle plant. 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 for the entire plant. The commercial chemical process simulator, Pro/II® V8.1.1, is used to build the non-integrated and integrated systems and perform the system performance analysis.

#### Coal Hydrogasification for Aromatics and Methane

Guoqing Wang, Yongguang Nie, Zhichao Ma, San Zhou, Xuliang Jing, ENN Science & Technology Development Co., Ltd., CHINA

With the increasing concerns on energy and environment issues, many companies and organizations have paid attention to comprehensive utilization of coal. As an innovative technology, coal hydrogasification can co-produce substitute natural gas (SNG) and aromatic hydrocarbons, which is significantly more efficient and economical than other processes. ENN Co. has developed a 10t/d coal hydrogasification process development unit (PDU) plant. Many advanced key equipments and technologies have been applied in the PDU plant. The influence factors on the distribution of hydrogasification products also have been studied.

##### (1) Development of injector

The high pressure hydrogen combustion injector has been developed, which can supply high temperature hydrogen by partial combusting of hydrogen with oxygen, ensuring good mixing of coal and hydrogen. So far, the injector has been running more than 1500 hours, while its reliability has been proved.

##### (2) Development of dense phase conveying technology of coal

The pulverized coal is conveyed to the gasifier by hydrogen under high pressure. Conventional inert gas (such as nitrogen) is replaced by hydrogen as transport gas so that the composition of the syngas is improved. Thus, a new dense phase conveying system of coal was developed. In this system, many key factors including coal properties (moisture and particle size), pressure drop for conveying, gas species, pipe length and diameter have been tested and optimized. The results show that the highest ratio of solid to gas in this process can be as high as 200kg-coal/kg-H<sub>2</sub>, and the highest coal feeding rate could reach 150-200t/d.

##### (3) Research on hydrogasification process

About 40 tests have been carried out on the 10t/d PDU plant. The influence factors including reaction temperature, H<sub>2</sub>/coal ratio, various types of coal, gasification pressure and residence time, were studied. The results showed that under the suitable reaction condition, the total carbon conversion was between 45% and 60%. The yield of aromatic hydrocarbon was about 10-15% (dry coal based). The volume fraction of CH<sub>4</sub> and CO in the product gas (excluding H<sub>2</sub>) was 75-80% and about 15% respectively with small amount of C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub> left. Besides, a 72-hour-operation test has also been accomplished. During the long term test, the PDU plant was running very stably, in which the feasibility and reliability of this advanced process of coal hydrogasification for aromatics and methane has been validated.

##### (4) Design of industrial demonstration plant

Based on the PDU experimental results, a 400t/d coal hydrogasification plant design has been launched for demonstrating the feasibility of commercial scale plant. The construction of the demonstration plant is planned to be completed in 2017.

## SESSION 28

### Combustion Technologies: Co-Firing

#### Estimating Biomass Yield and Co-Combustion of Coal Discard/Middling with Different Biomasses

S. O. Bada, R. M. S. Falcon, L. M. Falcon, University of the Witwatersrand, SOUTH AFRICA

The thermal behavior and physicochemical characteristics of a discard coal (DC) and middling coal (MC) products, along with different biomasses such as a 4 years plus Bambusa balcooa (BB) and Dendrocalamus Asper (DA), Olivestone, Sawdust, Macadamia shell, Wood knots and shavings were investigated using thermogravimetric analysis (TGA). In addition, the estimated DA biomass yield (tons/hectare) and quantity (kg) required to generate 1 kWh of electricity at a certain energy conversion was presented. The aim of the study is to enhance the utilization of the million of tons of discarded/middling coal as co-fired fuel and to determine their combustion potential solely, along with the above mentioned seven different biomasses. The ash composition of all the biomass was analyzed in order to determine the propensity of the ash to slagging and fouling. The co-firing of the seven biomass fuels with DC 78.31% and MC, 39.45% ash content were conducted in air using a ratio of coal inclusion of 10%, 30%, 50% and 75%.

The proximate and ultimate analysis results show a significant difference in the quality of the six biomass fuels. The ash content and total carbon "As-received" of the biomass fuels were found to be Macadamia (0.32% & 49.70%), Olivestone (0.90% & 53.10%), Wood Shaving (0.62% & 47.55%), Sawdust (6.10% & 44.41%), Wood Knot (2.72% & 45.39% and the 4 years Bambusa balcooa (1.94% & 46.80%), respectively. The total sulphur content of all samples was found to be in the range of 0.018% to 0.65, with the wood knot having the highest sulphur content.

The influence of biomass on the thermal characteristics of the DC and MC was illustrated on the DTG curve. The Olivestone, followed by macadamia and BB samples were the fastest and easiest fuel to ignite with very low peak temperatures. Whilst, the wood shaving has the highest reactivity of 15.30 %/min of all the fuels utilized, and the DC with the lowest calorific value of 1.84 MJ/kg compared to 19.64 MJ/kg obtained from the macadamia nut shell.

#### Preliminary Studies on Biomass Co-Firing Targeted to Demonstration in a Commercial Pulverized Coal Power Plant

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Biomass co-firing becomes more and more important in Korea, for coping with the RPS (Renewable portfolio standard) which has been implemented since 2011. In this presentation, several studies on biomass co-firing to commercial pulverized coal power plants are introduced. The target power plants have 500 MW in scale and different boiler configurations. One of the plants was designed to use bituminous coal and the other was to use sub-bituminous coal which contains higher moisture content and lower heating value than the bituminous coal. In both plant, biomass co-firing tests have been performed, just adding a biomass handling system to the existing plants. This study is aimed to improve performances of the biomass co-firing system in the sense of enhancing biomass co-firing ratio, diversifying co-fired biomass fuels, and in-furnace NO<sub>x</sub> reduction through reburning technology. In this presentation, several studies on biomass co-firing to those commercial pulverized coal power plants are introduced. First, results of performance evaluation for the two plants are presented for various co-firing methods, co-fired fuels and co-firing ratio. The evaluation was performed by process simulation as well as boiler efficiency calculation for all cases. Second, some CFD (computational fluid dynamics) results are to be shown for various co-firing cases. NO<sub>x</sub> reduction characteristics, temperature profiles in the furnace and heat flux distributions are predicted and evaluated for various co-firing cases. Finally, selected pilot-scale (80kWth) test results will be shown, and future demonstration plan will be briefly introduced.

## SESSION 29

### U.S. EPA's Coalbed Methane Outreach Program (CMOP) Coal Mine Methane Conference Track: General - 5

#### Development and Implementation of Ventilation Air Methane (VAM) Projects

Clark Talkington, Advanced Resources International, Inc., USA

Estimated worldwide coal mine methane (CMM) emissions total 589 million metric tons of carbon dioxide equivalent (MMTCO<sub>2</sub>E), or about 41.2 billion cubic meters (BCM) and emissions are expected to grow to 671 MMTCO<sub>2</sub>E (46.9 BCM) by 2030 according to the U.S. Environmental Protection Agency (USEPA 2012). Mine

ventilation accounts for the largest share of emissions from coal mines with an estimated 70% of all coal mine methane emissions.

Methane concentrations in ventilation air methane (VAM) are very low, generally below 1.0 percent CH<sub>4</sub>, although some countries including the United States allow CH<sub>4</sub> concentrations as high as 2 percent in certain return shafts. The coal industry in many countries has a long history methane capture and use from degasification systems, but the low concentrations in VAM have inhibited its use despite the enormous energy potential of the large volumes of methane emitted to the atmosphere. Beginning in the early 1990's, substantially more effort was directed at identifying, designing and testing various technologies for VAM capture and use. This effort led to the adaptation of regenerative thermal oxidation (RTO) to VAM. RTO technology is common in manufacturing for oxidizing low concentration volatile organic compounds, and the same approach is used for VAM. Today the RTO technology is a commercially viable option for destroying VAM emissions and generating thermal energy for other uses.

Although the RTO technology is generally straight-forward and not overly complex, development and implementation of VAM projects requires access to significant capital, effective preparation including a thorough mine gas audit and mine gas forecasts, and coordination with the mining operations. Strong off-take agreements for energy produced and emissions reduction purchase agreements (ERPA's) for emission reductions are necessary to sustain the project. Safety is paramount, and VAM projects must have extensive and redundant safety features.

Given its very large share of coal mine methane emissions, success in reducing greenhouse gas emissions from the global coal sector must include VAM abatement on a wide-scale. This paper will: (i) global VAM emissions including the countries with the largest VAM resources; (ii) review RTO technology and also identify other technologies that are in development and close to commercialization; (iii) identify and examine the key considerations in siting, developing and implementing a VAM project; and (iv) present indicative project economics for VAM projects.

### **Estimating VAM Concentration Based on Coal Tonnage Forecast and Ventilation Flow Rate**

Dominique Kay, Guy Drouin, Biothermica Technologies, CANADA

Underground coal mining activities generate methane gas that must be vented to the atmosphere for safety purposes. Thereby, nearly 20 million tonnes of methane are emitted each year by the ventilation systems of underground coal mines around the world. Since methane is a greenhouse gas (GHG) 25 times more potent than CO<sub>2</sub>, these VAM (Ventilation Air Methane) emissions are equivalent to 500 million tonnes of CO<sub>2</sub>.

The abatement of VAM has been recognized by major carbon frameworks as an eligible activity for the generation of carbon credits. With the adoption of the Mine Methane Capture Protocol by ARB on July 1, 2014, VAM projects in the U.S. are now eligible to produce offset credits that can be sold on the regulated California-Québec carbon market, which provides a source of revenue fostering the implementation of VAM abatement measures such as Regenerative Thermal Oxidation (RTO) systems.

The range of VAM concentration to be discharged by the ventilation shaft is a critical project input dictating the design and profitability of such VAM abatement projects. VAM concentration depends on various geological and operational factors including coal rank, coal seam depth, method of mining, coal tonnage and ventilation conditions. The individual contributions of each of these factors may significantly vary and are often difficult to determine, which makes the prediction of VAM concentration very challenging. However, for a given ventilation shaft, coal tonnage and ventilation flow rate are the two main factors impacting methane concentration over time, since most other factors (coal rank, coal seam depth, method of mining, etc.) remain relatively constant.

In preparation for its next VAM abatement project planned to be implemented at shaft 7-14 of Walter Energy mine in Alabama, Biothermica has setup a methane analyzer system which has allowed continuously monitoring the concentration released at shaft 7-14 for 20 months. Concentration data were coupled with coal tonnage and shaft ventilation flow rate data provided by Walter Energy. Flow rate data were coupled with the monthly average methane concentration to estimate the total volume of methane release per month. Then, these monthly volume of methane were correlated with the coal tonnage produced during each month. A linear correlation was confirmed between the amount of methane released at shaft 7-14 and coal tonnage in the specific mine area ventilated by shaft 7-14. Based on this correlation, an equation was developed allowing predicting the average methane concentration to expect at shaft 7-14 as a function of clean coal tonnage and shaft flow rate forecasts.

### **Addressing the Technology and Standards Gaps for VAM Abatement in Australia and Elsewhere**

David Cork, Rod Peet, Corky's Sustainable Energy; Peter Yallamas, Aerison Pty Ltd, AUSTRALIA

Ventilation air methane can be abated in a Regenerative Thermal Oxidizer (RTO). Coal mines in Australia have asked for a safer RTO technology which is affordable and capable of exceeding the base needs of the Australian Coal Industry. A modified RTO, called VAM RAB, has been developed to resolve the design challenges raised by Australian Coal mines. The VAM RAB technology has been

developed, via a seven year path, from a small pilot plant, to two larger demonstration plants, to the design of an even larger commercial scale plant. The aim has been to develop a flame arrestor with a different operating mechanism to the traditional very-small aperture flame-arrestor. This new flame-arrestor has a low pressure drop and will not fail in the presence of mine dusts or sustained VAM concentration above the Lower Explosive Limit. This development is technically difficult given the variability of VAM, high air flow rates and other constraints such as not impacting the existing mine ventilation system. The core research has indicated that isothermal venting for deflagrations occurs differently compared to that described in NFPA 68 "Standard on Explosion Protection by Deflagration Venting". For this application there is a lack of accepted standards and guidelines in Australia and this is compounded by the uniqueness of each coal mine. These types of observations have led to one of the biggest challenges faced during the VAM RAB technology development. That is; "How do Corky's know that Aerison is building the right thing and how does the mine know they are building it correctly?" Therefore, a design assurance methodology was needed to match the other research. The proposed scale-up project will use an engineering design development and verification framework that is based around the guidelines in aerospace standard DO254.

### **COMET™ – A Versatile Economic Low Temperature Catalytic Solution For Ventilation Air Methane Abatement**

Ian Mitchell, David Watson, Suzanne Ellis, Peter Hinde, Alec Miller, Johnson Matthey Davy Technologies Limited, USA

JM and Anglo American, and in particular its AngloCoal business unit have collaborated in developing technology for Catalytic Oxidation of METHane (COMET™) for coal mine ventilation air methane abatement. COMET is a catalytic technology capable of abating the low levels of methane seen ventilation air methane (VAM) streams. This is the culmination of efforts in research and development by mining engineers, process engineers and catalyst scientists to create a robust system that can flamelessly oxidize >99% of ventilation air methane at low temperatures. This presentation will consider the benefits of this concept for VAM abatement, and describe some of the work by JM's catalyst scientists and engineers to demonstrate the potential of the technology.

Combining the mining know-how of a world renowned mining company together with the catalytic knowledge and process technology expertise from a world leading catalytic technology company has allowed the partners to develop a robust and safe, low temperature solution to the emission of methane from the ventilation air from active or abandoned coal mines. The concept utilizes a simple scalable design with modular sub components that allows for a unit with a small footprint that is also able to leverage economies of scale when addressing larger flow rates. The supported precious metal catalyst is a development of one of JM's leading commercial large scale stationary catalysts. The catalyst has been developed specifically to match the VAM duty in order to ensure satisfactory operation under the varied conditions experienced during the treatment of ventilation air. The catalyst formulation has undergone extensive examination in the laboratory and has been demonstrated under industrially relevant conditions for over 2 years. The technology is now ready for commercial application.

### **VAM with CMM Injection and Power Generation Update**

Jason Schroeder, Karl Walby, Durr Systems, Inc., USA

In many countries and regions of the world, no regulation to limit VAM has been established. However, carbon reduction requirements are becoming ever increasing. Many forward thinking companies and venture capital firms are seeing the ability to abate methane voluntarily to obtain carbon offset credits that can eventually be sold or traded in potential carbon credit markets.

Another potential source of profitability and sustainability that can be generated by the abatement of VAM is the creation of energy. At methane concentrations above 0.3% methane, an RTO can operate with no supplementary fuel in a self-sustain mode and generate a substantial quantity of excess heat. However, a system must be implemented to shed the excess heat from the combustion chamber. The excess heat can be directed to a heat utilization device for use. With VAM projects, this is a steam boiler. Steam is generated and sent to a steam turbine to generate power which can be used locally or sold back to the power company.

In 2014 Dürr presented on its VAM abatement project located at the Gaohe Mine in Changzhi City of the Shanxi Province in China. Dürr will provide an update on the 1,040,000 Nm<sup>3</sup>/hr (700,000 scfm) project which is now operating, connected to the power grid and generating up to 20 MW of electricity.

In addition Dürr will present on the next VAM / CMM / Power project in China for the Sangzhang Coal mine. This project incorporates new features handling 720,000 Nm<sup>3</sup>/hr of VAM and 25,000 Nm<sup>3</sup>/hr of CMM with a refined inlet VAM collection system, improved CMM injection system and upgraded RTO technology. The project is currently in the design engineering phase and is slated for startup in the second quarter of 2016.



**SESSION 30**  
**Coal Science: General - 3**

**Hazardous Elements in Agricultural Soils Surrounding a Coal Power Plant from Santa Catarina (Brazil)**

Matheus S. Civeira, Luis F.O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North-West University, SOUTH AFRICA

In general the hazard element contamination coming from coal power plants is something obvious, but when this contamination is accompanied by other contamination sources, such as, urban, coal mining and farming activities the study gets complicated. This is the case of an area comprised in the southern part of Santa Catarina state (Brazil) with largest private power plant generator.

After the elemental analysis of 41 agricultural soils collected in an extensive area around the thermoelectric (from 0 to 47 km) high presence of As, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Sn, Tl, V and Zn was found in some specific areas around the power plant. Nevertheless, as the NWAC (Normalized-and-Weighted Average Concentrations) confirmed, only soils from one site were classified as of very high concern due to the presence of potential toxic elements. This site was located within the sedimentation basin of the power plant. The spatial distribution obtained by mapping in combination with the analysis of the data by Principal Component Analysis (PCA) revealed three important hotspots in the area according to soil uses and geographic localization: the thermoelectric, its area of influence due to volatile compound deposition, and the area comprised between two urban areas. Farming practice turn out to be an important factor too for the quantity of hazard element stored in soils.

**SESSION 31**  
**Sustainability and Environment: General - 1**

**Effects of Cotton Waste Addition on the Oxidation Characteristics of High Sulfur Turkish Lignites**

Arzu Kanca, Ataturk University, TURKEY

Low rank brown coal "lignite" is one of the major domestic energy resources in Turkey, with significantly high amounts of sulfur limiting its potential uses. The best known coal process, combustion, causes serious sulfur emission problem, especially for the high sulfur lignites. The study aims to examine the effects of blending of lignite with cotton waste on the oxidation characteristics of Turkish lignite. Cotton waste including cotton stalks and shells has high energy potential due to its high cellulose content [1, 2]. Although it is one of the large scale agricultural residues in Turkey, the harvesting cotton residue for energy production is not common. The preliminary analysis of the cotton waste obtained from the Southeastern Anatolia Region of Turkey showed that the carbon and sulfur contents of the cotton waste samples are 6.63% and 0.13%, respectively. Heating value of cotton waste was determined to be 3595 cal/g by bomb calorimeter. Additionally, no ash formation was observed during the combustion process.

When the low sulfur and ash contents and high calorific value of cotton wastes are considered, the blending of cotton waste with brown coal may be as an alternative pathway to decrease the sulfur content by preserving the heating value of lignites. In order to indicate the combustion characteristics of coal and cotton waste blends, coal and cotton residues are mixing in different weight ratios and Thermal Gravimetric Analysis (TGA) is employed at a temperature between 25°C and 900°C, under air flow. Additionally, heating values of the coal and cotton waste blends are determined by the bomb calorimeter. The effects of cotton waste amount on the sulfur content and heating value of Turkish lignite will be discussed.

**SESSION 32**  
**Carbon Management: Post Combustion Capture**

**Optimization of Amine-Based Solid Sorbent Chemistry for Post-Combustion Carbon Capture**

Qianwen Gao, David C. Miller, DOE/NETL, USA

Numerous solid sorbent materials have been proposed for application to post-combustion carbon capture. These include both physical sorbents such as zeolites and MOFs as well as chemical sorbents such as amine-impregnated silica. To effectively understand the potential of these materials, they need to be evaluated within the context of a complete process that includes both adsorption and regeneration of the capture material. In addition, that process needs to be synthesized and optimized for the particular material. To help guide the discovery and selection of new materials for

carbon capture, this paper describes an approach to not only optimize a carbon capture process, but to also optimize the material reactivity parameters for a class of amine-based solid sorbents. A diversity of opinion has been expressed in the literature regarding the desire to have a higher or lower enthalpy of reaction. Our approach enables the enthalpy of reaction for all three reactions associated with amine-based solid sorbents to vary, allowing insight into their interaction and providing guidance for tuning the reactivity of future systems.

CO<sub>2</sub> adsorption on amine-based solid sorbents consists of three reactions [1]: (1) water physisorption, (2) bicarbonate formation, and (3) carbamate formation. The reactions can be expressed as  $K_i = \exp(\Delta S_i/R) \cdot \exp(-\Delta H_i/RT)/P$ , where  $K_i$  is the equilibrium constant,  $\Delta S_i$  is the entropy of reaction,  $\Delta H_i$  is the enthalpy of reaction,  $R$  is the gas constant,  $T$  is the temperature, and  $P$  is the overall pressure. Preliminary sensitivity analysis indicates that the entropy and enthalpy of the bicarbonate and carbamate reactions ( $\Delta S_2$ ,  $\Delta S_3$ ,  $\Delta H_2$  and  $\Delta H_3$ ) have the largest impact on the overall cost of capture. We utilize a solid sorbent system model developed under the Carbon Capture Simulation Initiative (CCSI) [2] in conjunction with the CCSI-developed Framework for Optimization and Quantification of Uncertainty and Sensitivity (FOQUS) [3] to simultaneously optimize process design variables and reaction parameters to determine how much the cost of electricity (COE) could potentially be reduced by a hypothetical sorbent exhibiting different reactivity. Our preliminary results indicate that a reduction in COE of approximately 10 \$/MWh can be achieved compared with the base case sorbent. The improvement results from increasing the fraction of the overall working capacity resulting from the bicarbonate reaction, which arises from an increase in the absolute value of  $\Delta H_2$ .

