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PITTSBURGH COAL CONFERENCE

**ABSTRACTS BOOKLET**

COAL - ENERGY, ENVIRONMENT AND  
SUSTAINABLE DEVELOPMENT



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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 Twenty-Ninth Annual International Pittsburgh Coal Conference, we wish to express our sincere appreciation to Ms. Heidi M. Aufdenkamp for her dedication and professionalism; and Dr. Laurent Sehabiague and Mr. Gun Kositchaiwat for their invaluable assistance in preparing this Abstracts Booklet.

Thank you,

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

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

## TABLE OF CONTENTS

<b>Oral Sessions</b>	<b>Page</b>	<b>Oral Sessions</b>	<b>Page</b>
1: Clean Coal Demonstration and Commercial Projects: Financial .....	1	41: Carbon Management: CO <sub>2</sub> Storage - 1 (Coal) .....	34
2: Sustainability and Environment: General - 1 .....	1	42: Coal Science: General - 4 .....	35
3: Gasification: General - 1 .....	2	43: Clean Coal Demonstration and Commercial Projects: Technical - 5 (Industrial CCUS) .....	35
4: Combustion: Chemical Looping and Oxy-Combustion - 1 .....	2	44: Coal-Derived Products: General - 6 .....	36
5: Carbon Management: Carbon Management Policy and Legislation/Regulation .....	3	45: Gasification: Modeling - 2 .....	37
6: Coal Mining and Coal Gas: General - 1 .....	4	46: Gasification: Low Rank Coal .....	38
7: Clean Coal Demonstration and Commercial Projects: Financial Risk Management .....	6	47: Carbon Management: CO <sub>2</sub> Storage - 2 (Coal) .....	39
8: Sustainability and Environment: General - 2 .....	6	48: Coal Science: General - 5 .....	41
9: Gasification: General - 2 .....	7	49: Clean Coal Demonstration and Commercial Projects: Technical - 6 (Combustion & Post-Combustion CO <sub>2</sub> Capture) .....	42
10: Combustion: Chemical Looping and Oxy-Combustion - 2 .....	8	50: Coal-Derived Products: General - 7 .....	42
11: Carbon Management: CO <sub>2</sub> Capture - 1 .....	9	51: Gasification: Modeling - 3 .....	43
12: Coal Mining and Coal Gas: General - 2 .....	10	52: Carbon Management: CO <sub>2</sub> Use and Methane Abatement .....	44
13: Clean Coal Demonstration and Commercial Projects: Path Forward for CCUS .....	10	53: Carbon Management: CO <sub>2</sub> Storage - 3 .....	45
14: Gasification: General - 3 .....	10	54: Coal Science: General - 6 .....	47
15: Gasification: Gas Cleaning .....	11		
16: Combustion: Chemical Looping and Oxy-Combustion - 3 .....	13		
17: Carbon Management: CO <sub>2</sub> Capture - 2 .....	14		
18: Coal-Derived Products: General - 1 .....	15		
19: Clean Coal Demonstration and Commercial Projects: Technical - 1 (Commercial Projects) .....	16		
20: Coal-Derived Products: General - 2 .....	17		
21: Gasification: Modeling - 1 .....	18		
22: Combustion: Ash and Combustion - 1 .....	19		
23: Carbon Management: CO <sub>2</sub> Capture - 3 .....	20		
24: Coal Science: General - 1 .....	21		
25: Clean Coal Demonstration and Commercial Projects: Technical - 2 (Polygeneration) .....	21		
26: Coal-Derived Products: General - 3 .....	22		
27: Gasification: General - 4 .....	23		
28: Combustion: Ash and Combustion - 2 .....	23		
29: Carbon Management: CO <sub>2</sub> Capture - 4 .....	24		
30: Coal Science: General - 2 .....	25		
31: Clean Coal Demonstration and Commercial Projects: Technical - 3 (CCUS) .....	26		
32: Coal-Derived Products: General - 4 .....	27		
33: Gasification: Coal and Biomass - 1 .....	28		
34: Combustion: Ash and Combustion - 3 .....	29		
35: Carbon Management: CO <sub>2</sub> Capture - 5 .....	29		
36: Coal Science: General - 3 .....	30		
37: Clean Coal Demonstration and Commercial Projects: Technical - 4 (Polygeneration) .....	31		
38: Coal-Derived Products: General - 5 .....	32		
39: Gasification: Coal and Biomass - 2 .....	32		
40: Combustion: Mainly Mercury .....	33		
		<b>Poster Sessions</b>	<b>Page</b>
		1: Combustion .....	48
		2: Gasification .....	48
		3: Sustainability and Environment .....	49
		4: Carbon Management .....	50
		5: Coal-Derived Products .....	52
		6: Coal Science .....	53

## SESSION 1

### Clean Coal Demonstration and Commercial Projects: Financial

#### Future Opportunities for Clean Energy Power Projects

Tom Fogarty, Co-author of “Investing in The Renewable Power Market”, USA

One investment banker likes to say “When times are good I take my boys and girls out of the restructuring group and place them in mergers and acquisitions. When times are bad I do the reverse.” Skills used to evaluate healthy and distressed power deals will be discussed, with a focus on coal-fired power plant financings.