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**Membrane Properties Required for Post-Combustion CO<sub>2</sub> Capture at Coal-Fired Power Plants**

Simon Roussanaly, Rahul Anantharaman, Karl Lindqvist, Jana Jakobsen, SINTEF Energy Research, NORWAY; Haibo Zhai, Edward Rubin, Carnegie Mellon University, USA

Gas separation membranes are considered among one of the most promising technologies for post-combustion carbon dioxide capture. However, to compete with solvent-based systems for CO<sub>2</sub> capture, development of membranes with improved performances (e.g. selectivity and permeance) is strongly needed. Even if membrane development experts have a good idea of what membrane properties are desired for membrane-based CO<sub>2</sub> separation [1], no benchmark has been performed to quantify the membrane properties (permeance and selectivity) required for membrane process to compete with solvent-based CO<sub>2</sub> capture. Considering the high investments of membrane processes and their strong dependence on membrane properties, a cost-based comparative approach as proposed here shall be developed and applied to identify the range of membrane properties that are required for membrane processes to compete with solvent-based CO<sub>2</sub> capture.

Although membrane processes are conceptually very simple, in practice, complicated membrane process configurations are often employed to meet the product purity and capture ratio constraints. To minimize the cost of CO<sub>2</sub> capture of such membrane systems, multiple process design decisions among process configuration, operating conditions, and membrane properties have to be made to ensure suitable driving force for gas separation and determine the optimal trade-off between the separation work and membrane area requirements.

A graphical analysis, called the Attainable Region approach, has been developed by Lindqvist et al. [2-4] in order to easily design a cost-optimal multi-stage membrane separation system for given membrane properties. Here, a numerical version of the analysis proposed by Lindqvist et al. [2-4] is developed to identify membrane properties required for membrane systems that are economically competitive with the commercial MEA-based capture technology. Specifically, for each set of membrane permeance and selectivity considered, the numerical model is employed to optimize the membrane capture process with a configuration up to three stages and evaluates if the best membrane process with the given properties can be economically competitive with the MEA-based CO<sub>2</sub> capture process.

Using the methodology discussed above, Figure 1 illustrates the membrane properties targets necessary to meet the capture CO<sub>2</sub> cost goal in comparison with the Nth-of-a-kind MEA process for post-combustion CO<sub>2</sub> capture at an European-based coal-fired power plant. The green areas indicate the properties which lead to a membrane process with up to three stages that can directly compete with MEA capture. The blue areas correspond to the conditions in which more complex configurations (with for example recycle, sweep, counter-current flow pattern, etc.), which can lower the cost up to 10%,

are required to compete with MEA CO<sub>2</sub> capture. Finally, the purple areas correspond to the conditions in which membrane processes cannot compete with MEA capture while the red area corresponds to the condition in which the membrane processes cannot reach the purity and capture ratio requirements.

The results are directly useable to identify if a given membrane with specific characteristics can be cost-competitive with MEA CO<sub>2</sub> capture (for a given application). Thus, the assessment results can guide the development of membrane materials for cost-effective CO<sub>2</sub> capture, as well as help the industry to select membranes that can compete with solvent-based capture systems.

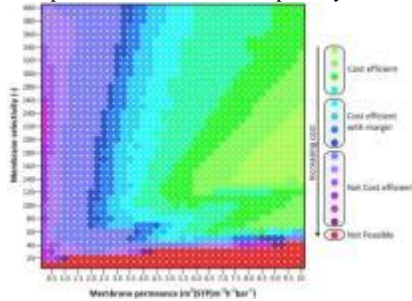


Figure 1: Illustration of the membrane properties under which membrane capture process is cost-competitive with MEA for a European-based power plant considering a Nth Of Kind Plant and a membrane cost of 50 \$/m<sup>2</sup>

Furthermore, to illustrate the influences of flue gas CO<sub>2</sub> concentration, plant location (Europe [5] or USA [6]), and technology maturity, we will comparatively evaluate three additional cases along with different membrane costs and discuss their effects on the of membrane properties required.

Acknowledgements: This publication has been produced with support from the BIGCCS Centre, performed under the Norwegian research program Centres for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Gassco, Shell, Statoil, TOTAL, GDF SUEZ and the Research Council of Norway (193816/S60).

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### Aspen Modeling for MEA-CO<sub>2</sub> System: Solution Approach for Rate-Based Column Model

Zhen Fan, Kun Liu, Heather Nikolic, Reynolds Frimpong, Guojie Qi, Kunlei Liu, University of Kentucky, USA

CO<sub>2</sub> capture by amine absorption and stripping is currently considered as the most viable option for the removal of CO<sub>2</sub> from power plant fired with coal or natural gas. MEA is the benchmark solvent for this application because of its high absorption rate. For performance evaluation, rate-based column models are specially developed such as the Ratefrac™ model from Aspen Plus® that incorporated vapor-liquid-equilibrium, reaction kinetics, film resistance and mass transfer properties.

Solving rate-based column model will not only provide overall column performance, such as capture efficiency and rich solvent C/N loading, but also provide column profiles, such as temperature, concentration, and absorption rate profiles. A recent paper concluded that various simulation tools and setups for same test column and operation predicted properties with the variation in an order of 5-10%, often less than the uncertainty in experimental measurements. Despite of all having a general good resemblance on the final C/N and capture efficiency among modeling, however, column temperature and concentration profiles vary more than expected. Essentially for a rate-based column simulation, to correctly predict rate determined column profiles is more important than to predict the overall column performance, since the column profiles are intrinsically rate determined.

It is believed that the dominant CO<sub>2</sub> absorption occurs at the top of the column because of high mass transfer enhancement factor from the fast kinetics and the high feed MEA concentration. While the absorption rate reduces with increase of solvent loading C/N

as solvent flows down along the column. This induces a high gradient of temperature profile along column with a sharp bulge at the top of column as observed from test and modeling result. Sometime for solving column model these high gradients cause convergence and accuracy issues. Our study indicates that solution approach to numerically solve column model has significant impact on the column profiles, and thus on the convergence and the final results. To reach convergence, dynamic cell sizing in corresponding to gradients is applied in this paper. Fine cell is used for high gradients while a coarse cell for the rest to reduce the total cells. This success allows more cells to be applied locally for study of the impact of very high number of cells on profile. When high resolution applied, the absorption rate profile and the corresponding temperature profile show significant improved, even though the overall column performance is sometime less impacted from a tall column.

In summary, right solution approach for solving column model will be presented in obtaining the appropriate result for performance analysis. The successful in convergence relies on the match of gridding with gradients.

### SESSION 33 Gasification Technologies: General - 3

#### Economic Evaluation of Dry Solids Feeding an Entrained Flow Gasifier

Timothy W. Saunders, Aerojet Rocketdyne Inc., USA; Christopher A. Higman, Higman Consulting GmbH, GERMANY

The coal gasification industry has long been seeking a solution to poor and unreliable performance of lock hoppers for feeding coal into pressure. This is particularly so with very low rank coals which are frequently being used in China, the market center for coal gasification implementation.

Aerojet Rocketdyne has developed a linear Dry Solids Pump (DSP), which provides an alternative to conventional lock hoppers for charging a pressurized coal gasifier. The key to successful implementation of the DSP solution will be capital and operating cost benefits arising from improved availability of the continuous feed DSP and elimination of gas compression costs associated with lock hopper operation.

Aerojet Rocketdyne, in association with Higman Consulting GmbH, has undertaken a study to develop a suitable DSP configuration and plant layout/installation to determine DSP impact on the economics (CAPEX and OPEX) of an overall entrained flow gasification system with syngas cooler for a China location. The study has identified benefits of dry feed and the opportunities for plant reconfiguration and cost reductions reflecting the advantages of continuous solids feeding. The determined configuration and economic benefits identified will be presented. The study will also address benefits associated with solids feeding for water-quench gasifier configurations where the savings for dry solids pump feed are expected to be even greater due to the potential elimination of select support equipment.

#### Comparison of Simulating NGCC/IGCC Power Plants between Using Thermoflex and Aspen Plus

Henry A. Long, Ting Wang, Energy Conversion & Conservation Center, University of New Orleans, USA

During the course of an introductory study meant to analyze the feasibility of an Integrated Mild Gasification Combined Cycle (IMGCC) plant, different segments of the plant were constructed using the commercial software package Thermoflex®. In order to verify the Thermoflex results, they were compared to results from the corresponding segments in both NGCC and IGCC plants modeled by Aspen Plus in a report from the United States Department of Energy (DoE). Both Thermoflex and Aspen Plus are recognized as established commercial software. Thermoflex is a suite of the Thermoflow package, which is widely used for designing power plants and thermoflow processes, while Aspen Plus is a broadly used for designing thermoflow components and chemical reaction processes.

The study begins with the examination of the natural gas combined cycle (NGCC), and the effects of various fuels including low-BTU synthesis gas. During the course of this study, the topics examined and discussed include comparing different design of HRSG & deaerator, investigating the effect of low-Btu gas on gas turbine mass flow rate, inlet temperature and turbine polytropic efficiency, studying the effect of back pressure on compressor performance due to increased mass flow rate in the combustor, and discussing an apparent mass imbalance in the steam turbine block of DoE's case.

The convenience of using built-in modules in Themoflex is also discussed in comparison with Aspen Plus. These modules include an air separation unit, a gasification island, a Selexol® process for acid gas removal, and a carbonyl sulfide hydrolysis unit. The overall conclusions are: (a) the baseline case results are comparable to the DoE results within 1% difference, and (b) Thermoflex is more convenient for building the various subsystems, but is less versatile in modeling chemical processes; whereas Aspen Plus is more flexible in modeling these chemical processes, but requires extensive knowledge of all relevant subsystems and a lot of effort to model them adequately.

## Gasification of PRB Coal Liquefaction Residue

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

Direct and indirect coal liquefaction are two processes used to produce liquid products from coal. These processes have been studied for decades and have enjoyed renewed interest as demand for liquid fuels increases. Indirect liquefaction, through gasification of the coal and subsequent conversion of the syngas to liquids via such processes as Fischer-Tropsch, is expensive and energy intensive. Direct coal liquefaction is less energy intensive, but produces a "dirtier" product requiring more refinement. In addition, a substantial amount of insoluble residue remains after extraction. This residue still has a high concentration of organic material as well as remaining mineral matter and sulfur making disposal a problem as well as contributing to the overall inefficiency of the process.

One potential method for utilization of the remaining direct coal liquefaction 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 the direct coal liquefaction process. 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 which would be used in a commercial direct liquefaction process. Extraction of the coal sample was continued until the solvent passing through the sample no longer showed signs of any coal compounds. The remaining residue was dried and then gasified in a drop-tube type reactor at various temperatures and pressures. Both carbon dioxide and/or steam were used in the gasification process. Results were then used to fit kinetic models to the gasification process. These models were compared with those obtained from gasification of untreated PRB coal to see the relative ease of gasification of the extraction residues.

Results of these studies should provide important information about the possible use of residues remaining from direct coal liquefaction 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 the direct liquefaction process more feasible since the remaining residue could be used effectively and possibly provide needed energy and hydrogen for the direct liquefaction process.

### SESSION 34

#### Combustion Technologies: General

#### Determination of Devolatilization Kinetics in Inert and CO<sub>2</sub>-Enriched Atmospheres in a Plug Flow Reactor

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In recent, utilization of low-grade coals including sub-bituminous coals in Korean power boilers which were originally designed to use bituminous coals of high-quality. These low-level coals contents high moisture contents & sulfur contents, lower heating value & ash fusion temperature (AFT), which may cause of additional environmental problems such as increasing CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> emissions and ash deposit inside boiler. Ash deposit may seriously effect operational life of PC boiler which related with slagging and fouling. Utilization of renewable fuels such as biomass (including wood pallet, walnut shell etc..) in coal-firing power generation system is most promising way to solve previous environmental problems commonly refer as biomass co-firing. In however, one of the major problems using biomass co-firing are increasing corrosion of boiler tube which associated with increasing ash deposit in fouling zone and chlorine contents. There have been limited research papers reported related to investigation of biomass co-firing ash deposit behavior caused by blended biomass and coal combustion. Therefore, purpose of this study is to observe ash deposit behavior (including slagging and fouling characteristics) using a pilot-scale (80 kWh) down-fired pulverized coal combustion system. Three different biomass samples with one bituminous coal are used in present study. In order to observe behavior of ash behavior, the measurement of X-ray diffraction (XRD) and inductively coupled plasma (ICP) are performed in present study.

#### Influence of Different Steam Concentration on Carbonation Reaction of the Carbide Slag

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To mitigate CO<sub>2</sub> emissions from human activities, various technologies have been proposed for CO<sub>2</sub> capture in different energy conversion stages, i.e., pre-combustion, post-combustion CO<sub>2</sub> capture and oxy-fuel combustion. Recently, the calcium looping technology has been intensively studied as a promising technology for CO<sub>2</sub> capture due to its advantages such as low energy penalty, inexpensive and nontoxic sorbent derived from limestone and the potential of integrating with hydrogen production or cement

production. Steam is typically present in the gas stream in either pre-combustion, i.e., hydrogen production, or post-combustion in the carbonation reaction, in the range of 0-40%. The previous works focused on the relative low steam concentration and the high steam concentration above 40% has rarely been reported. Carbide slag is a by-product of acetylene production, which is mainly composed of Ca(OH)<sub>2</sub>. The previous works of our group have proved that the carbide slag can be used as CO<sub>2</sub> sorbent in calcium looping. However, it has not been reported that the CO<sub>2</sub> capture performance of the carbide slag with high steam concentration during the carbonation.

In this work, the effect of the various steam concentrations in the carbonation reaction on the CO<sub>2</sub> capture performance of the carbide slag was investigated in the multiple calcination/carbonation cycles. The effects of the calcination conditions (including temperature and atmosphere) and the carbonation conditions (such as steam concentration, carbonation duration and CO<sub>2</sub> concentration) were studied in a dual-fixed bed reactor. In addition, the microstructure of the carbide slag in the CO<sub>2</sub> capture cycles was studied. It is found that the calcination under pure CO<sub>2</sub> reduces the carbonation conversions of the carbide slag during the calcination/carbonation cycles.

In the presence of steam, the decay of the carbonation conversion occasioned by the calcination conditions is relatively smaller than that without steam in carbonation atmosphere. It is also observed that the higher steam concentration results in higher carbonation conversion, with remarkable difference, of the carbide slag with the short carbonation duration (e.g. 5 min); however the effect of the steam concentration on the carbonation becomes unapparent with the long carbonation duration (e.g., 20 min). In the presence of 60% steam in carbonation atmosphere, the pore volume of the calcined carbide slag is smaller than that in the presence of 20% steam. It indicates that higher steam concentration leads to the worse pore structure of the carbide slag in the cycles.

The results indicate that steam has a two-side effect on the carbonation reaction of the carbide slag. On one hand, the steam has great positive influence on the carbonation conversion of the carbide slag. On the other hand, the presence of steam deteriorates the pore structure of the carbide slag. Therefore, there should be a suitable carbonation duration for the carbide slag in the presence of steam for better cyclic carbonation performance.

#### Slagging Characteristic of Easy to Slagging Coal, Zhundong Coalfield, China

Heng Chen, Yungang Wang, Haidong Ma, Qinxin Zhao, Xi'an Jiaotong University, CHINA

Slagging characteristic is one of the main factors affecting the safety and economic operations of boilers in power plants. The Zhundong coalfield is a very large coal deposit with coal reserves amount to 164 Gt, currently under exploration, and promises to be the most important coal mining resource of China. Zhundong coal is characteristic of low mining cost and fine reactivity. However, the serious slagging occurring on the heating surfaces leads to very dangerous and uneconomical operation of Zhundong coal-burning boilers. In this paper, we discuss the slagging characteristic of Zhundong coal of China. We analysed the slagging samples taken from two boilers (a circulating fluidized bed (CFB) boiler and a pulverized (PC) boiler) burning Zhundong coal. The slag samples on different parts of each boiler were analysed. The results show that some melting ash particles adhere to tube walls and form the initial slag layer. Then the minerals of coal ash begin to decompose, quartz (SiO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and other compounds form low melting point eutectics and bond to the inner layer of the slag body. Fly ash are absorbed and the outer slag layer forms. The study is supposed to be helpful in reducing the slagging of the boilers burning Zhundong coal.

### SESSION 35

#### U.S. EPA's Coalbed Methane Outreach Program (CMOP) Coal Mine Methane Conference Track: General - 6

#### Preliminary Results of Coal Methane Resources Assessment in Mongolia

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This paper provides brief background to Mongolian's coal resources and preliminary results of Coal methane assessment in Mongolia. This study has two parts. The first part reflected coal resources, coal types as well coal production, export and consumption in Mongolia. In Second one reflected the preliminary results of Coal mine methane (CMM) resources assessment for some coal mine sites as well main coal basin of Mongolia. Mongolia has geological coal reserves of 150 billion tons in 300 deposits and occurrences in 15 coal basins, falling in 3 major regions.

In June of 2012 a team comprised of Mongolian Nature and Environment Consortium (MNEC) and Ravin Radge Resources (RRR), USA carried out a series of field visits to three surface coal mines Baganuur, TavanTolgoi, and NarynSukhait. The primary objective of the research was to collect information and data for the CMM resource assessment, which included coal samples, maps, and other data and sample collection, was dictated by the drilling being. The team tested gas samples obtained from the manometer during desorption testing in the field at NarynSukhait and Baganuur mine sites.

Methane desorption and adsorption tests were conducted at the above two mines to determine the gas content of coal. Coal resource estimates served as the basis for

calculating in-place gas resources for each Mongolian coal basin. We estimate the percentage of p50 CMM resources by rank. The majority of CMM resources are contained in bituminous coal (63.9 percent), with subbituminous coal estimated to contain the second largest volume of CMM resources (24.4 percent). Lignite and anthracite contain the least amount of CMM resources with 10.6 percent and 1.0 percent, respectively. The p50 CMM resource estimation of the coal resources potentially lying within 1200 m of the surface is for Mongol-Altai coal basin is 538,022 million cubic meters, for South goby coal basin is 592,936 million cubic meters and for Tamsag coal basin is 470.2 million cubic meters. The total estimated CMM resources of main coal basins is 3,117 trillion cubic meters.

### **Coal Mine Methane Projects in Southwest China: Opportunities and Barriers to Development**

Raymond C. Pilcher, Candice L. M. Tellio, James S. Marshall, Boni Jiang, Raven Ridge Resources Incorporated, USA

Since 2008 EPA contractors and grantees have conducted six pre-feasibility studies and one feasibility study at coal mines in southwest China. These studies explore the technical feasibility and forecast the economic performance of potential improvements to existing gas drainage strategies and options for beneficial uses of gas. Southwest China has been the focus of these studies as the region is one of the fastest growing coal production centers in China, providing raw materials and energy for a rapidly expanding industrial base. Mining authorities estimate more than 350 billion tonnes, or about 6.3 percent of China's minable coal reserves are located in southwest China. In 2014, 3.87 billion metric tons were extracted in China, 10 percent of which was produced from mines located in western Guizhou, southern Sichuan, and eastern Yunnan provinces. Coal mine methane (CMM) extracted from the unusually gassy coal seams mined in this region comprises about 25 percent of that produced in the country, but utilization of the extracted gas represents only about 10 percent of the CMM used nationwide. One fact tells the story of the challenge of gas management at these mines: the amount of methane liberated per tonne of coal mined is about 4 m<sup>3</sup>/t of coal mined as compared to the national average of 1.5 m<sup>3</sup>/t of coal mined. Faced by the lowest coal prices in six years, coal mine operators in China are looking for ways to offset operating losses, service their debt, and maintain operations under difficult market conditions. Progressive mine operators, whose mines were subjects of the EPA funded studies, are investigating options outlined in the reports. Some of these operators are becoming industry pathfinders by making significant efforts to effect transition from commodity producers to integrated energy companies. Yet, this is not an easy path to take as there are institutional and market barriers that limit options for use of produced CMM. Many mines in China generate electricity from produced methane, and several of the mines that are the subject of the EPA studies have chosen this option, but are not always satisfied with the outcome. In southwest China during years when rainfall is plentiful there is an abundance of hydropower, and even though policy and regulations require that regional grid operators purchase electricity from operators generating power from CMM, this is not a reliable market option. The central government of China recognizes the importance of unconventional gas resources and continues to promote the development of CMM projects. If policy and practice become more aligned, coal mine owners will adopt new business models and CMM projects will become more highly valued as a part of their investment portfolio.

### **VAM at Russian Coal Mines**

Oleg V. Tailakov, Institute of Coal of SB RAS/KuzSTU; Peet M. Sööt, CMM Energy LLC, RUSSIA

VAM (Ventilation Air Methane) at Russian Coal Mines was a project funded by the Global Methane Initiative (GMI). The project accomplished all four goals of resource definition, technology assessment, economic analysis and dissemination of results. The focus of this project was on the Kuznetsk Coal Basin (Kuzbass) which is the site of most of the underground mining in Russia. There are about 1.6 billion (109) cubic meters of methane emitted from these mines every year into the ventilation air and into the gas drainage systems. The annual coal production is nearly 200 million tons. This project provided individual mine estimates of methane emissions for all (about 40) coal mines in the Basin. It was also noted that these mines use bleeder boreholes more frequently than coal mines in other countries. Since the methane concentration of air from bleeder boreholes is allowed to be as high as 3.5%, this can provide a much better source of fuel for utilization systems than what is available from ventilation air shafts. Ventilation air shafts are only allowed to emit a maximum of 0.7% methane in the ventilation air. A broad spectrum of technologies were considered for utilization of the ventilation air methane (VAM) from the Kuzbass coal mines. This included VAM as a secondary fuel, as in power plants and industrial fuel applications, as well as VAM as a primary fuel. The primary fuel options that were considered included regenerative thermal oxidizers (RTO - both conventional and catalytic), lean fuel gas turbines (LFGT), chemical looping, porous burners, enzymatic and bacterial consumption of methane and concentration of the methane with adsorption systems. RTO and LFGT were the only commercial systems that were considered in detail. The other technologies are in various development stages and need further improvement and proving before they can be applied commercially. RTO is the only technology which has already been implemented at various coal mines. And those installations exist at numerous mines in

Australia, China and the USA. There are a number of companies that have provided commercial equipment for these installations, including Megtec (Sweden/USA), Biothermica (Canada) and Dürr (Germany). Several more companies claim to have RTO equipment ready for commercial deployment, with additional companies still developing more RTO options, both conventional and catalytic. Kawasaki (Japan), FlexEnergy (USA) and Enercore (USA) are all developing LFGT equipment for VAM utilization. Kawasaki is still in the development phase for their equipment whereas both FlexEnergy and Enercore have commercial equipment ready. FlexEnergy has relatively small turbines available (250 kW) whereas Enercore is offering 2 MW turbines.

Economic analyses were completed for all viable VAM utilization technologies. This included calculation of ROI, NPV and sensitivity analyses. Monte Carlo simulations were also run for the most promising technology options. Unfortunately, none of the technologies were found to be economically viable without some subsidization from carbon credit sales. Enercore LFGT provides a 7.7% ROI, even without subsidies, but will need carbon credit support before the ROI is suitably large for general commercial application. However, LFGT has shown the potential of improvement in ROI as new equipment is developed so it has a significant future potential as the technology of choice for VAM applications – as long as methane concentrations of 1.5% to 2.5% can be made available. And, that is available with bleeder boreholes at Kuzbass mines, or VAM at other mines with sweetening from gob wells or other sources.

### **MEXICO CMM Project from Design to Reality, Who to Implement and Operate Flaring**

Mario Santillan, Adrian Huerta, Brenda Soto, Minera del Norte, MEXICO

AHMSA thru his subsidiary MINOSA has more than 20 year of experience to degas the double coal seams at the Sabina's Basin to prevent accidents in the Northern portion of the country where the only Mexican coal sector in operation are. After mining law modification back in 2006 a gas utilization plan started, currently we are operating three flares in our underground coal mines at MIMOSA unit, this project has been register as a CDM project under to the UNFCCC in 2013 (Reference 3751: "Mimosa Coal Mine Methane Project"). AHMSA operate success the first phase of the project, flaring, and then with the volume of gas register, proceed to generate electricity as a second phase. CATERPILLAR and AHMSA signed a contract to generate for 1.5 Megawatt as a pilot phase on implementation, once we evaluate AHMSA will decide to complete 8 MW in total according with the PDD. Great changes happened in the mining sector 2014, Mexican laws & policies derivate from our Mexican President Peña Nieto's energy reform, who provided an excellent frame work that's allows to use the coal mine methane gas, based on that legal status AHMSA has another four PDD's on validation at the UNFCCC that includes the VAM for the operative mines and CBM, CMM and VAM for the future mines (Concha's complex mines IX, X y XI) including flaring, power generation (12 MW) and high quality gas pipeline sales. The project are considered in total an emission reductions of 3.5 MM tons of CO<sub>2</sub> equivalent.

## **SESSION 36 Coal Science: General - 4**

### **Coal Mining Residues and Sulphide Oxidation by Fenton's Reaction**

Adilson C. Dalmora, Luis F.O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North-West University, SOUTH AFRICA

In this work the Fenton's reaction is utilized as an accelerated weathering test for concentrated sulphides associated with Brazilian Coal Cleaning Rejects (CCR), that are exposed to oxygen and water during the mining of coal. X-ray diffraction (XRD), High Resolution-Transmission Electron microscopy (HR-TEM)/(Energy Dispersive Spectroscopy) EDS/(selected-area diffraction pattern) SAED, Field Emission-Scanning Electron Microscopy (FE-SEM)/EDS were used to evaluate the nature, occurrence and distribution of minerals, organometallics and mineraloids in coals and other lithological units, before and after applying the test. Oxidation of CCR's was observed by studying the soluble sulphur (with sulphate) and dissolved elements by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major and selected trace elements and for additional trace elements inductively coupled plasma mass spectrometry (ICP-MS) was used. As dissolved SO<sub>4</sub><sup>2-</sup> increased, dissolved Zn, Cd, Cu and Co concentrations increased, leading to undetectable amounts of the remaining solid phases. Dissolved Ni and Mn also increased with the mobilized sulphur, with the remainder in the solids being the most significant fraction; Fe and Pb were not mobilized due to precipitation as iron sulphates or iron hydroxides (e.g. jarosite or hematite) in the case of Fe or as SO<sub>4</sub><sup>2-</sup> in the case of Pb. Agreement between the detected results and the calculations by geochemical modelling is debated. Presented results demonstrate that in restoration practice the selective management of spills can be considered to offer the best protection against contamination of surface and subsurface water and is the method which should be applied in the future construction of dump facilities.

## The Influence of Drying Conditions on Processing Properties of Lignite

Albrecht Matthes, Hans-Werner Schröder, Jens-Uwe Repke, TU Bergakademie Freiberg; Bastian Lehmann, RWE Power AG, GERMANY

Lignite is a widely used energy resource. Its natural deposits are near to surface making lignite easy to mine as it is done in vast surface mining areas. This also brings a couple of problems as the coal seams are located in water-bearing formations. Due to that fact lignite has a high water content of up to 60 wt.-% when mined. In Germany 183 Mt were mined in 2013. About 90 % of that were used for electricity generation without any processing. The remaining 10 % of the mined coal are refined. Though for utilization and refining a drying process is advised, as it is necessary to increase the lignite's heat value, improve handling and refining properties or even to reduce the mass and volume for transportation purposes. As is already known for decades, the grade of drying has a significant influence on the processing properties of lignite. In the field of lignite refining by briquetting, for example, the water content of the coal has a remarkable effect on the achievable briquette strength by influencing the formation of particle-particle bonds. But not only the final water content itself, also the process to reach it, is an important factor for the following processing steps. Experimental investigations with lignite using a lab-scale tube dryer have shown that the drying atmosphere influences the drying result significantly. Drying of lignite in an air and water steam containing atmosphere, as is normally applied, delivers a dried lignite with different physical properties compared to drying in a nearly pure steam atmosphere. Due to changing surface reactions and changing gas/steam pressure in the pores the drying atmosphere influences lignite substance parameters such as porosity, specific surface, hardness and pore size distribution. Consequently the mode of drying also influences processing properties like grindability, specific surface formation during pyrolysis and briquetability. Experiments have shown a slightly reduced pressure strength but a considerably increased water resistance of the briquettes when predrying of lignite is performed in a water steam atmosphere.

## Coal Drying Characteristics in Fluidized Bed Dryer

Wonjae Lee, Dongmin Jang, Jaehoon Choi, POSCO, SOUTH KOREA

Coal drying technology has been used for many years in coal power plants and for domestic purposes. Recently coal drying technology has been adopted on the coke making to increase coal charging density in coke oven. In this study the drying characteristics of coking coal was investigated using a continuous two stage fluidized bed dryer (0.15m I.D x 2.5m-high) with a particular focus on the effect of fluidization parameters on coal moisture content. In the batch test, the moisture content of coal drastically decreased with increasing drying time in different conditions of flow rate and hot gas temperature. The drying rate of coal linearly increased with increasing inlet gas temperature and fluidization gas velocity, but decreased with increasing static bed height. In continuous process, the moisture content decreased with increasing fluidization gas velocity and decreasing coal feeding rate. The entrainment rate of dried coal fine increased with increasing fluidization gas velocity, but decreased with increasing coal feeding rate. The ratio of captured coal fine increased with increasing fluidization velocity. By using a two stage fluidized bed, coking coal can be effectively dried and the coal fine separation rate was controlled by using different flow velocity for each fluidized bed. We confirmed that coal with about 10wt% moisture content could be dried to 2~3wt% moisture content by controlling fluidization parameters in a continuous two stage fluidized bed dryer

## SESSION 37

### Gasification Technologies: Bio-Conversion

## Biostimulation for Bio-Gasification for Converting Coal to Methane

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Coal mining generates about 55 million tons of waste coals annually in the US. Besides economic loss to the coal industry, coal wastes are either piled up at mine sites or dumped in ponds where the environmental risk is extremely high but difficult to assess. In order to address the coal waste issue and utilize mined out coals for methane production instead of burning for electricity, we seek to convert coal to methane through bio-gasification.

Bio-gasification, the process of transforming coals to gases by microorganisms takes place naturally in coal seams and mined out coals. This process is one of the driving forces for methane released from coal mines. If it happens in coal waste ponds or surface coals, the resulting methane will be emitted to the atmosphere, severing the greenhouse effect. To take advantage of bio-gasification and reduce emission of methane to the atmosphere, we seek to stimulate microbial activities to turn coal into methane, a cleaner fuel than coal itself.

To achieve this purpose, we took water samples from a coal mine and characterized the microbial composition in terms of distribution of bacteria and archaea through use of next-generation DNA sequencing. Based on the presence of different microbial

species, different nutrient solutions were tested and compared. In addition to methane yield and productivity, the nutrient solutions were also investigated regarding their costs. Based upon these two criteria, methane yield and cost, two nutrient media were selected for further optimization. This optimization considered physical parameters, such as temperature, coal loading, mixing and other non-physical factors, for example, pH, size of inoculum, effect from adding surfactants, carbon sources, etc. A total of 12 parameters were initially screened to identify significant factors through use of Design of Experiment (DOE) software. This screening step also evaluated effects from individual parameters and interactions between and among different ones. Once the important parameters were finalized, response surface methodology was adopted to identify the optimal value for each parameter. According to our results so far, the addition of a nutrient solution can result in a methane productivity of 680 ft<sup>3</sup>/ton coal in 62 days, which is 88 times higher than that without the supplement of any nutrients. Apart from the fact that coal can be converted to methane successfully *ex situ*, the developed approach can also be employed for stimulating methane production *in situ*. Our recent development on both scenarios will be discussed fully through this presentation.

## HUMAXX MicGAS™ Coal Bio Refinery Techno-Economic Analysis for Deployment in Wyoming

Daman S.Walia, ARCTECH Inc., USA

A Techno-Economic feasibility analysis will be presented for a HUMAXX Bio Refinery in Wyoming, using our MicGAS™ Coal Biotechnology to increase monetization of both mineable (61 Billion tons) and un mineable deep coal seams (estimated to be about one trillion tons by the Wyoming Geological Survey). MicGAS™ Coal Biotechnology is an environmental safer approach of using coals that capitalizes on the carbon-rich organic humic matter in coals, which originated from plant matter over geological time. The MicGAS™ technology uses microbes derived from termite guts and naturally enhanced, which convert mined coal, in anaerobic bioreactors, to hydrogen-rich methane biogas, carbon-rich liquid co-products for agriculture, and solid humic co-products used as highly effective filters that remove toxic contaminants from waters and wastes. For the deep coal seams, this bioconversion is affected in the seam geo bioreactor itself and biogas is recovered gradually. The biogas is used "as is" or converted by commercially proven Fischer Tropsch process, to jet fuels, diesel and chemicals. Feasibility tests will be presented with core coal samples obtained from deep un mineable coal seam and sub-bituminous coal samples a mine in the Powder River Basin in Wyoming. Applicability tests with organic humic products agriculture use and wastes treatment along with a market analysis will also be presented. An economic analysis will be presented based on a design of a 100,000 Tons Per year HUMAXX Bio Refinery. This integrated approach to coal bioconversion results in use of the total value chain of coals and yields no solid and liquid process wastes. It offers an approach of achieving negative carbon footprint for production of liquid fuels as well as at a cost which remains competitive with falling oil prices. This study was performed for the State of Wyoming who is seeking technological approaches for moving the Wyoming minerals up the value chain.

## Thermogravimetric Assessment of Coal, Biomass and Their Blends to Support Pilot-Scale Gasification Tests

Alberto Pettinau, Alessandro Orsini, Mauro Mureddu, Francesca Ferrara, Sotacarbo S.p.A, ITALY

Carbon-rich fuels (coal, oil and natural gas) currently represent the primary energy source in the modern society. The depletion of non-renewable resource and stricter environmental regulations, along with increasing of the energy demand, has led to the need to find alternatives to conventional fuels. Biomass, if properly used, could potentially provide approximately 25% of the current energy demand. Moreover, biomass has the lowest risk and capital required to be used in energy generation and it can be considered carbon- neutral. Co-combustion and co-pyrolysis of biomass/waste with coal are two of the most beneficial ways for replacement of fossil fuels for stationary energy conversion. Furthermore, co-firing biomass with coal results in a net reduction of CO<sub>2</sub> emissions. So, the knowledge of the thermal decomposition of coal and biomass is essential to evaluate the performance of carbonization, combustion and gasification processes, as well as its reactivity.

In this work, thermogravimetric analysis (TGA) has been used to investigate both the pyrolysis and combustion behavior of coal, biomass and their blends in order to find a correlation between the results of such analysis and the gasification data from pilot-scale experimental tests. This kind of correlation could be used to optimize the test campaigns. As a matter of facts, due to the relatively high cost of each pilot-scale run, a first step is represented by pyrolysis and combustion characterization performed by a thermogravimetric analysis: this typically allows to qualitatively predict the fuel reactivity and to optimize the design of test campaigns, with a subsequent reduction of the overall experimental cost.

In this study, seven kinds of fuel, selected as the most representative among those tested in the Sotacarbo pilot plant, have been characterized: (i) a high ash South African bituminous coal; (ii) a high sulphur Sardinian sub-bituminous coal; (iii) a lignite from Usibelli coal mine (Alaska); (iv) a high sulphur brown coal from Hungary; (v) stone pine (*Pinus pinea*) wood chips from Sardinian forests; (vi) corn cobs and (vii) corn stover, both from Southern United States. Among all the tested coals, Alaskan

lignite and Sardinian coal are the most reactive ones. They present a well-defined combustion peak in the DTG profiles, corresponding to 358 and 437 °C respectively. An opposite behavior is shown by South African coal, which does not present a real peak in the DTG curve (a weight loss of only 25% can be observed during the combustion tests by TGA): it indicates a very low reactivity, as a consequence of the very high carbon content in the fuel structure. A different trend can be noticed for Hungarian coal, whose performance is affected by the very high moisture and ash contents. As for biomass, all the tested fuels present a very high peak in the DTG profile, thus indicating a high combustion rate (10.98, 14.05 and 9.29 wt.%/min for stone pine, corn cobs and corn stover, respectively), which is typically an order of magnitude higher than the coal combustion rates (between 1.20 wt.%/min for the low reactive South African coal and 2.80 wt.%/min for the high reactive Usibelli lignite). Finally, with reference to fuel blends, the slight synergic effects between the considered fuels observed during pyrolysis TGA seems to be confirmed during combustion tests.

Overall, a significant correspondence can be observed between the combustion rate measured by TGA and the specific gasification rate calculated by the pilot-scale gasification experimental data.

#### **Synthesis of Polymer Encapsulated Porous Kaolinite Proppant for Microbially Enhanced Coalbed Methane Recovery**

Taylor D. Sparks, Kyu Bum Han, John Fuertez, John McLennan, University of Utah, USA

Many coal reservoirs are too deep to safely, economically, and environmentally extract. It has been proposed to convert these coal reservoirs into methane in-situ using methanogenic bacteria. Electric power plants fueled by natural gas have many benefits. They emit 54% less greenhouse gas emissions, have very low levels of NO<sub>x</sub> and SO<sub>2</sub> pollutants, have virtually no mercury, soot, or other solid particulates, and use 60% less water than coal fired plants.

Our approach to this biogasification challenge is to redesign the current proppant for enhancing coal seam permeability. Methanogenic microbial consortia can be loaded into this proppant and delivered directly to the coal seam. The microbes have a size range of 5-10 μm, consequently, the pore size of at least this diameter are necessary for effective loading of this organism. The creation of anhydrous structures from water containing structures has proven to be an effective method for creating and controlling porosity of a ceramic material. Kaolinite-iron oxide particles are synthesized with a high population of pores with an average size of 24 μm (+/- 12 μm). The open and apparent porosities are 29.3% and 54.7% respectively. To create the pores on the surface, aluminum oxide is coated on the kaolinite proppant, mixed with iron oxide, before sintering. The size of surface pores is 8 μm (+/- 3μm) with low density (1.7g/cm<sup>3</sup>) and high inner porosity (36%). This porous proppant is impregnated with a tracer dye molecule, Rhodamine 6G, and then encapsulated with a polymer film made up of sodium alginate and calcium lactate. We demonstrate >96% efficiency in retaining the dye molecule during polymerization encapsulation and have tested the time release character of dye from this impregnated, encapsulated proppant. Proppant is also evaluated for crush strength and conductivity. The next step is to optimize the encapsulation system for loading the bacteria and evaluate the final product in the simulated conditions.

The creation of microbial consortia that are able to use different coal sources offer multiple opportunities in the field. We retrieved microbial populations from hydrocarbon-rich environments and locations characterized by natural methanogenesis. Different pulverized coal and coal waste materials are combined with selected microbial inoculum and various types of nutrient amendments under three levels of screening tests. A pool over 500 initial combinations is generated to identify the top producers of methane and carbon dioxide. Incubation periods up to 24 weeks at about 23°C are considered and headspace concentrations of CH<sub>4</sub> and CO<sub>2</sub> are analyzed by using gas chromatography. Concentrations of 873438 ppm for methane and 176376 ppm for carbon dioxide are measured for one of the best set of consortia identified at 2 weeks of incubation in last phase of screening test. A variance analysis (ANOVA) is conducted to identify possible trends and levels of higher significance or impact during experimental development.

### **SESSION 38 Carbon Management - CO<sub>2</sub> Storage**

#### **Comparing Adsorption Behavior of Carbon Dioxide, Methane and Nitrogen on Coal and Shale: Particle Size Effect on Pore Characterization of Coal from Low Temperature Nitrogen Adsorption Test**

Xu Tang, Nino Ripepi, Virginia Polytechnic Institute and State University, USA

Carbon dioxide sequestration and storage in geological formations such as coal seams, shale formations and saline aquifers is one of the promising approaches to reduce carbon dioxide in the atmosphere. Since enhanced shale gas recovery (ESGR) and enhanced coalbed methane recovery (ECBM) from carbon sequestration can help

offset the cost of capture and storage, these techniques are likely to gain popularity. Carbon dioxide sequestration pilot tests in coal seams were initiated in the early 1990s, and the knowledge of carbon sequestration in coal seam has been gained from both laboratory and field projects. However, ESGR from carbon sequestration is still in its infancy stage, and both laboratory and field research are needed to understand the carbon dioxide storage mechanism in shale, the gas transport mechanism and best practices for field operation management. Even though coal and shale have similar physical properties such as adsorption behavior, the knowledge gained from coal cannot be directly transferred to shale. Thus, it is imperative to distinguish the adsorption properties between coal and shale. This study investigates the adsorption behavior of carbon dioxide, methane, and nitrogen on both shale and coal via isothermal adsorption tests; both the adsorption kinetics and adsorption capacity will be studied. This research is helpful for understanding the carbon dioxide storage process and estimating the carbon dioxide storage capacity in shale formations, development of future pilot field tests, and lays the foundation to understand the specific adsorption properties of shale compared to coal.

#### **Development of the First Internationally Accepted Standard for Geologic Storage of Carbon Dioxide Utilizing Enhanced Oil Recovery (EOR) Under the International Standards Organization (ISO) Technical Committee TC-265**

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

The Carbon Capture Utilization & Sequestration (Storage) (CCUS) marketplace is lacking standardization and therefore the ability to allow CCUS projects to be advanced as Clean Development Mechanism (CDM) projects as well as to advance to full scale commercialization. An international effort between the United States and Canada, funded by and the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide, and managed by CSA Standards, have developed the first internationally recognized Standard for the geologic storage of CO<sub>2</sub> entitled Z-741. The Z-741 Standard has been adopted by the Standards Council of Canada and is available to American National Standards Institute. As a direct result of Z-741, the International Standards Organization (ISO) has created a technical committee (TC-265) to advance the development of comprehensive standards that address carbon capture, utilization, and storage. A Working Group within TC-265 has been created (WG 6, CO<sub>2</sub> EOR) focusing on standardization in connection with enhanced oil recovery (EOR) related carbon dioxide storage. The new working group will focus on standardization efforts associated with low-pressure subsurface oil field operating environments and related CO<sub>2</sub> recovery operations, as well as the harmonization of CO<sub>2</sub> supplies with EOR operations both on a daily basis and over multi-year operational horizons, among other topics. Additionally, the working group must address buffer storage and plans to continue the international call for expert participation in its development of standards and other documents related to CO<sub>2</sub> EOR. ISO TC 265 was first established in 2011 with a focus on advancing standardization in connection with CCS worldwide, including the development of related standards, technical specifications, and technical reports. Since its creation, six (6) working groups have been established to address various aspects of CCUS. In addition to the sixth working group on CO<sub>2</sub> EOR, the other five working groups include capture (WG1), transportation (WG2), on & off shore storage (WG 3), quantification & verification (WG4), and crosscutting issues (WG5). This paper will address key issues experienced in the standard development process, which is a technical, consensus-based facilitated process as well as social issues and a social license to operate as part of the stakeholder engagement, which include general interest, operators/industry, regulatory, and consultant/service providers.