Material will be referenced from Tom’s book entitled “Investing in The Renewable Power Market” by Tom Fogarty and Robert Lamb (Wiley 2012).

#### The Financial Side of Combustion: How Do Coal and Natural Gas Compete on the Margin as Fuels for Electricity?

John M. Hynes, Excidian, LLC, USA

This session will address the direct competition between natural gas and coal for power generation based on fuel cost and heat rate. This will enlighten the audience as to just how high natural gas prices could go before a combined cycle power plant could no longer compete on the margin with a coal plant. Likewise the audience will also be able to see how low coal prices would have to go before a combined cycle power plant could no longer compete on the margin with a coal plant. This should lead to an interesting, audience-involved, discussion on the realistic range of coal and natural gas prices that the market will see over the next five to ten years as well as the realistic heat rates that one would expect to see from coal and combined cycle plants over the same time period.

#### A View From Wall Street on U.S. Debt Financings

Hans L. Christensen, MJX Asset Management LLC, USA

Over the next two decades, hundreds of billions of dollars will be invested in the US Power sector to support both replacement and expansion of electricity in this country. A significant portion of this capital will be provided by debt investors. Mainstream debt investors are examining the opportunities to invest in this sector, just as it does each dynamic sector such as healthcare, oil & gas or chemicals.

Investors are measured against objective investment hurdles with constraints to minimize risk of the third-party investor funds they manage. I will describe the types of analysis debt investors use to measure industry, issuer and debt instrument risks, how new ideas and debt structures can reward both issuer and investor and broadly discuss the regulatory issues that can make debt investors reluctant and demanding of yield.

#### Project Financing Insights – Texas Clean Energy Project

Jeffrey D. Brown, Summit Power Group, USA

The Texas Clean Energy Project (TCEP) is a carbon capture, utilization and storage (CCUS) commercial demonstration facility featuring integrated gasification combined cycle (IGCC) poly-generation. As a first-of-a-kind commercial demonstration, the project presents real and varied challenges with respect to achieving project financing in today’s economic conditions. This 2012 Pittsburgh Coal Conference presentation will provide a summary discussion with respect to project financing of energy projects in today’s economy based on the experience with TCEP.

## SESSION 2

### Sustainability and Environment: General – 1

#### Chemistry Modeling of Dry Sorbent Injection for Acid Gas Removal

Guisu Liu, Liming Shi, Lewis Benson, Nalco Mobotec, USA

Dry sorbent injection (DSI) is often used to reduce acid gases such as SO<sub>3</sub>, HCl, SO<sub>2</sub>, and HF from combustion flue gas in boilers. Sorbents for injection are usually calcium- or sodium- based, such as hydrated lime and trona. Multiple reactions between acid gases and hydrated lime were evaluated thermodynamically. The reaction preference by the sorbent is however partially explained. Its removal efficiency is directly affected by sorbent properties and the extent of sorbent mixing with flue gas. Computational fluid dynamic (CFD) modeling can be used to optimize sorbent dispersion in a flue gas duct. However, chemistry between acid gas species and sorbent is also critical to designing an injection system with high reduction efficiency. In this paper, a SO<sub>3</sub>/sorbent chemical reaction sub-model is developed and validated, which is then

coupled with the CFD model for industrial applications. Both mass transfer and chemical reaction between sorbent and SO<sub>3</sub> are included in the sub-model. This enhanced CFD based chemistry model can predict sorbent injection rate and SO<sub>3</sub> profile in the duct. Sensitivity analysis has been conducted to evaluate the effect of particle size, porosity, surface area, inlet SO<sub>3</sub> concentration, and residence time on SO<sub>3</sub> removal. The model has been applied to an industrial-sized flue gas duct, where injection designs between air heater and electrostatic precipitator were modeled and optimized by varying the number of lances, injection depth of lance, and vanes in the duct. The SO<sub>3</sub> removal efficiency for each injection design is predicted.

#### Ferromagnetic Properties of Pyrite From the Southern Brazil Coal Mining Industry at Different Heating Temperatures

Michael Peterson, Márcio Antônio Fiori, Adilson Oliveira da Silva, Universidade do Extremo Sul Catarinense; Regina de Fátima Peralta Muniz Moreira, Paula Hahn Concer, Engenharia Química – UFSC; Cíntia Máximo Cardoso, Curso de engenharia química – UNESC, BRAZIL

The Southern of Santa Catarina State is the leading coal producer at Brazil. In The region of Criciúma city are the more important coal mine industries representing a great amount of the Brazil coal production. Years of coal mining were extremely detrimental for the environment at this region. Acid Mine drainage (AMD) is still a problem and the coal mine industries are doing treatment systems for this dangerous effluent. The AMD behavior in the nature is well known and at the southern Santa Catarina region are a lot of problems with it; the pyrite oxidation from the coal mining produces 1m<sup>3</sup> of AMD for each ton of coal mined (ROM). The LMPP (Materials laboratory of Universidade do Extremo Sul Catarinense) had developed new ways for the pyrite use as a material. This study was done with a sample of pyrite from the coal mining industry. The characterization took place with chemical and mineralogical analysis (XRF and XRD) and the determination of magnetic properties of the “In Natura” samples and the samples that were heated at several temperatures in a reactor under controlled atmosphere (with N<sub>2</sub> – 50 cm<sup>3</sup>/min). The objective of the thermal treatment was the production of a ferromagnetic phase from the In Natura pyrite sample, the reaction studied was the loss of sulfur under controlled atmosphere conditions at a reactor. The results showed temperatures around 550°C for the first ferromagnetic properties for this reaction. The LMPP Laboratory is now studying the possibility to use this material in other industries at the region. Acknowledgments: Carbonífera Criciúma, Centro de Tecnologia Mineral – CETEM, FINEP.

#### Co-Briquetting of Coal and Biomass

Darrell Taulbee, Robert Hodgen, Nicholas Aden, University of Kentucky Center for Applied Energy Research, USA

The co-briquetting of coal and biomass has been under evaluation at the University of Kentucky Center for Applied Energy Research (CAER) for the past decade. Early studies focused on the co-briquetting of bituminous-coal fines with sawdust but have since expanded to include sub-bituminous and lignite coals as well as biomass from a variety of sources including agricultural wastes, energy crops, and bio-char.

Co-briquetting biomass with fine coal provides an avenue for moving biomass into the energy markets at a meaningful scale using the infrastructure now used to transport, store, and utilize coal. It can also serve to convert low-market-value coal into a lower-emission premium fuel that is suitable for the steam or stoker markets or serve as a single-source feedstock for gasification and/or liquid fuels production.

Selected results for two prior co-briquetting projects are presented along with a description and initial results from three current projects.

#### Evaluation of Methods Used to Quantify the Durability of Coal-Biomass Briquettes

Erich Dohm, Gerald Luttrell, Robert Bratton, Nino Ripepi, Virginia Polytechnic Institute and State University; Darrell Taulbee, University of Kentucky, Center for Applied Energy Research, USA

The emergence of the coal-biomass briquette industry is currently limited by the absence of standard characterization methods to quantify briquette durability. In light of this issue, the following paper identifies and evaluates methods used to quantify the durability of coal-biomass briquettes to determine ideal testing configurations. Durability properties investigated include compressive strength, impact resistance and attrition resistance. The compressive strength test method exhibited poor precision without the use of an automated test stand; however, a simple modification to the manual test stand configuration reduced the standard deviation of results by more than 75% and produced a normal distribution of data from 50 briquette measurements. The briquette attrition resistance test method was found to be well designed. The ideal configuration requires tumbling 20 briquettes in a standard sized drum at a rotational speed of 40 rpm for a period of 5 minutes. Finally, a modified ASTM drop-shatter test that involves dropping 20 briquettes twice from a height of 6 ft was confirmed to be

well suited for briquette evaluations. To ensure statistically significant results and alignment with other ASTM procedures, recommendations are made for repetition of procedures and reporting of results.

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

**ITM Oxygen Technology: Scale-Up Toward Clean Energy Applications**

John M. Repasky, Lori L. Anderson, VanEric E. Stein, Phillip A. Armstrong, Edward P. (Ted) Foster, Air Products and Chemicals, Inc., USA

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

The team has successfully demonstrated expected performance of commercial-scale modules in a prototype facility that produces up to 5 tons-per-day (TPD) of oxygen. Continued operation of this unit has verified thermal and pressure cycle performance, and tested a number of component designs and operating scenarios for next phase scale-up. Next phase pilot unit is in construction, and major operation is planned in 2013. This Intermediate Scale Test Unit (ISTU) is designed to produce up to 100 TPD of oxygen integrated with turbo-machinery and co-production of power. Data from the 100 TPD unit will provide the design basis for a much larger plant that could produce 2000 TPD. In parallel, work has also begun to expand ceramic fabrication capacity to support these developments.