#### **Pressure Data and Interference Testing at the Citronelle SECARB Phase III Site, Alabama USA**

Hunter Jonsson, George Koperna, Jr., Advanced Resources International, Inc.; Rob Trautz, EPRI; Barry Friefeld, Lawrence Berkeley National Laboratory, USA

The Southeast Regional Carbon Sequestration Partnership (SECARB) Anthropogenic Test is a demonstration of the deployment of CO<sub>2</sub> capture, transport, geologic storage, and monitoring technologies. This project is the first and the largest fully integrated commercial prototype coal-fired carbon capture and storage project in the United States. This demonstration, which is primarily funded by the United States Department of Energy, Southern Company and Mitsubishi Heavy Industries and the Electric Power Research Institute, has reached a milestone of 100,000 metric tons (tonnes) of CO<sub>2</sub> injection and is in the second year of injection operations. Two Class V Experimental Injection Well underground injection control (UIC) permits were issued in November 2011 and the project's injection wells were installed shortly thereafter. A pressure data monitoring and interference testing regime has been developed and applied at the site as part of the project's robust Monitoring, Verification, and Accounting (MVA) plan to help in understanding the subsurface movement of CO<sub>2</sub> and the associated pressure field generated by the injection. To monitor the CO<sub>2</sub> movement in the subsurface at various distances from the injection well, a new observation well was drilled and two existing oil field wells were converted to observation wells. Downhole memory readout gauges were placed in the converted observation wells and surface readout gauges were placed in the newly drilled observation well, respectively. Two gauges are installed in each well (primary and backup) and are used to collect formation pressure and temperatures. The new observation well and one of the converted wells is

perforated in the CO<sub>2</sub> storage formation, allowing for in-zone pressure interference testing. The second converted observation well collects bottom hole pressure and temperature data from a porous zone lying directly above the storage interval's primary confining unit. Spatially, these data are collected in close proximity (870 feet to east) to the injection well and at some further distance (3,100 feet to the northwest) from the injection point. These downhole pressure data have proven to be a useful monitoring tool to observe the impact of the CO<sub>2</sub> injection as well as for refining the modeling efforts through injection history matching. When the pressure and temperature data is paired with injection rate data, the observation wells also provide the opportunity to conduct interference testing. Interference testing is a well-testing analysis method used to interpret the pressure variations at an observation well based upon injection rate data from the injection well. Standard pressure transient testing techniques allow the analysis of this pressure behavior in order to determine estimates of the formation's intrinsic permeability, how this permeability changes over time and also to determine the degree of communication across parts of the reservoir. This can, in turn, be used to validate or make improvements to the injection program as well as to improve the numerical history matching. The operational impact of intermittent injection and shut-in periods at the SECARB Test Site, due primarily to maintenance and dispatch demands, provided for multiple injection and pressure falloff periods for well test interpretation. These opportunities provided enhanced interference testing data points to observe changes over time that may be a result of the injected CO<sub>2</sub> volume. This paper will discuss the operational implications of the methodology as well as share data and interpretation results to date.

**SESSION 39**  
**Gasification Technologies – General - 4**

**High Pressure, Entrained Flow Studies of Gasification of Rhenish Lignite**

Daniel G. Roberts, Lucio N. Fogliari, Matthew J. Langley, David J. Harris, CSIRO Energy Technology, AUSTRALIA; Christian Schneider, Markus Walter, Technical University Bergakademie, GERMANY

There is growing interest in increasing the efficiency and cost-effectiveness of utilisation options for low rank coals such as lignites. Some of the most attractive and flexible options include gasification-based systems for the production of chemicals, fertilizers or liquid fuels. While air-blown lignite gasification systems are often suitable for power generation in IGCC systems, the presence of large amounts of nitrogen in the product syngas adds additional cost and complexity to downstream gas cleaning and conversion processes to produce hydrogen, chemicals or liquid fuels. For this reason, the use of low rank coals in oxygen-blown gasification technologies, commonly used with higher rank bituminous and sub-bituminous coals, is receiving renewed attention. There are several important coal specific issues associated with oxygen-blown gasification of low-rank coals which need to be considered and understood so that technology selection and project decisions can be made with confidence. While there have been extensive studies on fundamental aspects of brown coal gasification reactions at lower temperatures and with larger particles more suited to fluidized bed systems, there is insufficient information available in the public domain on the performance of oxygen-blown gasifiers using low rank coals such as lignites. Issues around increased temperatures and pressures, finer particle sizes, and how these impact gasifier performance are important. This paper presents some recent results from a study into the gasification behaviour of a German lignite using laboratory and larger-scale facilities. A pressurized entrained flow gasification reactor is used to study conversion behaviour at high pressures and different temperatures, O:C stoichiometries, and residence times. This work is supported by insights into the fundamental aspects of high heating rate devolatilisation and intrinsic char reactivity. Characteristics of partially-gasified chars (particle size, density, surface areas etc) are presented alongside these data, providing some unique insights into the entrained flow gasification behaviour of lignites.

**SESSION 40**  
**Shale and Coal Bed Gas -1**

**Regulation of Methane Emissions from Coal Bed Methane and Shale Gas Operations**

Stephen C. Smith, Steptoe & Johnson PLLC, USA

Coal bed methane production and hydraulic fracturing of shale gas produce methane, which is generally intended to be captured for use as an energy resource. However, some methane escapes, leaks or is otherwise released in the course of production and transmission operations. President Obama has identified methane reduction as an important goal in his strategy for addressing climate change. On January 14, 2015, US EPA announced that it intended to issue proposed regulations in the summer of 2015

and a final rule in 2016 addressing methane reduction in the oil and gas sector. The same day the White House announced a new goal to cut methane emissions from the oil and gas sector by 40-45% from 2012 levels by 2025, and a set of actions to put the U.S. on a path to achieve this ambitious goal. US EPA has developed a "Coalbed Methane Outreach Program" which encourages voluntary reductions of methane emissions. This presentation will explore the regulation of methane emissions from coal bed methane and shale gas operations and potential future regulatory and administrative initiatives that may be proposed to reduce methane emissions from coal bed methane and shale gas operations.

**From Venting Skyward to Moving Forward: A Historical Perspective on the Regulation of Coal Bed Methane Development**

Jon C. Beckman, Steptoe & Johnson PLLC, USA

Removal of coal mine methane was once intended only to provide for safe and effective coal removal. Operators remove coal bed methane (CBM) by proactively drilling wells into the coal seam prior to mining. CBM is both a potential greenhouse gas and a valuable source of clean-burning energy. Since 1994, the United States Environmental Protection Agency (EPA) Coalbed Methane Outreach Program (CMOP) has cooperated with the coal mining industry both in the United States and internationally to foster development of CBM in an effort to voluntarily reduce atmospheric methane emissions. CBM regulation recently gained national attention when President Barak Obama identified methane emission reduction as a critical component of his strategy for addressing global climate change. EPA promulgated regulations in an effort to achieve the goals of reducing methane emissions as an air pollutant and promoting the development of CBM as a fuel source. While these goals are not mutually exclusive, the regulatory framework demonstrates the tension between successfully protecting the environment while providing the energy society needs through cleaner and more sustainable sources. This presentation will analyze the historical regulation of methane emission from CBM operations. The purpose of the presentation is to establish a solid foundation from which the synthesis of CBM development policy can continue.

**SESSION 42**  
**Coal Science: General - 6**

**Detailed Characteristics of Coal Ash from the Largest Coal-Fired Power Plant in South America**

Adilson C. Dalmora, Luis F.O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North-West University, SOUTH AFRICA

The utilized feed coals, and remaining coal fly ashes (CFA) and bottom ashes collected from seven different units in a major Brazilian PF power plant have been subjected to comprehensive mineralogical, geochemical, and petrographic studies to investigate the links between feed coal and ash characteristics. Ashes from two of the units were collected while the coal was being co-fired with oil as part of the boiler start-up procedure, allowing the impact of oil co-firing on ash characteristics also to be evaluated. X-ray diffraction (XRD), High Resolution-Transmission Electron microscopy (HR-TEM)/(Energy Dispersive Spectroscopy) EDS/(selected-area diffraction pattern) SAED, Field Emission-Scanning Electron Microscopy (FE-SEM)/EDS, inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) were used to evaluate the nature, occurrence and distribution of elements, minerals, organometallics and mineraloids in coals and coal by-products.

High proportions of un-burnt carbon and high proportions of retained sulphur were found in the fly ashes produced during oil co-firing, probably reflecting less efficient combustion and associated lower combustion temperatures. Higher concentrations of a number of relatively volatile trace elements were also noted in these fly ashes, compared to the fly ashes collected from units under normal operating conditions.

In general, the CFA produced during oil co-firing gave rise to acid pH conditions in water-based leaching tests, in contrast to the alkaline pH associated with fly ashes produced during normal operations. This probably reflects higher SO<sub>3</sub> contents relative to the total CaO + MgO for the co-fired ash samples. Many trace elements that are typically mobilised as cations were also more abundant in leachates from the co-fired CFA. This is due, most likely, to the more acid pH conditions involved. Despite similar or even higher total concentrations, however, elements that are typically released from coal ash as oxy-anions were less mobile from the co-fired fly ashes than from the normally-fired CFA.

**The Fixation Capabilities of Fly Ashes Formed in Spanish Facilities Compared to that in the Israeli Facilities**

Roy Nir Lieberman, Oriol Font, Xavier Querol, Institut de Environmental Assessment and Water Research (IDÆA) Consejo Superior de Investigaciones Científicas (CSIC), SPAIN; Haim Cohen, Ariel University, ISRAEL

In recent studies it was found that coal fly ash could act as a scrubber and fixation reagent for acidic waste. Furthermore, the aggregate product formed was studied as a partial substitute to sand in concrete. The results indicated that the scrubbed product could serve as a partial substitute to sand and cement in concrete. The mechanical strength and ion penetration test of the bricks formed with the new concrete, have shown that it was within the concrete standards, and even stronger than regular concrete. Today, the energy consumption in Spain is ~178.1Mtce in 2012. It decreased by approximately 13% since the economic crisis started in Spain. As the only fossil fuel Spain possesses, as a resource is coal, the use of it increased in recent years up to 12.2% of the total energy demand. In 2012 the coal consumption in Spain was ~6Mt of domestic coal, and ~21.5Mt of imported coals (most of them from Colombia, South Africa, and Indonesia). Due to high ash content in the coals (~40%), there are large amount of coal fly ashes formed (<10Mt per year). In Israel ~13Mt of bituminous coal are used annually in 4 coal power plants, producing 1.3Mt of coal fly ash. The Israeli coal fly ashes are considered as Class F, therefore have pozzolanic behavior. In this study we have compared the fixation capabilities of the fly ash formed in Spanish energy facilities for wastes compared to that of the fly ashes formed in Israeli energy facilities. Furthermore, initial calculation show that utilization coal fly ashes as a chemical scrubber to wastes in Spain will increase appreciably its' economic value by at least 3 times better than its present value as construction material.

#### **Recycling of Fly Ash in Construction Projects Using Modifiers for Trace Metal Attenuation**

Matthew M. Bernacki, Cody W. Barnes, Brandon P. Goold, Kevin T. Fitzgerald, Gautham P. Das, Wentworth Institute of Technology, USA

Heavy metal leaching from improperly disposed fly ash remains a concern to human health and the environment as a result of their toxicity. The objective of this experiment is to evaluate the performance of calcium stearate to encapsulate heavy metals in fly ash to prevent chemical leaching. To assess the ability of the additive to solidify heavy metals, batch leaching tests and column leaching tests were performed. The methodology involved testing fly ash with various amounts of additive. The fly ash with the additive was evaluated by measuring the concentration of heavy metals such as Chromium, Lead and Cadmium that leached from the fly ash. Batch leaching results indicated that the concentration of chromium was 65 µg/L for fly ash alone. However, with 1% calcium stearate the concentration dropped to 45.5 µg/L. Column leaching results revealed that the concentration of cadmium was 166 µg/L for 3% calcium stearate. On the other hand, with 1% calcium stearate the concentration fell to 93.4 µg/L. Further testing revealed that 1% calcium stearate reduced the amount of heavy metal leaching from fly ash. It is hypothesized that the calcium stearate attacks the transition metals rendering the metal essentially inactive due to the free lime hydration.

#### **Evaluation of Strength of Subgrade Treated with Fly Ash & Calcium Stearate**

Devin Howe, Ryan Marshall, Michael Mooney, Gautham Das, Wentworth Institute of Technology, USA

The emphasis of this research was to evaluate the strength characteristics of subgrade with varying percentages of fly ash and calcium stearate. Calcium stearate, a common water repellent, was identified as a potential additive to reduce the leaching and potentially increase the strength of subgrade with fly ash additions. Laboratory testing with Boston Blue Clay used as a subgrade material with combinations of 20%, 30%, and 40% fly ash was evaluated for this research. Initial testing included fly ash treated with 1% and 2% calcium stearate. Modified proctor tests results indicated the optimum moisture content of the subgrade treated with 20% fly ash was 22% with the maximum dry density of 122 lbs/ft<sup>3</sup>. The highest strength results were observed for the sample containing 20% fly ash and 1% calcium stearate. Unconfined compression testing results for this combination indicated an average strength of 6,209 lbs/ft<sup>2</sup>. For subgrade with 20% fly ash and 2% calcium stearate the average strength dropped to 4,250 lbs/ft<sup>2</sup>. It was noticed that the higher additions of calcium stearate caused a decrease in the unconfined compressive strength due to the weak bonds formed between calcium stearate and Boston Blue Clay.

### **SESSION 43 Clean Coal and Gas to Fuels - 1**

#### **Advanced Process Intensification Approaches for Production of JP-8 Jet Fuel from Coal with High Productivity and Selectivity**

Andrew Lucero, August Meng, Brittany Koob, Kelly Mastro, Kevin McCabe, Santosh Gangwal, Southern Research, USA

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 U.S. Air Force and DOE/NETL sponsored cooperative agreement, Southern Research is leading a team consisting of Precision Combustion, Inc. (PCI),

Intramicon, Southwest Research Institute, and Nexant, inc, along with Chevron as selective Fischer-Tropsch (FT) catalyst supplier and the National Carbon Capture Center as the host site for technology demonstration. 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. This not only allows for CTL to be cost competitive at typical large scales, but also opens up opportunities for CTL to be viable at smaller scales. Research is specifically targeted towards two advanced cost-effective technologies: a compact auto-thermal reformer (ATR) from PCI to reduce syngas cleaning and water gas shift requirements, and a selective and active cobalt-zeolite hybrid Fischer-Tropsch (FT) catalyst from Chevron that predominantly produces liquid range C5-C20 hydrocarbons with high productivity (5X conventional FT catalysts) while eliminating the production and associated handling of solid C21+ wax. High fractions of the liquid product are in the desired C8 to C16 range for jet fuel. The ATR is used to (1) reform tar and light hydrocarbons, (2) decompose ammonia in the presence of H<sub>2</sub>S and other coal syngas contaminants, and (3) deliver the required hydrogen (H<sub>2</sub>) to carbon monoxide (CO) ratio for Fischer-Tropsch (FT) synthesis. Heat management associated with the highly exothermic FT reaction is carried out using a novel fixed-bed heat exchange reactor system. This work will present results from lab-scale development of H<sub>2</sub>S tolerant reforming catalysts and results from tests of the hybrid FT catalyst using simulated coal derived syngas.

#### **Conversion of Coal and Biomass to Liquid Hydrocarbons Using Molten Salt Gasification and a Hybrid Fischer Tropsch Catalyst**

Lyman Frost, Joseph Hartvigsen, S. Elangovan, Jessica Elwell, Ceramtec; Paul Dimick, Hongyun Yang, IntraMicron, Inc.; Neil Camarta, Western Hydrogen, USA

Ceramtec is leading a team to develop a two (2) BPD (barrel per day) Fischer Tropsch system to produce jet fuel. Funding is provided by the United States Air Force, through the US Department of Energy - National Energy Technology Laboratory. The feedstock for the system will be coal – water – slurry (CWS) with some biomass to meet carbon emission limitations. The CWS will be gasified using an innovative molten salt gasification (MSG) system being operated by Western Hydrogen in Alberta, Canada. The MSG system uses a mixture of sodium salts at high pressure and temperature to catalyze the gasification reaction and generate synthesis gas at pressures suitable for Fischer Tropsch (FT). The output MSG synthesis gas stream will be cleaned using a sulfur removal system provided by IntraMicron, a company located in Auburn, AL. The clean synthesis gas will be fed to a 2 BPD modular FT reactor designed and assembled by Ceramtec. IntraMicron will also provide a catalyst support structure for the FT reactor. Ceramtec is currently operating a smaller (~ ¼ BPD) GTL facility at its Salt Lake City laboratory. The sulfur removal system and the 2 BPD FT reactor will be tested at this facility prior to shipment to Canada for testing with the coal derived synthesis gas.

The objectives and challenges of the 2 BPD CTL (coal-to-liquids) project will be described in the presentation. The presentation will describe the capabilities of the team to address the issues associated with development of that integrated 2 BPD CTL system. The laboratory scale test data generated to date will be presented to demonstrate how the issues are being addressed. The design for the integrated CTL facility will be described and individual components highlighted. Other relevant technical data from associated projects will be presented.

#### **Development of a One Barrel per Day Coal to Liquids Pilot Research Facility and the Lessons Learned**

Andrew Placido, Rodney Andrews, Don Challman, University of Kentucky – Center for Applied Energy Research, USA

Laboratory facilities, and particularly research-scale pilot plants, are complex, technically sophisticated, and mechanically intensive structures that are expensive to build and maintain. The facility, nearing completion at the University of Kentucky, consists of a coal feed to finished fuels process train including: gasification, water-gas shift, acid gas cleanup, and Fischer-Tropsch reactors. The plant complex also includes ancillary systems for power generation, utilities, effluent treatment, ash disposal, and automated control systems. In order to maximize flexibility, the facility is of a modular design with skid mounted process units – and is intended to be adaptable to change-out of equipment and capabilities. This facility will be used for a range of investigations including: feed preparation, coal and biomass gasification, gas cleanup and conditioning, gas conversion by FT synthesis, product work-up and refining, systems analysis and integration, and scale-up/demonstration. The facility will also produce research quantities of FT liquids and finished fuels for subsequent fuel quality testing. In addition to training operating personnel, the facility will be used as a test bed for new technologies and concepts, will provide open-access facilities and information in the public domain to aid the wider scientific and industrial community, and provide a means to independently review vendor claims and validate fuel performance and quality. An entrained flow gasifier, which was procured from East China University of Science and Technology (ECUST), comprised of four opposed burners uses a coal/water slurry to provide syngas for the



facility. Syngas workup and condition for the facility is performed using a conventional water gas shift process followed by an aqueous amine system consisting of a traditional absorber/stripper model with additional sulfur cleanup using hydrolysis catalysts and activated carbon. Finally, the cleaned syngas is sent to a Chart Energy micro-channel FT reactor where liquid fuel is produced at a rate of 1 barrel per day. The design and construction of a facility such as the one described above comes with inherent risks that must be managed throughout the project and the lessons learned from the development of this facility can be used to improve future projects of this nature.

#### Comparison of Iron-Based Fischer Tropsch Catalysts Prepared Using a Simple, Inexpensive, Solvent Deficient Preparation Method

William C. Schaffers, University of Wyoming; William Hecker, Morris Argyle, Brigham Young University; Kyle Brunner, Sasol North America, USA

The Fischer-Tropsch process has been used for decades as a means of producing liquid products, primarily fuels, from coal and natural gas. The process has gained renewed interest in recent years due to the increased cost of petroleum and continuing political instability in oil producing regions. Most recently, the increased abundance of natural gas due to new drilling and extraction technologies has fueled growing interest in Fischer-Tropsch technology.

One of the most important aspects of the Fischer-Tropsch process is selection and preparation of the appropriate catalyst. Iron based catalysts are typically used for coal-to-liquids processes due to their water-gas shift capability and the hydrogen deficient nature of coal derived syngas. Iron based Fischer-Tropsch catalysts typically have a short life measured in months rather than years, thus making economic considerations very important. Recently, a new, solvent deficient, proprietary co-precipitation method of catalyst preparation (SDP) has been developed by Cosmas, Inc. of Provo, UT. This method involves the mixing of salts with the addition of no, or a minimal amount, of solvent. The process is relatively simple and inexpensive compared to traditional catalyst preparation techniques.

Ten catalysts were prepared using the above SDP method. Four different iron salt precursors were used with copper and/or manganese as the primary promoters. Additional components such as potassium and fumed silica were also added. The resulting catalysts were then dried, calcined and reduced based upon profiles determined by thermal gravimetric analysis. Surface area, extent of reduction, CO uptake, and catalyst composition were investigated for each catalyst. Activity and selectivity characteristics for the catalysts were determined using a fixed bed reactor under typical conditions for iron based Fischer-Tropsch processes.

Results of the studies showed wide variations in catalyst properties based upon the iron precursor used for synthesis. The best catalyst once again showed activity equal to or greater than typical iron catalysts. In addition, certain combinations resulted in catalysts with low methane selectivity even at elevated temperatures.

It is hoped that this research will aid in the manufacture of effective, low cost iron based catalysts for the production of Fischer-Tropsch fluids. The SDP method has the potential to allow for quick, inexpensive synthesis of effective catalysts. This will benefit the utilization of coal, as well as biomass and natural gas, resources to produce clean, affordable fuels and chemicals.