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

**Dry Solids Pump Development and Commercial-Scale Testing**

Timothy W. Saunders, Scott McVey, Craig Tang, Alex Olaguez, Pratt & Whitney Rocketdyne, USA

A reliable, cost-effective feeding system is one of the largest impediments to lowering gasification process costs and commercial acceptance of the technology. Pratt & Whitney Rocketdyne (PWR) has a cooperative agreement with the U.S. Department of Energy to design and develop a Dry Solids Pump (DSP) for use in the gasification industry. The objective of this program is to develop a machine with the capability of injecting coal or other dry solid fuel continuously, and at commercial scale, into gas pressures up to 1,200 PSI or 83 Bar. This pressure level is the operating target for the PWR Compact Gasifier. The gasifier has been successfully tested at the pilot plant scale.

The program has advanced design and development of a novel and patented feeding concept, testing of key pump components at near full-scale level and design and manufacture of a prototype. This full commercial-scale prototype has been manufactured and installed at the Energy and Environmental Research Center in Grand Forks North Dakota. Testing of the first prototype DSP is due to begin in March 2012 and should achieve significant operating hours by the summer of 2012. This paper will summarize the pump design and development; provide an overview of the data collected from the start of the test program to the conference date, and provide status of commercialization of the technology.

**Material Issues in Slagging Gasifiers Caused by Carbon Feedstock**

James P. Bennett, David E. Alman, Kyei-Sing Kwong, DOE/NETL, USA

Gasifiers are used to process carbon feedstock such as coal, petcoke, or mixtures of them at elevated temperature, high pressure, and in a reducing atmosphere (low oxygen partial pressure); forming CO and H<sub>2</sub> – also called synthesis gas or syngas. Syngas is used in power generation or as feedstock raw material for chemical production.

By-products of the gasification process include: 1) unreacted carbon, 2) hot gases such as CO<sub>2</sub> and H<sub>2</sub>S, and 3) slag formed from mineral impurities or organic metallic compounds in the carbon feedstock that have liquefied during gasification. The first by-product, unreacted carbon of the gasification process, is called char. It is carbon feedstock that has lost its volatile components and has not interacted with hydrogen/oxygen in the gasifier to form syngas. Essentially, it is bloated carbon that may have some mineral matter associated with it. The quantity of this material impacts process efficiency, is recovered at some sites, and can interfere with other components

within the gasification chamber or in the gasification process, such as temperature sensing devices.

The second by-product, hot gases, can impact gasifier efficiency by requiring high containment vessel temperatures to prevent dew point condensation of gas phases on the steel gasification vessel; can attack sensors used to monitor gasifier temperature; or can cause films to build up on syngas coolers. Films on syngas coolers contribute to fouling, which decreases heat exchange efficiency.

The third listed by-product, slag, is one of the leading causes of gasifier shutdown and premature component failure. Molten slag particles from the carbon feedstock contact the gasifier sidewall to form a thick molten film that flows down the refractory liner - a film that flows into a chamber at the base of a gasifier, solidifies, and is removed from the process. This liquid slag interacts with and dissolves/corrodes the gasifier lining causing one type of failure, can penetrate the porous refractory lining leading to structural spalling, or can cause particulate erosion and abrasive wear of the refractory lining. A small fraction of the solid particles are also carried in the process gas to the syngas coolers where they can coat components and reduce heat transfer, a process called fouling.

A discussion on how all three by-products of gasification currently impact material wear or process efficiency during gasification and a discussion on some of the NELT research in these areas will be presented. Reducing material interactions is critical to improving gasification process efficiency and RAM (reliability, availability, and maintainability).

**Testing Optical Gasifier Sensor at Wabash River Gasifier**

Serguei Zelepouga, Vitaly Gnatenko, Gas Technology Institute; Alexei Saveliev, North Carolina State University, USA

The objective of this research work is the development of reliable and practical means to optically monitor coal gasifier flames. This sensor technology is expected to allow better control of coal gasification process and predict burner wear and need for replacement. The paper presents the results of GTI sensor testing performed at Wabash River Coal Gasification Repowering Plant located in West Terre Haute, IN.

**PWR Compact Gasifier Development Status**

Steven Fusselman, Alan Darby, Pratt & Whitney Rocketdyne, USA

Pratt & Whitney Rocketdyne (PWR) is developing a compact gasifier technology with the potential to offer significant performance, availability and economic advantages relative to existing technologies. A very successful initial test campaign was completed on the 18 tons per day (TPD) pilot plant gasifier, with testing on four different feedstocks (ranging from sub-bituminous to petcoke) accumulating over 750 hours hot fire testing and characterizing 53 individual operating points. Test results will be reviewed, along with their significance relative to technical feasibility, technology readiness for scale-up to 400 TPD gasifier design, and anticipated economic benefits of the technology at a commercial scale.

**SESSION 4**  
**Combustion: Chemical Looping and Oxy-Combustion – 1**

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

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

Under the United States (U.S.) and China Clean Energy Research Center (CERC) collaboration initiative aimed to accelerate the development of clean energy technologies, Babcock & Wilcox (B&W) Power Generation Group, Inc. and Huazhong University of Science and Technology (HUST) are jointly investigating the fundamental reaction kinetics of coals from both countries under oxy-coal combustion conditions. Oxy-coal combustion is a viable technology for carbon dioxide (CO<sub>2</sub>) emissions control from coal-fired power plants. It produces a concentrated CO<sub>2</sub> stream by way of burning coal with oxygen instead of air. Since combustion of fuel with pure oxygen results in very high flame temperatures, flue gas recycling is applied to control the temperature and provide adequate gas flow over the heat absorption surfaces. "Cold-recycle" and "warm-recycle" characterized by different moisture levels depending on the location of the recycled flue gas (RFG) stream extraction are two common modes of oxy-combustion that could have different combustion characteristics. Our previous studies have shown that char-CO<sub>2</sub> and -H<sub>2</sub>O gasification reactions can play an important role in char burnout during oxy-coal combustion. The relative importance of these reactions is both coal rank and flame condition dependent. In this paper, we report new char burnout experiments with US and Chinese coals of different ranks under simulated oxy- and air-firing conditions. Char samples at different residence times are collected from the reaction zone and their extents of burnout are determined by the ash tracer technique. In some tests, optical fiber based two-color pyrometer is applied to simultaneously acquire single particle surface

temperature and flow field velocity data. Using an optimization tool, kinetic rate parameters for char gasification and burnout are derived from the experimental data.

### **3D CFD Simulation of Chemical Looping Combustion with Interconnected Air and Fuel Reactors**

Yong Liu, Michael J. Gallagher, Jr., Stephen P. Carpenter, DOE/NETL/URS; E. David Huckaby, DOE/NETL, USA

Chemical looping combustion (CLC) is a promising method for energy production from fossil fuels with low cost CO<sub>2</sub> capture. The configuration consists of two interconnected fluidized bed reactors with circulation of a solid oxygen carrier between them. The air reactor is a fast fluidized bed connected to a riser, while the fuel reactor is a bubbling bed with an L-valve located at the bottom to control solids flow between the reactors. The configuration studied here is based on the design of a nominal 20kWth equivalent system which is being installed at NETL. Simulations using ANSYS-Fluent were performed to study the flow and the reaction behavior during consecutive oxidation and reduction cycles. User defined functions were written to simulate the simultaneous heterogeneous oxidation reaction in the air reactor and the reduction in the fuel reactor. Parameters such as the oxygen carrier particle size, initial bed height in the air or fuel reactor, and fluidization gas flow rates at the bottom of either fuel or air reactor were varied to study the effects on the performance of the whole interconnected system. The distributions of the gaseous components such as N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> were analyzed.

### **Reducible Supports for Oxygen Carriers in Chemical Looping Combustion**

Saurabh Bhavsar, Götz Vesper, DOE/NETL/University of Pittsburgh, USA

Chemical looping combustion (CLC) is an emerging technology for clean energy-production from fossil and renewable fuels. In CLC, an oxygen carrier (typically a metal) is first oxidized with air. The hot metal oxide is then reduced in contact with a fuel in a second reactor, thus combusting the fuel. Finally, the reduced metal is transferred back to the oxidizer, closing the materials "loop". In this way, CLC produces sequestration-ready CO<sub>2</sub>-streams without expensive air separation and hence without significant energy penalty. Combined with sequestration, CLC thus allows high-efficiency, CO<sub>2</sub> emissions-free combustion of fossil fuels, or combustion processes with negative CO<sub>2</sub>-footprint from biomass-derived fuels.

To-date, a wide range of oxygen carriers has been investigated with the aim of maximizing carrier and fuel conversion while making the carriers more thermally and mechanically stable to obtain sustained performance at the demanding operating conditions of CLC. Ni, Fe, Cu, and Co have emerged as the most promising metals from these studies. However, these investigations have almost exclusively focused on the use of non-reducible supports (such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>).