#### SESSION 44

#### Carbon Management: Conversions, Utilization or Heat Recovery from CO<sub>2</sub> Capture

#### Functionalized Metal Organic Frameworks for CO<sub>2</sub> Capture and Conversion

Jingyun Ye, Karl Johnson, University of Pittsburgh, USA

Metal organic frameworks (MOFs) are highly versatile nanoporous materials because of their structural and functional tailorability. We use density functional theory (DFT) methods to design functionalized MOFs that are capable of chemically binding and hydrogenating CO<sub>2</sub>. We employ UiO-66 as our starting base material because it is a MOF that has chemical and thermal stability, is highly selective toward CO<sub>2</sub> and can be functionalized post-synthetically. We design functional moieties for CO<sub>2</sub> hydrogenation based on frustrated Lewis pairs (FLPs) because these organic molecules have been shown to be very active for chemisorption of CO<sub>2</sub> and the heterolytic dissociation of H<sub>2</sub>. One candidate FLP is 1-[bis(pentafluorophenyl)boryl]-3,5-di-tert-butyl-1H-pyrazole (FLP1). We have modified FLP1 as our functional group, denoted as P-BF<sub>2</sub>. P-BF<sub>2</sub> is a Lewis pair without steric hindrance, which would form a dimer in solution, quenching the Lewis acid (B) and base (Nb) sites. However, binding P-BF<sub>2</sub> to BDC linkers of UiO-66 prevents migration and association of P-BF<sub>2</sub> groups. Our calculations indicate that the porous framework remains stable after functionalization. The Lewis pair retains its chemical activity when bound in the pore, being able to facilitate bind H<sub>2</sub> and CO<sub>2</sub>. Furthermore, CO<sub>2</sub> can be reduced via a low energy barrier pathway by first exposing UiO-66-P-BF<sub>2</sub> to H<sub>2</sub>, giving heterolytic dissociation, followed by exposure to CO<sub>2</sub>.

We have developed a family of Lewis pair functional groups for inclusion in UiO-66 by replacing the -BF<sub>2</sub> group of P-BF<sub>2</sub> with the following moieties: -B(CH<sub>3</sub>)<sub>2</sub>, -BH<sub>2</sub>, -BCl<sub>2</sub>, -BBR<sub>2</sub>, -B(CN)<sub>2</sub>, -B(CF<sub>3</sub>)<sub>2</sub> and -B(NO<sub>2</sub>)<sub>2</sub>. We investigated the reactivity of these materials for CO<sub>2</sub> hydrogenation to produce formic acid. We found a linear relationship between the H<sub>2</sub> adsorption energies and activation energies for CO<sub>2</sub> hydrogenation. Furthermore, the adsorption energies of H<sub>2</sub> were observed to scale linearly with the acidity of functional groups. The rationalized relationships provide an efficient and simple way to predict the reactivity of CO<sub>2</sub> hydrogenation and also H<sub>2</sub> binding energies in Lewis pair functionalized MOFs. More importantly, it provides significant insights for designing effective catalysts for CO<sub>2</sub> hydrogenation.

#### Advances on Carbon Dioxide (CO<sub>2</sub>) Capture on Alkaline Ceramics and its Catalytic Conversion to Added Value Products

Heriberto Pfeiffer, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, MEXICO

In the last two decades, different materials have been proposed as potential CO<sub>2</sub> captors. Among these materials, different alkaline ceramics (lithium and sodium) have been analyzed as possible high temperature CO<sub>2</sub> captors. The most studied ceramics are the lithium and sodium silicates (Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>8</sub>SiO<sub>6</sub>, Li<sub>2</sub>SiO<sub>3</sub> and Na<sub>2</sub>SiO<sub>3</sub>), lithium aluminate (Li<sub>5</sub>AlO<sub>4</sub>) lithium and sodium zirconates (Li<sub>2</sub>ZrO<sub>3</sub> and Na<sub>2</sub>ZrO<sub>3</sub>) and lithium cuprate (Li<sub>2</sub>CuO<sub>2</sub>), among others. All these ceramics are able to trap CO<sub>2</sub>, chemically, at different temperature ranges (30 - 820 °C) under different physicochemical conditions.

These ceramics trap CO<sub>2</sub> throughout a chemisorption process. Initially, the alkaline ceramic particles react with CO<sub>2</sub> at the surface. The superficial reaction implies the formation of an external shell of Li<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> and secondary phases. Once the external shell is produced, the reaction mechanism is controlled by different diffusion processes. Therefore, the correct understanding of all these phenomena is a very important step during the selection of the ideal CO<sub>2</sub> capture conditions.

Conversely, different catalytic reactions, where carbon dioxide (CO<sub>2</sub>) and/or methane (CH<sub>4</sub>) are used, have attracted the research attention because of environmental applications. Some of these reactions are the methane reforming (called dry reforming), the water splitting and the CO<sub>2</sub> reduction. All these reactions produce syngas (CO + H<sub>2</sub>). The syngas produced by these reactions can be used in different energetic and organic applications. Additionally, these reactions are also environmentally important, as CO<sub>2</sub> and CH<sub>4</sub> (perhaps the two most important greenhouse gases) are catalytically converted into added value products, such as hydrocarbons and oxygenated compounds.

Therefore, the aim of this presentation is to show some recent advances in the CO<sub>2</sub> capture on alkaline ceramics (under different physicochemical conditions) and to show as well how the CO<sub>2</sub> chemically trapped can be catalyzed to added value products through the syngas production at different temperature ranges.

#### Assessment of the Use of CO<sub>2</sub> Injection for Heat Mining in Geothermal Reservoirs in Mexico

Carlos E. Romero, Chunjian Pan, Pavel Ramírez, Edward K. Levy, Lehigh University, USA; Alicia Aguilar Corona, Oscar Chávez, Carlos Rubio Maya, Universidad Michoacana de San Nicolás de Hidalgo, MEXICO

A study was conducted to assess the feasibility of using supercritical carbon dioxide (sCO<sub>2</sub>) injection for heat mining from geothermal reservoirs in Mexico. Mexico is aiming at expanding the role of geothermal energy, and renewable energy in general, in the country's power generation matrix. Four high-enthalpy sites are currently under commercial ownership and production by the Federal Commission of Electricity (CFE) in Mexico, totaling 953 MW<sub>e</sub>. Traditional water-based geothermal systems require significant amounts of water, a high permeability and porous formation and sufficiently high subsurface temperatures. Supercritical CO<sub>2</sub> is recognized to have good mobility and flow properties that make it an excellent alternative to water for heat recovery from geothermal reservoirs, thus expanding the range of usable natural geothermal formations. CO<sub>2</sub> is expected to be available in the future from carbon capture systems added to fossil-fired power plants for greenhouse gases abatement. CO<sub>2</sub> as a geothermal heat mining fluid also provides the added benefit of carbon storage within the geothermal formation. Estimations of heat mining potential using sCO<sub>2</sub> were performed using the TOUGH2 computer software. Simulations for three representative reservoirs in Mexico (Hard Dry Rock, HDR - Acoculco (260°C, 160 bar), Deep Saline Aquifer, DSA - Puruandiro (165°C, 100 bar), and Low Enthalpy Reservoir, LER - Agua Caliente Comondú (95°C, 75 bar) indicate that CO<sub>2</sub>-based systems have better heat mining potential than H<sub>2</sub>O-based systems, corresponding to enhanced heat extraction rates as high as 160 percent with respect to the H<sub>2</sub>O-based systems, with the heat mining benefit by sCO<sub>2</sub> increasing in inverse proportion to the site subsurface temperature. Additional simulations for twenty-one characterized geothermal sites in Mexico estimate a total power generation potential with sCO<sub>2</sub> of 1,161 MW<sub>e</sub>. This represents 51.4 percent additional power generation that can be mined by the use of sCO<sub>2</sub>, in comparison to water. Additionally, a sCO<sub>2</sub>-based geothermal system would be able to sequester in these twenty-one geothermal reservoirs, over an expected 30-year life of the reservoir, approximately 72 million

tons of CO<sub>2</sub>, or about 10 percent of the current total CO<sub>2</sub> emissions inventory for the country.

### **Simulation and Evaluation of Heat Recovery Exchangers for Solid Sorbent Carbon Capture Systems**

Olukayode Ajayi, David C. Miller, DOE/NETL; Benjamin Omell, Debangsu Bhattacharyya, West Virginia University, USA

Thermal swing systems for carbon capture use heat to regenerate a capture material that is circulating between an absorber and stripper (in the case of solvent systems) or an adsorber and regenerator (in the case of solid sorbent systems). Recovery of heat from the lean capture material to preheat the rich material can significantly improve the energetics and economics of these systems. For solvent-based capture systems, heat exchangers designs are straightforward; however, heat recovery exchangers for solids are not well developed. This paper describes a rigorous, partial differential equation-based model of a solids heat exchanger in which the solids flow in a moving bed regime, moving downward by gravity while passing between plate heat exchange surfaces. The contact heat transfer coefficient was modeled as a series of contact resistances between the plate surface and particles and the penetration coefficient inside the moving bed. The penetration coefficient was obtained from Fourier's equation, where the contact time largely depends on the solid velocity and length of discretized element. The model also includes reactions to account for the potential evolution of CO<sub>2</sub> and water as the solid is heated. The model was implemented within the gPROMS modelling platform.

Two different configurations are possible when exchanging heat between two solid streams. The first is indirect contacting between the hot and cold solids streams in which a heat transfer fluid is used between two solids heat exchangers. The advantages of this configuration include enabling counter current contacting between the hot and cold sides of the heat exchanger. In addition, trim heating or cooling can be applied without the need for a separate solids heat exchanger. The alternate configuration is direct contacting in which the solids are on the hot and cold sides of a single exchanger. In order to enable gravity to drive the solids flow, this configuration is limited to co-current contacting, which reduces the total amount of heat that can be transferred. The model is used within the context of a solid sorbent carbon capture system to evaluate both configurations and to determine the trade-off between energy savings and capital cost.

## **SESSION 45 Gasification Technologies: Slag Analysis**

### **New Slag Management Models for Coal Gasification**

Kyei-Sing Kwong, James P. Bennett, Peter Hsieh, DOE/NETL, USA

The service life of refractory liners for gasifiers has been identified as a critical barrier to IGCC economics, reliability, and on-line availability. Service life is influenced to a large degree by slag chemistry of the carbon feedstock and the gasification temperature. High gasifying temperatures increase refractory degradation, while low gasification temperatures can lead to a buildup of slag on the gasifier sidewall or exit, which is problematic during operation. Thus, there is an optimal operating temperature that maximizes refractory service life and gasifier performance, which is a function of the coal slag chemistry plays and concomitant slag viscosity. Gasifier operators typically use a slag's T250 (temperature at a viscosity of 250 poise), T100 (temperature at a viscosity of 100 poise), T<sub>cv</sub> (temperature of critical viscosity), and/or fluid temperature to determine gasification temperature. NETL has built a slag management tool-set to determine an optimal temperature range for gasification of a carbon feedstock. The tool-set is based on a viscosity database and models using slag chemistry similarity and neural networks to predict slag properties for a given composition. Experimental viscosity and coal ash fusion temperature tests were conducted to determine the ability of the slag model to predict slag viscosity.

### **Prediction of Slag Formation during a UCG Process**

Christien A Strydom, Jackie Collins, Romanus Uwaoma, North West-University; Johan C van Dyk, African Carbon Energy, SOUTH AFRICA

The thermodynamic equilibrium FACTSAGE™ modelling program was used to investigate the influence of gasifier operating temperature and composition of coal on slag formation. The value of utilizing FACTSAGETM equilibrium simulation is its potential to analyse equilibrium conditions for reactions occurring between inorganic and/or organic material. It also provides insight into mineral transformation and slag formation under the conditions during an Underground Coal Gasification (UCG) process. The purpose of the investigation is to fundamentally understand, optimise and determine the most efficient operating conditions in the UCG cavity. Zones (oxidizing and reduction), as previously determined valid for the gasification process are combined and thermodynamic equilibrium reactions modelled to simulate the overall underground gasification process. The ultimate, proximate and XRD analyses results from a coal from the Free State Province in South Africa was used as input data. This

coal will be used for a UCG process in the near future. The modelled results were used to predict leaching of minerals and inorganic compounds from the ash formed in the UCG cavity during the influx of groundwater after closure of the UCG plant. Ash samples from the coal were prepared at temperatures between 1100 and 1400°C in an atmosphere to simulate typical UCG conditions. Leaching tests simulating underground conditions were performed and the leachate analysed using ICP methods to determine the amounts of inorganic compounds that leach out of the ash at the various temperatures. Tests confirmed that within the higher temperature range, most of the mineral matter and inorganic compounds are stabilised within the amorphous part of the slag, as predicted by FACTSAGETM. The temperatures reached within the cavity during a UCG process thus may be controlled in order for most of the mineral matter and inorganic compounds to be inactivated and not to pollute groundwater

### **Slagging Characteristics of Australian Brown Coal Ashes**

Alexander Y. Ilyushechkin, Daniel G. Roberts, David J. Harris, CSIRO Energy Flagship, AUSTRALIA

Consideration of the behavior of coal mineral matter is important in terms of matching coals to the most appropriate gasification technology. While non-slugging gasifier requires coal processing at temperatures below ash melting or ash softening, slugging gasifiers require the mineral matter to melt and have sufficient slag viscosity to achieve steady slag tapping. Some entrained flow gasifiers also have a requirement for the slag to form a protecting layer in the water-cooled wall of the gasification chamber.

Mineral matter compositions of Australian brown coals are highly variable and cover a wide range of compositions in the Si-Al-Fe-Ca-Mg-O system. In this work slagging characteristics, such as phase compositions and viscosity, of typical brown coal ashes from Latrobe Valley are studied.

Slag compositions were calculated using thermodynamic modelling tools and confirmed experimentally by analysis of the selected quenched slags. Experimental slag viscosity data were obtained over a temperature range from 1200–1600°C.

It was found that the liquid phase appearance in the low temperature slagging region (900–1100°C) strongly depends on the slag's chemical composition and the primary phase field, but not directly related to ash fusion temperatures, AFT.

High silica slags typically have Newtonian slag flow behavior and high viscosity which may require fluxing in order to reduce viscosity to be suitable for use in entrained flow gasification (5–25 Pa·s). High iron and magnesium, and high calcium and magnesium slags have low viscosities at high temperatures (above 1500°C), however the slag flow follows non-Newtonian behavior over the entire investigated temperature range. For those slags blending with other coals are required for use in entrained flow installations.

### **Mechanism of Coal Char Gasification Derived from Chinese Western Lignite in Mixture CO<sub>2</sub> and H<sub>2</sub>O**

Chao Ye, Qinhuai Wang, Zhongyang Luo, Mengxiang Fang, Zhejiang University, CHINA

Coal as a fossil fuel is widely used over the world which is the lowest kind of fuel among different fossil fuels and will be used for a relative long time, especially in China. What is more, the ratio of low rank coal in Chinese reserve and production is very high. But the modern pulverized-coal-fired power plant leads to low efficiency (38%–40%) and high pollutant emissions especially carbon dioxide. The efficient and clean utilization of coal has drawn people's attention. Coal gasification is a popular technology to produce syngas from coal that can be converted to synthesis gas. The syngas not only can be utilized in producing chemical material such as methanol but also for electricity. Therefore the low rank coal gasification will play an important role in clean utilization of coal. The mixture of CO<sub>2</sub> and H<sub>2</sub>O as common reactant gas has become more and more important. However, the mechanism of coal gasification in CO<sub>2</sub> and H<sub>2</sub>O has not been clear yet, Chinese western lignite char gasification is conducted at a modified PGTA. The paper present new data to clarify the common or separate active sites assumptions. Chinese lignite is pyrolyzed in Argon atmosphere at 873K, then gasified isothermally at four temperatures (1123–1223K in 50K increments) in atmospheric pressure. There are four kinds of environments in which the partial pressure of H<sub>2</sub>O ranged from 0.015MPa to 0.045MPa and fix the CO<sub>2</sub> partial pressure 0.015MPa. While in H<sub>2</sub>O or CO<sub>2</sub> (Ar as dilute), the higher temperature and partial pressure make the gasification occur more rapidly. When the partial of CO<sub>2</sub> is fixed, the added H<sub>2</sub>O resulting in higher reaction rate all along. The reaction rate increases, and then decreases as char converts to gas and there is a maximum reaction rate during the gasification which attributes to the variety of char reactivity. The volumetric model and Langmuir-Hinshelwood model are applicable to describe experiment data. The results show that when the temperature below 1173K, char-CO<sub>2</sub> and char-H<sub>2</sub>O occur on the separate active sites, while temperature is high than 1173, they share the common active sites.

## Study on Difference of Viscosity-Temperature Characteristic between Coal Ash and Slag

Qinfeng Liang, Jianliang Xu, Xin Gong, Haifeng Liu, East China University of Science and Technology, CHINA

The entrained flow coal gasification is a key technology for coal clean utility. The coal ash/slag viscosity-temperature characteristic is an important factor to the long period operating of entrained flow gasifier. The viscosity-temperature characteristic of raw coal ash and gasification slag from gasifier was investigated in order to achieve more information about change of coal ash melting characteristics during the gasification. The two typical sample used in coal gasification plant was as the research object. The ash fusion point determination meter, high-temperature rotational viscometer, X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to gain the physicochemical characteristics of raw coal ash and slag from entrained flow gasifier under high temperature and reducing atmosphere. The Equilib model in Factsage was performed to further understanding the reason on difference of viscosity-temperature characteristics between coal ash and gasification slag. The results indicated that the mineral crystal in raw coal ash is more noticeable but insignificant in slag. The gasification slag viscosity is higher than coal ash in low temperature but lower in high temperature, furthermore the gasification slag critical viscosity is lower and critical viscosity temperature is higher than coal ash. According to  $Al_2O_3$ - $SiO_2$ - $CaO$ - $FeO$  quaternary phase diagram the mineral in slag is located in high fusion temperature area. Some differences on type and quantity of minerals near the critical viscosity temperature due to viscosity variance between coal ash and gasification slag. More mineral crystal quantity in slag is main reason for higher viscosity of slag in low temperature. Analysis and experimental results are in good agreement, the chemical thermodynamic equilibrium analysis method was suitable for investigating the viscosity-temperature characteristics of ash/slag.

### SESSION 46 Shale and Coal Bed Gas: General - 2

#### A Flowback Simulator Tool for Horizontal Well Drilling

Mike Bockelie, Rand Pummill, Martin Denison, Reaction Engineering International; John McLennan, Ian Walton, Jim Guilkey, University of Utah, USA

The evolution of hydraulic fracturing has enabled development of unconventional natural gas resources that previously would not have been economical. The volume of water required for these operations is a major concern. Industry is actively seeking methods to reduce water usage and increase the amount of gas recovered per unit of water used to stimulate the formation. There is substantial evidence that the rate and method of flowback of the fracturing fluid has a significant impact on the amount of water recovered and well productivity.

Through funding from the DOE Reaction Engineering International, with assistance from the University of Utah (UofU) Energy and Geophysics Institute (EG&I) is developing a computational tool designed to allow engineers to optimize the injection and recovery of water used in hydraulic fracturing operations. A Computational Fluid Dynamics (CFD) model of the Flowback process. Initially the Flowback simulator will be developed using a commercial CFD code ; in later stages of the project the simulator will be transferred to a HPC framework. A database of CFD model solutions for Flowback will be generated and a reduced order model (ROM) tool will be created from the database of CFD solutions. The CFD solutions and the ROM tool will be benchmarked against field data.

### SESSION 47 Coal Science: General - 7

#### Mathematical Model of Lignite Devolatilization with Solid Heat Carrier

Fang-Zhou Li, Jie Feng, Wen-Ying Li, Taiyuan University of Technology, CHINA

To better understand the complex lignite devolatilization behavior with solid heat carrier, a comprehensive mathematical model was established, in which contains two correlative one-dimensional unsteady heat conduction equations of spherical particle and a two-pore-size mass transfer model. This mathematical model is with special consideration of the spatiotemporal temperature and concentration gradients inside coal particles. Distributed activation energy model (DAEM) was validated by thermogravimetric data of the Hulunbuir lignite and then adopted to describe the pyrolysis primary reaction kinetic. The physicochemical properties of coals and volatiles were estimated as a function of local position and temperature because of the presence of transient thermal profile. An implicit finite volume method (FVM) with a tridiagonal matrix algorithm (TDMA) is employed to solve the partial differential equation (PDE) of energy and mass conservation, while the genetic algorithm optimization toolbox (GAOT) based on Matlab software is used to refit kinetic

parameters. The model predictions were verified by comparing the calculated yield of volatiles with the experimental data. The four influencing factors including coal particle radius, pressure, the initial temperature, and the feed amount of solid heat carrier were set as variables of sensitivity analysis to elucidate the influence of macroscopically operation conditions on pyrolytic products distribution. The interactive influences between heat transfer and multicomponent diffusion combined with viscous flow in pores were illustrated. The calculation results allow a quantitative assessment of intraparticle heat and mass transfer in lignite devolatilization with solid heat carrier.