Here, we report a comparative evaluation of Ni-based oxygen carriers supported on reducible (CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) and non-reducible supports (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) with the aim of identifying possible contributions from the support itself to the oxygen carrying capacity of the carrier, as well as synergistic effects between metal and support. Ni-based carriers (40 wt% Ni) were synthesized by a simple incipient wetness technique on synthesized and commercial supports. These carrier samples were characterized by TEM, XRD, BET, and EDX. The reducible supports CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> were initially tested in thermogravimetric experiments (TGA) at 800°C for their inherent activity in CLC with H<sub>2</sub> as a model fuel, and this activity was then compared to the activity after Ni deposition. Although CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> themselves do not contribute significantly to the overall oxygen carrying capacity, a strong synergetic effect between the metal and the support was observed, resulting in complete utilization of the oxygen carrying potential of the metal on reducible supports vs incomplete utilization for Ni on silica and alumina supports (~91% and ~81% respectively) at identical conditions.

Ni-CeO<sub>2</sub> and Ni-Al<sub>2</sub>O<sub>3</sub> were then down selected based on reducibility, thermal stability, and cost, and further evaluated with CH<sub>4</sub> as fuel in TGA and fixed-bed studies at 800°C. In these TGA studies, Ni-CeO<sub>2</sub> again showed complete carrier utilization vs only ~77% utilization for Ni-Al<sub>2</sub>O<sub>3</sub> (~77% carrier conversion). Post-use characterization of carriers by TEM, XRD, and BET does not reveal significant sintering or formation of mixed oxide phases with the support for the two carriers. Further evaluation in fixed-bed reactor experiments confirmed the superior performance of Ni-CeO<sub>2</sub> not only due to complete carrier utilization, but also based on >90% fuel conversion and a significantly increased duration of the reduction half-cycle. Our results hence identify Ni-CeO<sub>2</sub> as a promising candidate for chemical looping combustion, and suggest that reducible supports can strongly enhance the operation range of metal-based oxygen carriers through synergetic effects between the metal and the support. Extension of the studies onto Fe- and NiFe-based carriers is currently under way.

### **CFD Study of Oxy Coal Combustion in a 100kW Downfired Furnace**

Albio Gutierrez, Alejandro Posada, Ismail Celik, West Virginia University, USA

This paper presents the results of a computational fluid dynamics (CFD) study for oxy coal combustion processes of pulverized lignite coal under air and O<sub>2</sub>/CO<sub>2</sub> oxidizing atmospheres. Simulations were performed using a commercial CFD software, Ansys-Fluent. The simulation is based on the experimental work performed in the 100kW

experimental furnace facility located at Chalmers University of Technology. This furnace is down fired with a cylindrical refractory lined reactor which has a 2.4m inner height and 0.8m of internal diameter. The burner consist of a central injection of pulverized coal feed by a carrier gas and primary and secondary swirl registers with fin angles of 45 and 15 degrees respectively.

The simulation was performed using the Standard k-ε model with standard wall functions for turbulence. Radiation was modeled using Discrete Ordinates model. Devolatilization and char burnout of pulverized coal particles were modeled using the Single Rate Devolatilization model and Kinetics/Diffusion Limited model respectively. Turbulence-chemistry interaction was modeled using the Eddy Break Up model. Walls were kept at constant temperature with the values reported in the experimental measurements and using a reflecting particle condition to account for wall- particle interaction. A grid independence study was performed. The values of parameters for char combustion and turbulence model were varied to investigate their influence on combustion. Results from simulations were compared against experimental results and previous CFD simulations. Preliminary results show that temperatures obtained from current study agree fairly well with data reported in experiments and previous simulations. However, differences in the temperatures and oxygen concentration along the centerline were detected. This maybe caused mainly by a lack of a well defined burner recirculation zone.

### **Syngas Chemical Looping Process: Design and Continuous Performance of 25 kW<sub>th</sub> Sub-Pilot Scale System for Gaseous Fuel Conversion and 99.99% Purity Hydrogen Generation**

Mandar V. Kathe, Andrew Tong, Deepak Sridhar, Liang Zeng, Rae Kim, Elena Chung, Liang-Shih Fan, The Ohio State University, USA

Chemical looping technologies are projected to have a higher cost-reduction benefit for power production from fossil fuels like coal in a carbon-constrained scenario as compared to conventional and other emerging technologies. Chemical looping processes (CLP) are envisaged as scalable and efficient next-generation clean-energy technologies validated by the numerous demonstration studies on a sub-pilot and pilot scale world-wide, with commercialization expected by 2020.

CLP provides oxygen for fuel combustion indirectly through a solid metal-oxide or metal-sulfide. This reaction scheme produces a concentrated sequesterable CO<sub>2</sub> stream and reduces the costs associated with the corresponding downstream purification steps. The Ohio State University (OSU) has developed multiple iron-based chemical looping technologies for processing gaseous and solid fuels like coal and natural gas. The iron-based CLP developed at The OSU utilizes a unique moving bed reducer reactor that provides for higher oxygen-carrying capacity utilization of the iron-based oxygen carrier. The enhanced oxygen carrying capacity utilization provides for the advantage of being product flexible. The OSU CLP systems can be adapted for high-purity H<sub>2</sub> production, retrofit to a Fischer-Tropsch process for liquid fuels production, and combustion operation for electricity generation. Amongst the novel CLP processes developed at OSU, the Syngas Chemical Looping (SCL) process is primarily designed to utilize any carbonaceous gaseous fuel like syngas, natural gas and methane for H<sub>2</sub> and/or electricity production with 100% in-situ CO<sub>2</sub> capture. The process has been demonstrated on a 25 kW<sub>th</sub> scale of operation for over 300 hours of integrated operation for complete syngas conversion with carbon capture and H<sub>2</sub> production. This operational result validates the chemistry of the SCL process and is one step towards the process commercialization.

The design, construction and operation of the SCL sub-pilot unit will be the focus of this presentation. The design philosophy behind the construction of the 25 kW<sub>th</sub> SCL sub-pilot unit will be elucidated initially, with key emphasis on influence of the mode of operation. Multiple parametric operation studies for various gaseous fuel flow rates with different solids conversion profiles and system performance with regards to fuel conversions and pure H<sub>2</sub> production in the oxidizer integrated system will also be presented. The experimental data obtained from the sub-pilot unit operations is compared with the ASPEN simulation and theoretical thermodynamic calculation results. Finally the scale-up design and construction of the 250 kW<sub>th</sub> pilot-scale unit will be discussed.

## **SESSION 5 Carbon Management: Carbon Management Policy and Legislation/Regulation**

### **Carbon Capture and Sequestration (CCS) Technology**

Frank Princiotta, U.S. Environmental Protection Agency, USA

Recent developments have highlighted the importance of reliable and affordable Carbon Capture and Sequestration (CCS) technologies. The planet continues to warm, worldwide CO<sub>2</sub> emissions are growing at an accelerated rate (5.9% in 2010) and recent analysis based on Recent Royal Society analysis, the planet could experience 4 °C warming as early as 2065. with highly undesirable consequences. Also, in light of the Fukushima disaster, nuclear power appears to be a less viable mitigation option than it

was before the disaster. A description of key capture technologies will be discussed as well as a summary of worldwide research, development & demonstration activities. Since coal will continue to be a major power generation source, and the single largest source of CO<sub>2</sub> emissions, it is desirable that multiple coal demonstrations be conducted consistent with the wide range of potential applications and technologies: coal type, new versus retrofit, storage via EOR versus deep saline reservoirs and pre-combustion, post combustion and oxy-fuel technologies. Also, given the likelihood that natural gas will play an increasingly important role for power generation in the near future, natural gas CCS demonstrations should be considered as well. For at least some of the demos, pipeline distances and quantities injected should be large enough to shed light on the communication programs needed to work with local jurisdictions and citizens to eliminate the potential for NUMBY (Not Under My Back Yard) resistance to these projects. The objective of the research component of such a program would be to support the demos & continually enhance efficacy, reduce costs, increase energy efficiency and understand the life-cycle environmental implications of current and next generation CCS technologies. An important example of such research would be to accelerate development of more energy efficient air separation technologies which could substantially reduce the cost of both oxy-fuel and gasification technologies.

### **Development of the First Internationally Accepted Standard for Geologic Storage of Carbon Dioxide: – Update from the Public Comment Period & Initiation of the ISO Process**

Steven M. Carpenter, Advanced Resources International, USA

The Carbon Capture & Sequestration (Storage) (CCS) marketplace is lacking standardization and therefore the ability to allow CCS projects to be considered as Clean Development Mechanism (CDM). There is an international push to change this and recognize CCS. This recognition will allow for standardized and ultimately address a much needed CDM option and international standardization.

The international effort between the United States and Canada, funded by and the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide (IPAC-CO<sub>2</sub> Research Inc.), and managed by CSA Standards, have partnered to develop the first internationally recognized Standard for the geologic storage of carbon dioxide (GSC). This Committee, with process and editorial support from CSA Standards, will be completely responsible for the content of the final standard. The process is a technical, consensus-based facilitated process. Membership of the Committee is drawn from experts with full GSC project life cycle knowledge and experience – general interest, operators/industry, regulatory, and consultant/service providers, which represent a balance of stakeholder needs.

The technical voting committee developed a draft that has been offered for public comment. The public comments have been received and incorporated into the draft Standard. This paper will provide an update on the development of the standard, discussion of the Standards Council of Canada (SSC) and American National Standards Institute (ANSI) process, implications of the completion of the process, as well as the impending International Standards Organization (ISO) follow-on process.