### SESSION 48 Coal Science: General - 8

#### High-Resolution Transmission Electron Microscopy and Time of Flight Secondary Ion Mass Spectrometry: An Initial Study of the Distribution of Hazardous Elements and Rare Earth Elements in Coal Combustion Product

Adilson C. Dalmora, Luis F.O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North-West University, SOUTH AFRICA

Moderately new analytical techniques can help in determining the occurrence of mineral species and the distribution of hazardous volatile elements (HVEs) and rare earth elements in coal combustion products such as minerals and amorphous phases. The continuous generation of carbonaceous matter and mixed crystalline/amorphous mineral ultrafine/nano-particles in the 1 to 100 nm size range by worldwide coal power plants represents serious environmental problems due to their potential hazards. In general the coal fly ash (CFA) that resulted from coal combustion in a thermal power plant was studied in this research. The geochemical classification of ultrafine/nano-particles present in the CFA samples and their interaction with environment are the aim of this work. The detailed methodologies applied for this work were field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy with energy dispersive X-ray spectroscopy (HR-TEM/EDS) and time of flight secondary ion mass spectrometry (ToF-SIMS). Hazardous volatile elements, C, N, S and Hg contents were also determined in the studied sample by inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and LECO equipment. The presented results about the CFA samples comprise carbonaceous, glassy and metallic solid spheres with some containing mixed amorphous/crystalline complex matrix. The EDS analysis coupled with the electron beam observations of the CFA particles with 100 to 0.1 nm demonstrates that these materials contain a small but significant proportion of encapsulated HVEs and rare earth elements. A wide range of organic and inorganic compounds was determined by chemical maps obtained in ToF-SIMS analysis. This work will help as a basis for further scientific research. New techniques such as spectroscopic imaging and transmission electron microscopy make it possible to check which CFA components retain HVEs and rare earth elements, thereby contributing to propose effective measures for the remediation of coal combustion products.

#### Strategies for Modeling and Simulation Aided Design of a Coal Washing Plant for Gasifier Feed Preparation

E. Caner Orhan, Ergin Gulcan, Ozcan Gulsoy, Levent Ergun, Metin Can, Hacettepe University ; Mücella Ersoy, Turkish Coal Enterprises, TURKEY

There has been an ever-increasing focus on a cleaner environment and more efficient use of fuel resources. With coal being a major source of fuel in most parts of the world, there is a continued interest in the efficient use of coal and development of clean coal technologies. This requires a detailed understanding of the fundamental properties of coal, thus making the area of coal characterization of paramount importance.

An ongoing research project, namely OPTIMASH (Optimization of IGCC Technologies For Use With High Ash Content Coal) supported by the European Union's 7th Framework Programme, aims to design and optimize a gasification plant for high ash coals. The efficient gasification of coal, regardless of the extent of ash content, requires well defined coal characteristics which will determine the outcome from gasification as well as the efficiency of gasification. On the other hand, the fluctuations on the specification of the run-of-mine coal which is the feed to a gasification plant, affects the gasification performance. Besides providing washed coal at the suitable quality, coal washing plants also reduce these fluctuations and provide regular feed materials to the gasifiers and hence significantly increase overall gasification efficiency.

In this study, the strategy and approach to the design of a coal washing plant that will produce gasifier feed material from run-of-mine coal are discussed. For this purpose, 500 kg of -60mm Indian coal sample was delivered to our laboratories and the size distribution of the sample is determined. Then, in order to determine the washability characteristics of the coal sample, on each size fraction sample (+50mm, -50+30mm, -30+18mm, -18+10mm, -10+5mm, -5+2mm, -2+1mm, -1+0.5mm, -0.5+0.2mm and -0.2+0.1mm), heavy liquid tests were performed in the density range of 1.3 – 2.3 g/cm<sup>3</sup> with 0.1 g/cm<sup>3</sup> density intervals. Based on the washability data, various coal washing

flowsheets with various coal washing equipment are simulated to prepare feed at the target quality to the gasification plant. The simulations are performed using Lave 2.0 software (an in-house developed coal washing plant simulator). The results of the simulations were compared and the advantages/disadvantages of each flowsheet were discussed in order to determine the optimum flowsheet for the preparation of the gasifier feed. The flowsheet and the design approach will be utilized in the preparation of the feed to the 1 MW pilot scale coal gasifier and the future plant scale application.

**SESSION 49**  
**Clean Coal and Gas to Fuels - 2**

**Production of Petrochemicals and ULSD via Direct Coal Liquefaction Technology**

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

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

**Increasing the Rate and Extent of Microbial Coal to Methane Conversion through Optimization of Microbial Activity**

Matthew W. Fields, Katie Davis, Hannah Schweitzer, Robin Gerlach, Al B. Cunningham, Montana State University; Elliott Barnhart, U.S. Geological Survey, Wyoming-Montana Water Science Center, USA

Coal bed methane (CBM) production is limited by the conversion of the organic fractions of coal into methane, and the process can occur thermogenically and biogenically. For biogenic methanogenesis, the process can be stimulated via microbially-enhanced coal bed methane (MECBM) production. Currently, CBM wells have a limited lifetime since the rate of methane removal via the installed wells is most likely faster than the in situ methane production rates. A significant amount of research has been dedicated to understanding the in situ microbial system involved in converting subsurface coal to methane, but most studies have relied upon formation water that does not always reflect the full microbial community. In addition, core samples can be expensive and/or logistically challenging to obtain. Therefore, we have employed a down-well incubation technique with a diffusive microbial sampler to target and obtain coal-associated microbial populations. The coal-associated microbial communities (bacterial and archaeal populations) have been characterized via pyrotag analyses of the SSU rRNA gene sequences from wells with different methane levels and water geochemistry. On-going analyses include the identification of bacterial and archaeal populations unique to different coals and/or geochemical conditions. The down-well samples were also used to inoculate on-going enrichment cultures to elucidate microbial community dynamics and activity in response to different constraints, and the enrichment cultures are also being analyzed via pyrotag sequence analysis to identify potential population networks that contribute to coal-dependent methanogenesis under non-stimulated and stimulated conditions (i.e., nutrient amended). Pyrotag analysis indicated organisms capable of methylotrophic and hydrogenotrophic methanogenesis dominated the archaeal community from the CBM well while the bacterial community was diverse. Within the enrichments, coal maintained a much greater bacterial diversity compared to enrichments without coal, and these results indicated that a diverse and coal-specific bacterial community was needed to support coal-dependent methanogenesis. Nearly 25% of the bacterial OTUs had low similarity to any known cultured bacteria and may represent novel species specifically adapted to coal bed ecosystems. In stimulated enrichments, coal-dependent methanogenesis more than doubled from native microbial populations from Powder River Basin (PRB) coal beds when yeast extract (YE) and several individual components of YE (proteins and amino acids) were added to laboratory microcosms. Microbial populations capable of hydrogenotrophic methanogenesis were detected in situ and under non-stimulated conditions, whereas stimulation with YE caused a shift in the community to microorganisms capable of acetoclastic methanogenesis. In conjunction, a high proportion of cyanobacterial and algal SSU rRNA gene sequences were detected in a CBM well within a major recharge area where previous isotopic analysis indicated that acetoclastic

methanogenesis was the major methanogenic pathway, suggesting that these phototrophic organisms naturally stimulate acetoclastic methane production. In laboratory studies, adding phototrophic (algal) biomass stimulated CBM production by Powder River Basin microorganisms in a similar fashion to YE. Biomimicry of this natural process could lead to technologies that utilize coupled biological systems (photosynthesis and methane production) to sustainably enhance CBM production and generate algal biofuels while also sequestering carbon dioxide (CO<sub>2</sub>).

**Direct Natural Gas-Fueled Hybrid Fuel Cell System for Producing Liquid Fuel and Power**

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We are developing a fuel cell technology that operates on excess natural gas being produced at a natural gas well-pad to generate electrical power and ethylene, which, when integrated with a chemical process, produces a liquid fuel or higher value chemical that is more readily transported to market. We will accomplish this by integrating a catalyst for the non-oxidative coupling of methane (NOCM), to convert methane to ethylene and hydrogen, into the anode of a proton-conducting fuel cell (PCFC). The hydrogen will be oxidized within the anode, generating protons which will migrate to the cathode where they react with oxygen, thus driving the thermodynamically unfavorable coupling reaction by reducing the hydrogen partial pressure in the anode and by the heat generated by the fuel cell, generating electricity in the process. The technical benefits of our hybrid fuel cell system are: (1) higher levels of methane conversion can be realized at a lower temperature than in a conventional chemical reactor by using a fuel cell to remove hydrogen thus helping to overcome the thermodynamic limitations of the NOCM reaction and (2) using a proton-conducting electrolyte eliminates the loss of carbon due to the formation of CO and CO<sub>2</sub> that occurs when oxygen is either co-introduced with methane, as in conventional oxidative methane coupling (OCM), or when an oxide ion-conducting electrolyte is employed. One of the keys to this technology is the development of a novel proton-conducting fuel cell that is capable of operating efficiently at 500-700°C. Proton-conducting oxides have attracted considerable attention as an electrolyte for SOFCs that operate at intermediate-temperature (≈600°C). We have fabricated a solid oxide fuel cell (SOFC) using a BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>x</sub> (BCY) proton conductor as the electrolyte. A dense BCY film (≈10-μm thick) was deposited on a porous Ni/BCY cermet (i.e., ceramic/metal composite) substrate by a dip-coating process. The gas-permeable Ni/BCY cermet substrate backed with nickel mesh was used as the anode, and platinum paste backed with platinum mesh served as the cathode. The current-voltage characteristics of the BCY-based SOFC were measured in the temperature range 450-800°C using wet air on the cathode side and hydrogen on the anode side. The open-circuit voltage was close to the theoretical value at lower temperatures (<600°C) and was about 85% of the theoretical value at 800°C. The lower measured voltages at high temperature may be due to the development of electronic conductivity in the BCY electrolyte. Gas leakage due to an incomplete seal may also contribute to the deviation from the theoretical voltage at high temperature. The peak power density of the fuel cell was ≈90 and ≈1500 mW/cm<sup>2</sup> at 450 and 800°C, respectively. The power density increased as temperature increased because the cell resistance decreased. Our efforts to develop SOFCs based on proton conductors will be summarized in this talk.

Work supported in part by the U.S. Department of Energy, Advanced Research Projects Agency – Energy (ARPA-E) under Contract DE-AC02-06CH11357

**Syngas Generation via Chemical Looping Dry Reforming**

Amey More, Götz Vesper, University of Pittsburgh, USA

‘Chemical Looping Combustion’ (CLC) is an emerging clean combustion technology which offers an efficient route for fossil fuel combustion with inherent CO<sub>2</sub> capture based on the cyclic oxidation and reduction of an ‘oxygen carrier’ (typically a metal) with air and a fuel, respectively. We have recently shown that this process can also be used for CO<sub>2</sub> activation by replacing air with CO<sub>2</sub> as the oxidant for the process, resulting in the reduction of CO<sub>2</sub> to CO which is a useful chemical feedstock, and thereby offers an alternate pathway to carbon sequestration. We had previously identified Fe as the most suitable metal for the process due to its good reactivity with CO<sub>2</sub> at realistic process operating conditions. However, Fe shows poor reactivity with methane as a typical fuel for this process. Ni and NiO, on the other hand, are well known as efficient catalysts for methane combustion, but do not show significant reactivity with CO<sub>2</sub>. We hence hypothesized that a physical mixture of Fe- and Ni-oxides would show combined good reactivity with both CH<sub>4</sub> and CO<sub>2</sub> in the reduction and oxidation half cycles, respectively.

Supported Ni, Fe oxygen carriers with 40wt% metal loading were synthesized using a simple wet-impregnation procedure. Thermo-gravimetric analysis (TGA) of the carriers combined with X-Ray Diffraction (XRD) gave insight into oxidation states, and carrier conversions and reaction rates were evaluated in fixed-bed reactor experiments. TGA experiments with CH<sub>4</sub> revealed that the physically mixed oxide carrier was reduced at a much higher rate than the corresponding bimetallic oxide, while the fixed-bed experiments confirm excellent methane conversions and syngas

yields. This points towards an interesting cooperative reaction mechanism, where methane is first cracked over Ni carriers, resulting in the formation of carbon and H<sub>2</sub>, and the H<sub>2</sub> is then oxidized in a (very fast) reaction with Fe<sub>x</sub>O<sub>y</sub>. The produced H<sub>2</sub>O then gasifies the carbon deposit on Ni, yielding syngas as final product. Individual reduction experiments of Fe-carriers with H<sub>2</sub> and CO, and experiments in a structured bed composed of two sequential monometallic Fe and Ni beds further confirm this cooperative reaction mechanism. Finally, the impact of Ni:Fe ratio and reaction temperature was investigated and the stability of the carriers over at least 50 redox cycles was confirmed. Overall, our results thus indicate that the combination of these two carrier materials enables a highly efficient process for syngas production via CLDR.

**SESSION 50**  
**Carbon Management: Other Topics on CO<sub>2</sub> Capture**

**Evaluation of Ionic Liquids for Supported Ionic Liquid Membranes: Application in Pre-Combustion Carbon Capture**

Alexander Horn, Elliot Roth, DOE/NETL; Megan K. Macala, AECOM, USA

Ionic liquids (ILs) are room temperature organic salts which are known to dissolve large amounts of carbon dioxide. They are attractive materials for carbon capture since they are generally non-flammable, thermally and chemically stable, exhibit extremely low vapor pressure, and their physical properties can be tuned by structural modifications. One significant disadvantage of ILs is their projected cost, which would limit their use as solvents. To reduce the amount of IL required, the IL can be incorporated onto a hollow fiber support as a Supported Ionic Liquid Membranes (SILM). With SILM technology, a thin layer of IL is held within the porous support by capillary forces. The thin layer of IL is used to selectively separate the gases. A series of ILs have been synthesized, characterized, and their physical and thermal properties were determined. The ionic liquids were evaluated for CO<sub>2</sub> solubility and CO<sub>2</sub>/H<sub>2</sub> selectivity. Dynamic Mechanical Analysis was used to probe the interaction of the IL and support.

**Warm Gas Precombustion CO<sub>2</sub> Capture Using Hydrophobic Solvents**

Nicholas Siefert, DOE/NETL and Carnegie Mellon University; Hunaid Nulwala, Carnegie Mellon University; Wei Shi, Fan Shi, Jeffrey Culp, URS/AECOM/DOE/NETL; Elliot Roth, Victor Kusuma, ORISE/DOE/NETL; David Hopkinson, DOE/NETL, USA

A key way to improve the efficiency of IGCC-CCS power plants is to capture CO<sub>2</sub> at temperatures close to the temperature of the water gas shift (WGS) reactor, which is close to the temperature at which the hydrogen is sent to the combustor of the gas turbine (~200 °C). Instead, in baseline IGCC-CCS configurations [1], the syngas is cooled to 40°C and the physical solvent is chilled to 10°C prior to entering the CO<sub>2</sub> absorption column. NETL/ORD is researching a number of hydrophobic, physical solvents that can be used to capture CO<sub>2</sub> at partial pressures of 25-35 bar and at temperatures as high as 100°C so that there is a better match between the temperature of the absorber and the temperature at which the hydrogen must be sent to the gas turbine. This will improve the overall thermodynamic efficiency and could decrease the overall capital cost if the reduction in heat exchanger sizes overcomes the potential increase in the cost/size of the absorption/desorption vessels due to lower uptake of CO<sub>2</sub> into solvents at higher temperature. When operating at above room temperature, it is crucial to use a hydrophobic solvent rather than a hydrophilic solvent so that water does not build up in the solvent and reduce the CO<sub>2</sub> solubility of the solvent. Here, we will present both experimental measurements and computational simulations of the CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub>/CO/N<sub>2</sub>/H<sub>2</sub> solubility, viscosity, and density of a number of different hydrophobic, physical solvents at temperatures between 25°C and 100°C. In particular, we will focus on the following solvents: H-Siloxane and [aPy][Tf<sub>2</sub>N]. The first solvent is an amphiphilic solvent containing polar ethylene glycol segments and non-polar siloxane portion (H-Siloxane). This solvent has very high CO<sub>2</sub> solubility for a physical solvent. The second solvent is a hydrophobic ionic liquid: allyl-pyridinium bis(trifluoromethylsulfonyl)imide. [aPy][Tf<sub>2</sub>N] is a low viscosity ionic liquid that is extremely selective for CO<sub>2</sub> over CH<sub>4</sub>, CO, N<sub>2</sub> and H<sub>2</sub>, but has a slightly lower overall CO<sub>2</sub> solubility than H-Siloxane. We also will present data on mixtures of these two solvents, and will compare the solubility against commercial available solvents such as Selexol® (UOP LLC).

**Li- and K- Doped Na<sub>2</sub>ZrO<sub>3</sub> Sorbents for CO<sub>2</sub> Capture**

Yuhua Duan, DOE/NETL, USA

Carbon dioxide is one of the major combustion products which once released into the air can contribute to global climate change. Solid sorbents have been reported in several previous studies to be promising candidates for CO<sub>2</sub> sorbent applications due to their high CO<sub>2</sub> absorption capacities at moderate working temperatures. However, at a given CO<sub>2</sub> pressure, the turnover temperature (T<sub>t</sub>) of an individual solid capture CO<sub>2</sub> reaction is fixed. Such T<sub>t</sub> may be outside the operating temperature range (ΔT<sub>o</sub>) for a

particularly capture technology. For a solid, in order to shift such T<sub>t</sub> into the range of ΔT<sub>o</sub>, its corresponding thermodynamic property must be changed by changing its structure through reacting (mixing) with other materials or doping with other elements. As an example, by combining thermodynamic database searching with ab initio thermodynamics calculations, in this work, we explored the Li- and K-doping effects on the T<sub>t</sub> shifts of Na<sub>2</sub>ZrO<sub>3</sub> with different doping levels. The obtained results showed that compared to pure Na<sub>2</sub>ZrO<sub>3</sub>, the Li- and K-doped mixtures Na<sub>2</sub>-αMaZrO<sub>3</sub> (M=Li, K) have lower T<sub>t</sub> and higher CO<sub>2</sub> capture capacities. The Li-doped systems have a larger T<sub>t</sub> decrease than the K-doped systems. When increasing Li-doping level α, the T<sub>t</sub> of the corresponding mixture Na<sub>2</sub>-αLiZrO<sub>3</sub> decreases further to low temperature range. However in the case of K-doped systems Na<sub>2</sub>-αKZrO<sub>3</sub>, although doping K into Na<sub>2</sub>ZrO<sub>3</sub> initially shifts its T<sub>t</sub> to lower temperatures, further increases on the K-doping level α, causes T<sub>t</sub> to increase. Therefore, doping Li into Na<sub>2</sub>ZrO<sub>3</sub> has a larger influence on its CO<sub>2</sub> capture performance than the K-doped. Compared with pure solids M<sub>2</sub>ZrO<sub>3</sub>, after doping with other elements, their CO<sub>2</sub> capture performances are improved. These results demonstrate that although one single material taken in isolation might not be an optimal CO<sub>2</sub> sorbent to fit the particular needs and to operate at specific temperature and pressure conditions, by mixing or doping two or more materials to form a new material, it is possible to synthesize such new CO<sub>2</sub> sorbents which can fit the operating temperature needs for industrial applications.

**Advanced Process Control of Bubbling Fluidized Bed Adsorber-Regenerator Processes for Efficient Transient Operation**

Priyadarshi Mahapatra, Jinliang Ma, AECOM / National Energy Technology Laboratory; Debansu Bhattacharyya, Benjamin Omell, West Virginia University; Stephen E. Zitney, David Miller, DOE/NETL, USA

This paper highlights advanced process control (APC) strategies and software framework developed as part of the U.S. Department of Energy's Carbon Capture Simulation Initiative (CCSI). These APC strategies provide substantial benefits in comparison to conventional industrial control methodologies such as advanced regulatory and/or linear model predictive control. The advantages have been demonstrated through nonlinear control of an amine-impregnated solid sorbent-based carbon capture process. The APC framework utilizes detailed first-principles-based multi-scale pressure-driven non-isothermal bubbling fluidized bed (BFB) models to represent the actual capture process, while computationally-fast and accurate dynamic reduced models (D-RMs) are utilized within the control algorithms. The carbon capture process includes tightly integrated adsorber and regenerator subprocesses, each containing a BFB model and models of the balance-of-plant equipment items. The process dynamics involve control challenges such as multiple time-scale transients, process delays and positive feedback due to solid sorbent recirculation and fluctuating flue-gas flowrate, rendering conventional control methods inefficient. Mimicking the open-loop dynamic behavior of these interacting processes through D-RMs and utilizing their predictive capability for optimally controlled operation, the developed APC strategies provide significant benefits for efficient utilization of material and energy without violating environmental-emission constraints.

In this paper, we highlight a D-RM builder tool that automatically generates fast D-RMs using pre-computed results from repeated simulation of high-fidelity dynamic process models. The tool utilizes black-box nonlinear identification techniques such as decoupled AB-Net (DABNet) and nonlinear autoregressive moving average (NARMA). Dynamic uncertainty quantification (UQ) analysis is utilized to quantify confidence in the generated D-RMs especially in presence of large measurement noise. Furthermore, an APC framework is presented, which uses these D-RMs as fast predictive-models for implementing various nonlinear control strategies such as nonlinear model predictive control (NMPC) and multiple model predictive control (MMPC). A novel disturbance estimation technique is also highlighted, which can automatically categorize routine disturbances (such as random step, random ramp, periodic, etc.) through a multiple model disturbance estimation (MMDE) algorithm. The developed APC framework is designed to enable better responsiveness to demand-changes and superior disturbance rejection for otherwise slow capture processes.

**SESSION 51**  
**Gasification Technologies: Modeling - 2**

**Dynamic Simulation of Opposed Multi-Burner Coal-Water Slurry Gasification System**

Zhengkua Dai, Junyu Yang, Chao Li, Qinfeng Liang, Guangsu Yu, East China University of Science and Technology, CHINA

The opposed multi-burner (OMB) coal-water slurry (CWS) gasification system has advantages in large capacity, high carbon conversion and high operation flexibility. There are four burners in symmetrical distribution on middle-upper part of the OMB CWS gasifier. The high temperature syngas from the gasifier is quenched in the quench chamber and then purified by a mixer, a cyclone and a water scrubber. This work presents a steady-state model of a commercial-scale OMB CWS gasifier and a

dynamic model of the gasification system. A general reactor network model (RNM) with detailed reaction kinetics is established for the gasifier. The particle and gas residence time distribution (RTD) of RNM are obtained by the Markov chain stochastic model, which is validated by that of CFD model. The steady-state model is validated with the industrial data (6.5MPaG, 1500TPD gasifier). Then the steady-state model is transformed into the dynamic model which adopts pressure driven solution. Based on the dynamic model, the specific online reset process (ORP) of the gasifier is studied firstly. ORP means that one couple of burners may be out of service triggered by security system, through ORP, this couple of shut-off burners can be online reset; meanwhile, the other couple of burners are always running. In addition, a temperature control strategy is established by using oxygen flow rate as the control variable. The dynamic responses of gasification system to the  $\pm 1.5\%$  disturbances of the CWS concentration and  $\pm 5\%$  disturbances of coal calorific value are investigated for temperature controller. The tendency of inlet oxygen flow rate, operation pressure, operation temperature, carbon conversion and  $\text{CO} + \text{H}_2$  flow rate are obtained through the dynamic simulation. The simulation results indicate that the fluctuation ranges of the operation temperature ( $\pm 25^\circ\text{C}$ ) and pressure ( $+0.1\text{MPa}$ ) of the gasifier are reasonable and the gasifier can be operated in security with liquid slagging. The ORP and temperature controller are effective and feasible.

#### **Optical Experimental Study on the Characteristics of Impinging Reaction Region in Opposed Multiburner Gasifier**

Xudong Song, Yan Gong, Guangsuo Yu, Qinghua Guo, East China University of Science and Technology, CHINA

Diffusion flames have been used for a wide variety of industrial processes, especially for opposed entrained-flow gasification technology. The effective monitoring and control of flames is the core of achieving high energy efficiency, reliable diagnosis for gasification process and optimal gasification technology. Through emission spectral analysis of impinging zone during coal-water slurry gasification in the bench-scale opposed multi-burner gasifier, the criterion for dominant reactions was constructed. There were obvious radicals emission in the impinging zone, including  $\text{OH}^*$  emission at 309nm and  $\text{CH}^*$  emission at 430nm. Intense black-body radiation appeared where the wavelength was longer than 400nm. The emissions of  $\text{OH}^*$  and  $\text{CH}^*$  were not monotone changing with increasing  $\text{O}_2/\text{Fuel}$ , but showed maximal values at a certain  $\text{O}_2/\text{Fuel}$ , in accordance with the change of atmosphere, which could serve as a criterion for dominant reactions between gasification and combustion.

#### **Numerical Analysis of the Particle Residence Time Distribution and Flow Characters of the Opposed Multi-Burner Gasifier**

Chao Li, Zhenghua Dai, Guangsuo Yu, Jianliang Xu, Fuchen Wang, East China University of Science and Technology, CHINA

As one of the most efficient and reliable entrained flow gasification technologies, Opposed Multi-Burner (OMB) coal-water slurry gasification technology has been applied in 35 plants. Over 100 gasifiers are adopted to convert coal or petcoke to chemicals, liquid fuel or electric power, in which, over 30 gasifiers are on operation. With the enhancing of the gasifier capacity and the scaling up of the gasifier size, the characteristics of the gas-particle flow in the gasifier have great meanings in gasifier modeling and design. In this study, a 3D numerical modeling of the gas-particle flow of a commercial scale OMB gasifier is conducted. The calculated particle residence distribution (RTD) of the bench scale gasifier is compared with the experimental data to validate the model. The particle RTD and particle flow characters in different flow regions of the gasifier are analyzed in detail. Based on the particle RTD and mechanical analysis, a criterion of the dominant factor of particle flow is proposed. The effects of particle properties and operating conditions on the particle flow characters in different flow regions are investigated. The result shows that in the impinging flow zone and recirculation zone, with the increasing of the gasifier load and the decreasing of the particle size, the dominant factor of the particle flow changes from the gravity-drag force controlled into the drag force controlled. And in impinging zone of the gasifier, the particle flow is dominated by the inter-particle collision.

#### **SESSION 52 Shale and Coal Bed Gas: General - 3**

#### **Chloride and Bromide in Waters Associated With Production of Shale Gas, Coal Bed Methane, and Coal in the Northern Appalachian Basin**

Paul F. Ziemkiewicz, West Virginia University; USA

Chloride and, particularly, bromide, in source water for public drinking water treatment facilities are important since interaction with water treatment processes may result in formation of bromate ( $\text{BrO}_3^-$ ) or brominated trihalomethane (THM) disinfection byproducts (DBPs) (U.S. Environmental Protection Agency, 2002; Parker et al., 2014). The drinking-water maximum contaminant levels (MCLs) for bromate and total trihalomethanes (TTHM) are 0.010 and 0.080 mg/L, respectively (U.S.

Environmental Protection Agency, 2005, 2012). While the relationships between source water halogens and DBP formation are complex and poorly characterized, it is important to understand potential sources of chloride and bromide in order to better manage stream and source water concentrations.

In the Appalachian Basin, potentially important sources of halogens are thought to be conventional and unconventional oil and gas produced water (brines), coal-bed methane (CBM) produced water, and coal-mine drainage (CMD). Halogens are elevated in conventional and unconventional oil and gas brines. In their study of flowback water from shale gas development, Ziemkiewicz and He (2015) found that ion concentrations in general increased throughout the flowback cycle reaching concentrations of 1,500 mg Br/L and 80,000 mg Cl/L and. Dresel and Rose (2010) and Haluszak et al. (2013) reported similar or higher concentrations of chloride and bromide in produced waters from conventional oil and gas wells in Pennsylvania. The major halogen ions in CBM produced waters ranged from 20 to 12 mg Br/L and 2,800 to 14,700 mg Cl/L.

Cravotta and Brady (2015) studied CMD from selected permitted discharge facilities in Pennsylvania and found concentrations generally less than 0.5 mg Br/L with several notable exceptions between 3 and 12 mg Br/L. While halogen concentrations in CMD are much lower than in oil and gas produced waters the discharged volumes from coal mines are substantially higher.

In this paper we examine the major ion chemistry of potential halogen sources, particularly the concentrations of chloride and bromide. We also compare chemistries of oil and gas brines to that of CMD to gain a better understanding of the sources of chloride and bromide in regional streams and rivers and the role that these sources play in regional stream chemistry.

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#### **SESSION 53 Coal Science: General - 9**

#### **Release Behavior and Formation Mechanism of Polycyclic Aromatic Hydrocarbons during Coal Pyrolysis**

Meiqi Gao, Yulong Wang, Jie Dong, Liping Chang, Fan Li, Taiyuan University of Technology, CHINA

At present, Polycyclic aromatic hydrocarbons (PAHs) have attracted increasing attention due to their severe potential carcinogenic, mutagenic and genotoxic on human health during thermal conversion and burning of fossil fuels. Especially, they are trapped easily in  $\text{PM}_{2.5}$  which is considered as the main cause of atmospheric haze. With the development of clean coal technology and the demand of contaminant emission reduction, it is imperative to study the release behavior and formation mechanism of PAHs during coal pyrolysis because coal pyrolysis is one of the most important parts of the comprehensive use of coal and it occurs almost in all major coal thermal conversion processes. In this study, 4 coals with different degree of metamorphism from China were pyrolyzed by pyro-probe CDS 5250, which can be heated up to the given temperature at a rate of  $20^\circ\text{C}/\text{ms}$ . The release tendency of 16 PAHs were studied under different pyrolysis conditions online by GC-MS. The macromolecular structures of 4 coals were determined by CP/MAS  $^{13}\text{C}$  NMR, and then the influencing factors of the PAHs release and the formation mechanism of PAHs during coal pyrolysis were discussed combined with the structure characteristic of coals. It was shown that the emission amounts of PAHs during coal pyrolysis related to coal rank to a great extent and followed the order of medium rank coal > low rank coal > high rank coal. The concentration of total PAHs varied with pyrolysis temperature, which was first increased and then decreased and reached its peak at  $800^\circ\text{C}$ . Besides, the variation of different rings PAHs was shown with different temperatures. The temperatures which different rings PAHs reached maximum value were different. When the temperature was lower than  $800^\circ\text{C}$ , the thermolysis reaction was the major so that the small rings PAHs were the most abundant. However, the

polycondensation reaction played a dominant role after 800 °C, it made the proportion of heavy rings increase. It can be indicated from the results of CP/MAS 13C NMR that, the formation of PAHs during coal pyrolysis have great relationship with the coal structure. The types and amounts of PAHs generated during coal pyrolysis were closely related to the protonated aromatic carbon and bridging ring junction aromatic carbon.

**SESSION 54**  
**Coal Science: General - 10**

**Analysis of Relationships of Optimal Design Parameters of Cavitation Venturi Tube and Pico-Nano Bubble Size Distributions and Process Parameters of Column Flotation of Coal**

Felicia Peng, Yu Xiong, West Virginia University, USA

Pico and nano bubble generations by applying various techniques have been studied for decades in various fields due to their complexity phenomena for pico and nano bubble generations, and wide range of high potential applications. Those tiny bubbles have been used for environmental remediation, medical and biotechnology usages, industrial dewatering processes, catalysis, ultrasound imaging, etc., depending upon the bubble generation techniques applied. The pico and nano bubbles generated by cavitation venturi tube technique have been used to enhance the recoveries of coal and minerals in flotation processing. The advantages of using pico and nano bubbles generated by hydrodynamic cavitation venturi tube improve coarse particle and ultrafine particle flotation performance, as well as reduction of reagents, frother and collector, consumption. The functions of pico and nano bubbles are to act as the secondary collector, in addition to the oily reagent as primary collector. The characteristics of coalesces and bridging capabilities of those tiny bubbles between, themselves, hydrophobic surfaces of solids particles, and larger size bubbles - microbubbles, increase the probability of attachment between bubbles and hydrophobic solid particles, and reduce the probability of detachment, to enhance the recoveries of coarse particle and ultrafine particle in column froth flotation. However, both the optimum design parameters of the cavitation venturi tube and process parameters including, operation parameters, feed characteristics and reagent conditions, control the pico and nano bubble size distributions, and thus control the column flotation process and performance. In this study, analysis of parameters was conducted to examine the relationships between the optimal design parameters of cavitation venturi tube and, pico and nano bubble size distributions and, the process parameters of coal column froth processing. The bubble size distribution was obtained under different conditions by a laser particle analyzer using a special designed pico-nano bubble generation column. The four factors and three levels, central composite design of experiment method was used to investigate the four important design parameters of venturi tube, which govern the size distributions of pico and nano bubbles generation. The design parameters of the venturi tube are, the ratio of inlet venturi tube to diameter of throat ( $D_{in}/D_t$ ), ratio of the length of throat to the diameter of throat ( $L/D_t$ ), and input and output angles of cavitation venturi tube. The effects of process parameters including, feed solid concentration and flow rate, air flowrate, reagent conditions, washing water, on the pico and nano bubble generation and coal flotation were investigated using a lab flotation column. The flotation column has 2-in diameter and 260 cm height, equipped with a static-mixer and a venturi cavitation venturi tube for macro, and pico and nano bubble generations, respectively. The design of experiment of coal column flotation test is performed to determine the optimized process parameters. When 70 percent of pico and nano bubbles are produced, the flotation results show, that the clean coal product has 86% combustible material recovery and 12% ash content obtained from Pittsburgh seam raw coal with 31% ash content.

**Determination of Coal Ash Emissivity and its Application to Ash Deposition Model for Coal-Fired Boilers**

Miki Shimogori, Mitsubishi Hitachi Power Systems, LTD., JAPAN

This study presents a simplified methodology to determine coal ash emissivity and its application to ash deposition model for coal-fired boilers. Regarding the determination of coal ash emissivity, the original Konopelko equation was modified. The equation expresses spectral emissivities in relation to the wavelength and iron content in ash. Spectral emissivity of coal ash is known to have a positive wavelength dependence; it is low at short wavelengths and increases with an increase in wavelengths which then remains constant ( $\epsilon_{max}$ ) over a certain wavelength ( $\lambda_{max}$ ). In the modified equation, parameters are  $\epsilon_{max}$ ,  $\lambda_{max}$  and spectral emissivity in the shorter wavelength:  $1.6 \mu\text{m}(\epsilon_{1.6}(T))$ . Based on spectral emissivity data from previous studies, we determined  $\epsilon_{max}$ ,  $\lambda_{max}$  as 0.85 and 8  $\mu\text{m}$ , respectively. To verify our modification, we compared total emissivities obtained by calculated spectral emissivities with those obtained by measured spectral emissivity for several works. To obtain  $\epsilon_{1.6}(T)$  by calculation, we investigated dependences of iron content in ash and temperature on  $\epsilon_{1.6}(T)$  using a shield tube emissometer. With reflecting these results, this simplified equation determines total emissivities obtained in different studies with an error of almost 20 %.

Obtained coal ash emissivities were applied to a comprehensive ash deposition model for coal-fired boilers and heat absorption behaviors before and after soot-blowing were discussed.

**POSTER SESSION**  
**Gasification**

**Numerical Analyses of Coal Gasification in a Bubbling Fluidized-Bed Gasifier**

Hsien-Chi Tsui, Yu-Der Lin, Tsung Leo Jiang, National Cheng Kung University; Po-Chuang Chen, Yau-Pin Chyou, Institute of Nuclear Energy Research, Atomic Energy Council, TAIWAN

Fluidized-bed reactors are widely used in many chemical industries and power plants, since they are characterized by the features of high efficiency, high heat transfer rates, low combustion temperature, low pollutant emissions, and less limitations on fuel selection. Combustion and gasification technology of pulverized coal in a fluidized-bed gasifier is thus an essential one for clean-coal technologies. In the present study, a numerical model for the simulation of combustion and gasification of pulverized coal in a bubbling fluidized-bed gasifier has been developed by using the commercial CFD software, ANSYS/ FLUENT. The Eulerian-Eulerian approach is employed for the gas-solid multiphase flow, where different phases are treated as interacting continua. The transport exchanges of mass, momentum, and energy among different phases are taken into account in the present numerical model. The physical sub-models include the char oxidation model, the turbulent combustion model, and the thermal radiative model. The finite-rate and eddy-dissipation combustion models are employed for the gas combustion. A model-gasifier with a height of 200 cm and a diameter of 22 cm has been investigated by the present model. A Colombia bituminous coal is used as the feedstock in the present study to verify with the reference data. Preheated air and steam are supplied from the bottom, and coal is fed from the side tube of the gasifier. Sensitivity analyses for the parameters such as the air/coal ratio and the steam/coal ratio are conducted for evaluating the efficiency of coal gasification. The numerical results obtained from the present study show that the outlet gas compositions predicted by the present model are generally in agreement with the experiment data. The results also indicate that the bubbles generated in the reacting bed may break and vanish when they move up to the interface between the sand bed and the ambient gas. The particles carried by the bubbles then splash down back into the bed, confining them within the gasifier. The heterogeneous reactions of the char oxidation are predicted to take place generally in the lower region of the reactor. The C(s)-CO<sub>2</sub> and C(s)-H<sub>2</sub>O reaction processes become important only when the oxygen in the gasifier is depleted.

**Radical Reactors - Using Multiphase Models to Automate Optimal Gasifier Design**

William A. Rogers, Jenny Tennant, DOE/NETL, USA

The NETL Gasifier Optimization and Plant Supporting Systems key technology area is focused on improving the performance and reducing the costs of advanced gasifiers. This work supports development of advanced gasifiers and supporting systems which would incorporate the most aggressive and successful technologies resulting from both Gasification Systems program and other DOE programs. Anticipated improvements will allow much expanded use of low-cost, low rank coals, expanding opportunities for gasification systems and lowering feedstock costs. Optimization also includes the aim of reducing water consumption in gasification plants, and systems integration to increase efficiency and reduce costs plant-wide.

One important thrust in this area is the development of multiphase computational fluid dynamics models to better understand chemical kinetics and flow behavior of gas and solids inside a gasifier. NETL's Office of Research and Development (ORD) and its Multiphase Flow Science Team are developing validated models for advanced gasification technology so that new concepts can be developed with less empirical testing to yielding improved performance. Multiphase Computational Fluid Dynamics (CFD) models are being developed to simulate and understand performance before a design is finalized, which is critical for reducing cost of construction and operation. During new technology development, empirical scale up information is not available. Science-based models with quantified uncertainty are important tools for reducing the cost and time required for development because traditional scale-up methods do not work well for multiphase flow reactors, such as the ones used for gasification.

As an extension of this effort, NETL is developing a design optimization framework for investigating potentially radically new reactor geometries to significantly reduce plant construction and operating costs. These tools will allow for investigation of different reactor geometries and flow conditions to allow for more precise manipulation of solids and gas flow and characteristics for design optimization. This framework is being built on NETL's open-source MFIX Suite of Multiphase CFD models. When these advanced design techniques are coupled to novel manufacturing processes such as additive manufacturing, significant increases in the financial performance of gasification systems could result. This paper will describe the design optimization framework in greater detail and provide a demonstration of the automated

technique for small-scale, cold-flow applications representative of various fluidized bed gasification processes. Particle segregation is optimized in the demonstration to illustrate how particle mixing, contacting, and gas - solids mixing can be modeled to meet certain optimal performance criteria. The optimized design is then built and tested in the NETL Multiphase Flow Science Laboratory, with a comparison of resulting physical data to model predictions to validate the approach.

#### **Catalytic Effect of Na<sub>2</sub>CO<sub>3</sub> on CO<sub>2</sub> Gasification of Wyodak Coal**

Lei Bai, Xin He, Tuo Tang, Deping Xu, Yonggang Wang, China University of Mining and Technology (Beijing), CHINA; Fan Zhang, National Institute of Clean-and-Low-Carbon Energy, CHINA; Maohong Fan, University of Wyoming, USA

The objective of this work is to study the catalytic effect of Na<sub>2</sub>CO<sub>3</sub> on CO<sub>2</sub> gasification of a low-sulfur sub-bituminous Wyodak coal from the Powder River Basin (PRB) of Wyoming. All the gasification experiments were conducted in a fixed-bed laboratory gasifier at atmospheric pressure from 700 °C to 900 °C. The sample obtained after 30 min CO<sub>2</sub> gasification in presence of Na was investigated by SEM/EDS. Loaded as the catalyst precursor, Na<sub>2</sub>CO<sub>3</sub> greatly increased the rate of coal gasification with CO<sub>2</sub>. The catalytic effect was intensified with the incremental loading of Na (0 wt%, 3 wt% and 5 wt%). Integrated model was used for fitting the kinetic data obtained from both non-catalytic and catalytic reaction. The activation energy of the catalyzed CO<sub>2</sub> gasification (Na loading were 0 wt%, 1 wt% and 5 wt%, respectively) was calculated, which were 102.76 kJ/mol; 82.60 kJ/mol and 68.80 kJ/mol, respectively. The addition of sodium promoted the reaction kinetics of coal-CO<sub>2</sub> gasification. Furthermore, SEM/EDS images indicate different sodium status during the gasification. Some sodium combined only with oxygen and existed as the fibrous oxides; while another portion of sodium integrated with silicon or alumina and existed as sodium silicate or sodium aluminosilicate.

#### **POSTER SESSION Clean Coal Demonstration and Commercial Projects**

#### **Pulverized Fuel Production from Coal Slimes of Hema Kandilli Washing Plant under 0.5mm with Reichert Spiral**

Gunduz Atesok, Mustafa Ozer, Firat Burat, Onur Guven, Huseyin Basturkcuk, Istanbul Technical University, TURKEY

In HEMA Zonguldak coal washing plant located in Kandilli region which is owned by Hattat Energy and Mining Company Ltd., about 750 tons of ROM coal per day is produced by underground methods. After production, the ROM coal at -100+10 mm and -10+ 0.5 mm size ranges are washed in Drewboy Heavy Media Drums and Heavy Media Cyclones respectively. In addition, the coal slime under 0.5 mm, firstly dewatered by detritus tank and then fed to the pressure filters. After these processes, an ultimate product of 0.5 mm sized coal with 40-47 % ash content and 18-22 % moisture is obtained. Although, this product can not be used in industrial applications due to its characteristics, it can be sold under 70 TL per tonne price in particular to cement factories

Thus, in this washing plant, 200 tons which accounts for 30 % of daily production, stands out as slime (-0.5 mm) coal. After bringing the ash and moisture content of that slime coal into 10-12 % content, it can be sold under 240 TL per tonne price to particularly iron and steel industries.

In recent years, Reichert Spiral is one of the most widely used washing unit for beneficiation of fine and dust sized ores. The separation process in spirals is mainly utilized in terms of density and -3+0.075 mm size ranges which can be successfully used in the washing of coals. In addition, the absence of moving parts out of pump and less investment and operating costs make out the reasons for choice of spirals.

In this study, a pilot scale Reichert Spiral was utilized for evaluation of coal slimes from preparation plant which is under consideration. Experimental studies were carried out for two types of coal classified as slimed and deslimed (sample without 0.106 mm sized coal) coal products. The result of these tests indicated that after desliming coal samples about 34.6 wt. % of spiral feed could be produced as clean coal product with 9.76 % ash content and 63 % combustible recovery. On the other hand, the results of tests with slime coal, about 48 wt. % of spiral feed was produced as clean coal with 26.2 % ash content and 65 % combustible recovery. However by screening the clean coal of this process with 0.106 mm screen, the oversize product accounts for 34.6 wt. % of spiral feed where an ultimate clean coal with 8.8 % ash content with 58 % combustible recovery was produced

#### **POSTER SESSION Combustion**

#### **A Study on Ash Deposit Characteristics for Biomass Co-Firing in a Pilot Scale Pulverized Coal Combustion System**

Seuk Cheun Choi, Yeong Seok Jang, Taeyoung Chae, Jae Wook Lee, Won Yang, Korea Institute of Industrial Technology, SOUTH KOREA

In recent, utilization of low-grade coals including sub-bituminous coals in Korean power boilers which were originally designed to use bituminous coals of high-quality. These low-level coals contents high moisture contents & sulfur contents, lower heating value & ash fusion temperature (AFT), which may cause of additional environmental problems such as increasing CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> emissions and ash deposit inside boiler. Ash deposit may seriously effect operational life of PC boiler which related with slagging and fouling. Utilization of renewable fuels such as biomass (including wood pallet, walnut shell etc..) in coal-firing power generation system is most promising way to solve previous environmental problems commonly refer as biomass co-firing. In however, one of the major problems using biomass co-firing are increasing corrosion of boiler tube which associated with increasing ash deposit in fouling zone and chlorine contents. There have been limited research papers reported related to investigation of biomass co-firing ash deposit behavior caused by blended biomass and coal combustion. Therefore, purpose of this study is to observe ash deposit behavior (including slagging and fouling characteristics) using a pilot-scale (80 kWth) down-fired pulverized coal combustion system. Three different biomass samples with one bituminous coal are used in present study. In order to observe behavior of ash behavior, the measurement of X-ray diffraction (XRD) and inductively coupled plasma (ICP) are performed in present study.

#### **Comparative Performance Evaluation of Oxy-Fuel Combustion at Elevated and Atmospheric Pressure through Process Simulation**

Tae-Young Mun, Tefera Zelalem Tumsa, Uendo Lee, Won Yang, Korea Institute of Industrial Technology, SOUTH KOREA

The oxy-fuel combustion under pressurized condition has been recently emerging as one promising technology for an efficient carbon capture and storage (CCS). The main advantages of pressurized oxy-fuel combustion are high latent heat recovery in flue gas, a compact reactor due to the reduction of gas volume, the increase in convective heat transfer to boiler tubes and avoidance of air ingress, compared to the oxy-fuel combustion at atmospheric pressure.

The ultimate goal in this research is to evaluate performance of pressurized oxy-fuel combustion and compare with oxy-fuel combustion under atmospheric pressure without the recirculation of flue gas to combustor. To achieve this, case studies at different operating pressure (up to 30 bar) based on 1000 MWe oxy-fuel boiler are performed using a gCCS simulator as a newly released commercial tool. The net plant efficiency, power consumption of auxiliary system such as air separation unit (ASU), pulverizers, fans, pumps, compression and purification unit (CPU) and flue gas heat recovery predicted from case studies as the variation of operating pressure are compared to that of oxy-fuel combustion under atmospheric pressure.

As notable results, by considering power consumption of auxiliary systems and latent heat recovery of moisture content in the flue gas due to pressurization, the net plant efficiency increases by 2.72 % as compared to atmospheric condition (baseline case). In addition, the purity of CO<sub>2</sub> concentration increases from 53.4 % (baseline case) to 94 % in pressurization cases before sequestration. The detail results on power consumption of each auxiliary system, thermal heat recovery and efficiency improvement variation with different operating pressure will be presented in the conference.

#### **Experimental Studies on Slagging and Fouling Characteristics during Zhundong Coal Combustion**

Haidong Ma, Yungang Wang, Qinxin Zhao, Heng Chen, Xi'an Jiaotong University, CHINA

Zhundong coal is rich in reserves and with unique characteristics, but it can not be transported out cosmically for the geographical, economic and transportation conditions. It is seriously hampered the application of Zhundong coal. At present, some power plants in Xinjiang have partially or completely burned Zhundong coal. However, due to severe slagging and serious contamination characteristic of Zhundong coal, the heating surfaces of the boilers in these power plants encounter severe slagging and serious contamination problems and the units can not keep long-term safe operation. Therefore, it is necessary to carry out studies on slagging and fouling characteristics of Zhundong coal.

The slagging and fouling characteristics of Zhundong coal are investigated by a 0.65MW pulverized coal combustion test platform. During the experiment, a new type of Zhundong coal swirl burner was adopted. The slagging and fouling characteristics of Zhundong coal in swirling combustion are mainly deliberated, especially the influence of the coal fineness. Furthermore, the slag samples and ash samples in different combustion regions were characterized by XRD, XRF, SEM, and EDS



analysis. The results showed that the slagging of Zhundong coal has important relationship with coal fineness, and there is an optimum range of coal particle size which can reduce the slagging and also reduce the tail heating surface contamination. Additionally, the slagging mechanism in the furnace is selective deposition of calcium iron while the fouling mechanism in the tail heating surface initiates selective deposition of alkali metal element sodium.

The research achievements have important guiding significance for the design of partially or completely burning Zhundong coal boiler as well as its long-term safe and efficient operation.

**POSTER SESSION  
Clean Coal and Gas to Fuels**

**Oligomerization over Solid Phosphoric Acid: The Limitation of Catalyst for Carbon Chain Growth**

Yaru Yan, Jichang Zhang, William A. Turmel, Jie Feng, Wenying Li, Taiyuan University of Technology, CHINA

The oligomerization of short-chain olefins over solid phosphoric acid catalyst (SPA) has been practiced commercially. However, it's unable to regulate carbon numbers with the limitation of reaction mechanism. In order to realize the possible factors of this limitation coming from, reaction temperature, space velocity, hydration and raw material were adjusted to explore the limiting factor for carbon chain growth in oligomerization. It turned out that interactions between SPA and olefins and the active intermediates (alkyl phosphate) might be formed besides typical Brønsted acid catalyzed carbocation mechanism. The reaction conditions such as temperature, space velocity and hydration aren't the limitation factor for carbon chain growth. It is impossible to produce oligomers heavier than  $C_{12}$  compounds due to the decomposition of the reactive intermediates to  $C_{12}$ .

**The Prediction of Pyrolysis Products Distribution from Coal Molecular Structure**

LAN Yi, Jie Feng, Yuhong Qin, Qun Yi, William A. Turmel, Wenying Li, Taiyuan University of Technology, CHINA

The establishment of coal pyrolysis model is relevant to design the reactor and optimize the parameter of thermochemical process. Most of present kinetic models have considered coal as a lump no matter the detailed structure. In this study a detailed kinetic model of coal pyrolysis based on the coal structural unit was established. The structural unit was consisted of aromatic clusters, side chains (functional group) and bridges. The structure model was built based on the results of proximate and ultimate analysis,  $^{13}C$ -NMR spectra, the average molecular weight per aromatic cluster and the average molecular weight per side chain which were calculated using a correlation from  $^{13}C$ -NMR chemical structural analyses. The initial amount of each functional group is obtained by interpolation from the parameters corresponding to a Van Krevelen diagram, where  $0.047 < O/C < 0.299$ ,  $0.747 < H/C < 0.867$  in atomic ratios. The pyrolysis of coal was described with a kinetic mechanism that light gases were from the relevant functional groups and tars were from the small aromatic clusters. Comparisons between model prediction and experimental data validated this model in the compositions of char, gases and tar. The setting-up kinetic model can quantitatively predict the products distribution of sub-bituminous coal pyrolysis, which accord with the experiment data.

**CFD Modeling of the Local Hydrodynamics in a Pilot-Scale SBCR**

Omar Basha, Badie I. Morsi, University of Pittsburgh; Li Weng, Zhuowu Men, Yonglong Li, Cuiqing Zhang, National Institute of Clean and Low-carbon Energy, CHINA

A computational fluid dynamics (CFD) model was developed to elucidate the internal hydrodynamics in a pilot-scale Slurry Bubble Column Reactors (SBCR). The model accounts for the effects of superficial gas velocity, reactor pressure and temperature as well as catalyst concentration with the aim of quantitatively predicting the internal hydrodynamics in a pilot-scale SBCR (0.29 m ID, 3 m height). The liquid-phase used in the model was a molten Fischer-Tropsch (F-T) reactor wax and the gas-phase was a mixture of He and as  $N_2$  as surrogates for  $H_2$  and  $CO$ , respectively. Our CFD model is based on three-phase, three-dimensional multi-Eulerian formulation. It encompasses mass and momentum conservation equations, bubble size distribution and drag as well as turbulence models. The mass and momentum balances were written for the different chemical species in the gas and liquid phases, taking into account the liquid-side volumetric mass transfer coefficients. The bubble size distribution was predicted using the bubble population balance, and the effect of bubble induced turbulence was considered. Also, the drag and turbulence closure models were validated against experimental results obtained in our pilotscale SBCR operating under F-T conditions. Our CFD model was then used to predict, with high precision, the effect of superficial gas velocity, reactor pressure, temperature and catalyst concentration on the local hydrodynamics, including gas holdup, liquid and

gas velocity profiles, particle size distribution, and mixing intensity, etc. These unique predictions are crucial in understanding the overall hydrodynamic behavior of the pilot-scale reactor operating under F-T synthesis conditions.

**POSTER SESSION  
Carbon Management**

**Synthesis and Characterization of Novel Immobilized Amine Sorbent Pellets Utilizing Fly Ash and Poly (Vinyl Chloride)**

Walter Christopher Wilfong, ORISE Postdoctoral Researcher / DOE/NETL; Yee Soong, McMahan L. Gray, DOE/NETL; Brian W. Kail, AECOM, USA

Pelletized immobilized amine sorbents incorporating different inorganic additives and polymer binders have gained recent attention for capturing  $CO_2$  emissions from coal-fired power plant flue gas. Fly ash (FA) is a promising inorganic binder due to its high availability, low cost, and surface hydroxyl functional groups. High mechanical strength and long term  $CO_2$  capture stability of pellets utilizing the fly ash are necessary for using the pellets in an industrial setting.

Mechanical strength testing and thermogravimetric analysis (TGA) revealed that pellets containing an amine-based polymer binder and metal hydroxide achieved a crush strength of 0.70 MPa and  $CO_2$  capture capacity of 1.10 mmol  $CO_2/g$ -pellet. The objective of our study was to develop a robust immobilized amine sorbent pellet using FA and hydrophobic poly(vinyl chloride) (PVC). PVC could serve as a strong binding agent and potentially inhibit the removal of amine from the pellet by  $H_2O$  during steam regeneration.

Sorbents containing 50 wt% amine/silica were prepared by impregnating granular silica with different solutions containing tetraethylenepentamine (TEPA, T) or polyethylenimine (PEIx,  $x=Mw$ : 423 to 800) in methanol then drying in a rotary evaporator at 80 °C. A 1.0 g amount of the resulting powder sorbents was ground to  $<25 \mu m$  (dynamic light scattering) and mixed with FA ( $<2 \mu m$ ) at different FA/sorbent weight ratios. Following, 0.8-1.2 g of different binder solutions containing PVCx ( $x=Mw$ : 43k, 62k, or 80k) and TEPA were added to the ground FA/sorbent mixtures. The resulting pastes were extruded, dried at 25 or 100 °C for 90 min, and cut into cylindrical pellets (D~1.8 mm, L~5 mm). The pellets were characterized by microscopy, infrared spectroscopy, crush testing, and gas adsorption.  $CO_2$  adsorption of pretreated pellets and powder was performed using TGA with a 14%  $CO_2/N_2$  flow at 55 °C.

$CO_2$  adsorption of the powder sorbents revealed that TEPA/silica (TS) and PEI423/silica (PEI423S) exhibited the highest  $CO_2$  capture capacities, 2.9 mmol  $CO_2/g$ -sorb. Pelletization of these sorbents decreased their  $CO_2$  adsorption kinetics, and also their capture capacities between 34 and 70%, depending upon the PVC Mw and FA content. Normalized TGA weight profiles during adsorption over PEI423S and FA/PEI423S\_10/90 pellets revealed that increasing the PVC Mw slowed the rate of  $CO_2$  adsorption onto the pellets compared to that of PEI423S powder. Increasing the PVC MW also enhanced the mechanical strength of the pellets. The slower adsorption kinetics are attributed to diffusion limitations caused by the presence of long chain PVC molecules between the particles and agglomerated at the pore entrances.

Crush test results for pellets containing the various PVC Mw and different amounts of FA revealed that increasing the Mw from 43k to 80k for FA/PEI423S\_10/90 enhanced the crush strength from 0.77 to 1.08 MPa, resulting from hydrogen bonding of rigid PVC chains to -OH and potentially -NH<sub>2</sub>/-NH groups of FA and sorbent particles. The accompanying decrease in  $CO_2$  capture confirms the inability of  $CO_2$  to diffuse through thick layers of PVC covering the pores and access the amines. Raising the FA content from 10/90 to 30/70 strengthened the pellet (Mw=62k) by a factor of 2.1. These results show that waste fly ash from power plants can be recycled into pelletized sorbents, which are used to mitigate the plant's  $CO_2$  emissions.

**Co Oxidation and Subsequent  $CO_2$  Capture on Alkaline Ceramics**

Brenda Alcántar-Vázquez, Heriberto Pfeiffer, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, MEXICO

The elimination of harmful and toxic exhaust gases still remains as one of major challenges in the area of environmental catalysis. The most common approach for the elimination of these gases is by catalytic conversion in the exhaust. Within the exhaust gases, the carbon monoxide emitted from transportation activities, energy production, agriculture, chemical and steel industry, is considered as an important class of air pollutants. It directly takes part in the formation of the ground-level ozone and increases the greenhouse effect due to transformation to  $CO_2$  and stabilization of  $CH_4$  in the atmosphere. Therefore, various methods have been proposed for CO removal, such a selective diffusion, pressure swing adsorption, selective CO oxidation, and CO methanation. Among them, catalytic oxidation of carbon monoxide remains an intense and important research topic at present. Both noble metals and transition metal oxides have been found to catalyze oxidation reactions. Transition metal oxides are less costly alternatives to the precious metals-based catalysts for carbon monoxide oxidation. In

general, these materials require a support, such as zeolites and Al<sub>2</sub>O<sub>3</sub>, which complicates their preparation and increases the cost. In addition, the catalytic activity is reduced by contamination due carbon deposition on the catalyst surface.

In steam reforming (SR), the H<sub>2</sub>/CO ratio can be varied by manipulating the relative concentrations of CO<sub>2</sub> and O<sub>2</sub> in the feed, which can be achieved via selectivity adsorbing the co-generated CO<sub>2</sub> on a proper and affective sorbent and or by carbon monoxide oxidation. In this regard, some alternatives have been proposed using alkaline ceramics, for example; (i) sorption enhanced hydrogen production (SEHP) and (ii) membrane-based technology (considered as a potential separation and purification technique in the syngas production). Therefore, catalytic oxidation of CO in H<sub>2</sub>-rich gas is considered a promising method and the most cost-effective approach for eliminating CO from reformed fuels. In this context, some alkaline ceramics have been proposed as bifunctional materials; CO catalysts and subsequently as CO<sub>2</sub> sorbents. In the field of CO<sub>2</sub> capture, several alkaline ceramics have been proposed as possible CO<sub>2</sub> chemisorbents. Sodium and lithium alkaline ceramics have been extensively studied, because they exhibit good CO<sub>2</sub> capture properties, such as, CO<sub>2</sub> chemisorption temperature range, good cyclability and good kinetic properties. Moreover, the use of these materials may be linked to CO<sub>2</sub> capture and subsequent conversion to added value products. Therefore, in the current work, some alkaline ceramics as Na<sub>2</sub>ZrO<sub>3</sub>, NaCoO<sub>2</sub>, Li<sub>2</sub>CuO<sub>2</sub>, were studied as bifunctional materials.

The CO oxidation and subsequent CO<sub>2</sub> capture analyses were performed in a tubular continuous-flow fixed bed reactor at ambient pressure and temperatures between 30 and 850 °C. The feed stream contained 5 vol% CO and 5 vol% O<sub>2</sub> in N<sub>2</sub> as balance. The total flow rate was 100 cm<sup>3</sup>/min. The gas products were analyzed with a gas chromatograph with a Carboxen-100 column and an FTIR spectrometer connected to a ZnS gas flow cell. After that, isothermal CO oxidation analyses were performed at temperatures between 300 and 700 °C and the catalysts were recharacterized. Finally, the CO<sub>2</sub> capture were evaluated thermogravimetrically, the samples were heated to the desired temperature into a N<sub>2</sub> flow and then the same CO:O<sub>2</sub> gas mixture was used.

The results confirmed that CO can be oxidized and chemically trapped on alkaline ceramics in different temperature ranges. Finally, it must be pointed out that these materials may be a possible option for the development of gas-separation systems, where CO must be extracted at high temperatures.

#### POSTER SESSION Coal Science

##### **An Experimental Research on Desulfurization of Fine Coal of China Using an Enhanced Centrifugal Gravity Separator**

Tao Youjun, Song Ao, Man Zhongpei, Zhu Xiangnan, China University of Mining & Technology, CHINA

Desulphurization experimental study under the enhanced gravity force field has been described for - 0.5mm fine particle of high sulfur coal from Nan-tong in China. The sulfur component of Nan-tong fine coal and its distribution were analyzed. The pyrite inlay characteristics and desulphurization feasibility of Nan-tong fine coal by gravity separation were investigated by analyzing its petrographic constituents. The separation behavior of fine coal and desulphurization efficiency of different size fractions coals by the Falcon centrifugal separator were studied, the results indicate that the Falcon centrifugal separator can separate efficiently +0.045 mm coal. A poor separation efficiency for -0.045 mm fine coal was obtained because of ultra fine coal overflow with water current during the separation process.

##### **A New Map of Metallurgical Coal of the United States with New Geochemical, Rheological, and Petrological Data**

Michael H. Trippi, Leslie F. Ruppert, U.S. Geological Survey; Cortland F. Eble, Kentucky Geological Survey; James C. Hower, University of Kentucky Center for Applied Energy Research, USA

The U.S. Geological Survey (USGS) is compiling Geographic Information System (GIS) data on metallurgical coal occurrences (including currently producing mines and those with historical production) in the U.S. These data will be available as GIS data files for internet download, and may be used in a GIS for a variety of energy resource studies. These files were made by digitizing maps previously published by state and federal agencies, companies, and independent researchers. A table will be included in the report listing names of coal deposits, coal rank, presence or absence of coal mines and activity of those mines, coal-bearing stratigraphic units (groups and formations) ages of these stratigraphic units and historical information about the coal. GIS data will be saved in shapefile format, with metadata files included describing all GIS processing.

As a supplement to the GIS Data, new metallurgical coal samples from Alabama, Kentucky, Oklahoma (in cooperation the Oklahoma Geological Survey), and Pennsylvania (in cooperation with Rosebud Mining Company) were collected and analyzed for organic petrography; proximate and ultimate analyses; sulfur forms; ash-fusion temperatures; calorific value; free swelling indices; major-, minor-, and trace-

element abundances; Arnu-Audibert dilatation; and Geiseler plastometer analyses. The new analyses will be included with historic data into an accompanying chemical database.

The United States has produced metallurgical, or coking, coal for nearly 200 years. In 2013, the U.S. exported a total of 65,678,865 short tons of metallurgical coal to 37 countries around the world (Energy Information Administration, 2015). In 2012, the U.S. ranked second behind Australia in coking coal exports, and third behind China and Australia in coking coal production (World Coal Association, 2014).

Most of the coking coal in the U.S. occurs in the Appalachian basin, especially the states of Alabama, Kentucky, Pennsylvania, West Virginia, and Virginia. Ohio and Tennessee have, and continue to produce, metallurgical-grade coal. Illinois coals have also been important for coking in the past, but currently play a lesser role. Indiana coals may be useful for Pulverized Coal Injection (PCI) to enhance coke production in steel mills, but are not expected to be used directly as coking coals (Valia and Mastalerz, 2004). Western U.S. coals from Arkansas, Oklahoma, New Mexico, Colorado, Utah, Wyoming, Montana, Washington, and Alaska have all been used in the past for coking, but only Arkansas coals are currently mined for coking purposes. Western coals range in age from Pennsylvanian in Arkansas and Oklahoma, to Early Cretaceous through Eocene in New Mexico, Colorado, Utah, Wyoming, Montana, Washington, and Alaska.

These GIS data of the coking coal resources in the U.S. and the associated chemical and production data included in this product can provide researchers with a useful source of spatially-defined information for energy, economic, and other analyses.

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#### **Study the Effect of Pretreatment and Cosolvent on Coal Swelling Ratio**

Xiaohua Wang, Fuyao Zhang, Donghua Wang, Yonglin Chang, Xi'an University of Science and Technology, CHINA

Methanol used as swelling solvent, volume method is used to calculate the swelling ratio, the effect of pretreatment and cosolvent on Dongsheng coal and Dongsheng coal macerals was studied. The results showed that oxidation pretreatment of coal has greater effect on swelling ratio increase, oxidation/acid treatment and reduction/alkali treatment both have synergy. Cosolvent help to increase the swelling ratio. When cosolvent content is less than 0.25, the increase extent of swelling ratio is larger, when cosolvent content more than 0.25, the swelling ratio increase extent is smaller. Vitrinite is easier swelling than inertinite. Swelling ratio decreased with the degree of coalification increased.