### **The Development of a State-Based Legal and Regulatory Program for the Geologic Sequestration of CO<sub>2</sub>**

David M. Flannery, Jackson Kelly PLLC, USA

Even in the absence of a federal program, significant developments have occurred in defining the legal and regulatory framework for the geologic sequestration of CO<sub>2</sub>. This presentation will address the role that the existing Clean Air Act plays in driving these issues and the recent efforts that have been undertaken to address such critical issues as environmental protection, property rights and liability.

In particular, the presentation will discuss the model CCS program initially recommended by the IOGCC in 2007 as well as the recommendation of the National Coal Council contained in their report issues in 2011

The presentation will also address the two-year effort that was undertaken by the West Virginia CCS Working Group not only to make recommendations on important legal and regulatory issues, but also to advance a comprehensive piece of legislation related to such critical topics as:

- permitting
- pore space usage
- eminent domain and pooling
- property interests
- operational liability
- post closure liability
- post closure management
- cooperative agreements with other states; and
- the role of utility regulatory commissions.

### **New Precombustion Carbon Capture Process**

Arnold Keller, London Management, Inc., USA

A new energy efficient process for CCS (carbon capture and storage) is offered in a pre-combustion process. The new pre-combustion carbon capture process (patent pending) operates at high pressure. The bulk of the dry, sulfur free CO<sub>2</sub> is first

condensed at high pressure and low temperature above the CO<sub>2</sub> freezing point. The residual, uncondensed CO<sub>2</sub> is then removed via either a traditional solvent process or via adsorption by a PSA. Finally, all the captured (liquefied) CO<sub>2</sub> is purified to remove CO and other light-end gases prior to the liquid CO<sub>2</sub> being pumped to above its critical pressure for its ultimate disposal.

The study compares the new carbon capture (CC) process against a benchmark. The benchmark comparison process is a state-of-the-art physical process, followed by CO<sub>2</sub> compression to supercritical pressure.

Significant energy savings (about 50%) are demonstrated for the combination of the selective H<sub>2</sub>S removal process, followed by the new process. The new process also has applicability in CC from synthesis gas derived from shale “FRACKING” gas.

### **GHG Emission Reduction Measurement and Monitoring Methodology for CCS Projects**

Mahesh Gundappa, Ray Hattenbach, Blue Strategies, USA

A greenhouse gas (GHG) emission reduction measurement and monitoring methodology for carbon capture and storage (CCS) projects was developed for registering carbon credits with a US-based GHG registry. It is applicable to projects that capture CO<sub>2</sub> from industrial sources or direct air capture systems, and transport it via pipelines for use and storage during EOR operations and/or storage in saline aquifers. The methodology is based on the accounting framework developed by the Center for Climate and Energy Solutions (formerly the Pew Center on Global Climate Change) and is aligned with the principles and procedures contained in ISO 14064 Part 2. The methodology includes a rigorous accounting of all GHG emission sources associated with the capture, transport, and sequestration phases of the project, details of monitoring activities required to assure permanence, and a practical approach to address important issues related to CCS projects such as title and liability consistent with registry requirements.

The paper will present the details of the methodology and an independent review process conducted by the registry to gain acceptance of the methodology. The procedures for defining the physical boundaries of the project and GHG emission sources included in the assessment will be discussed. An evaluation of project baselines and project additionality will be presented in the context of the registry requirements. Details of the calculation procedures and parameters that should be monitored and their monitoring frequency will be included. Particular focus will be on monitoring, reporting, and verification (MRV) requirements for the storage sites, including details of baseline, operating, and post-injection monitoring for storage during EOR operations. Issues related to permanence, title, liability, and pore space ownership will be discussed.

The process conducted to gain acceptance of the methodology by the registry will be discussed. The process involves a public comment period and an independent scientific review process conducted by an expert panel appointed by the registry. The issues raised during those reviews and their resolutions will be discussed. At the completion of the process the methodology will become available for use by industry to monetize carbon credits associated with CCS projects.

## **SESSION 6 Coal Mining and Coal Gas: General – 1**

### **Pre-Mining Drainage of Coal Seams – US Practices and Applicability to Worldwide Coal Mine Methane Drainage Projects**

Felicia A. Ruiz, Coalbed Methane Outreach Program, US EPA; Jon Kelafant, Richard Lawrence, Clark Talkington, Advanced Resources International, Inc., USA

Hydraulic fracturing of coal seams to produce methane in advance of mining has been an established technique in the United States (U.S.) for over 30 years. Trial projects in the Black Warrior basin, initiated in the 1970’s by the U.S. Bureau of Mines, demonstrated reduction of up to 70% of in-situ methane, over a ten year period, using vertically stimulated wells. Large scale commercial production of methane from coal seams started in the 1980’s and once further study had demonstrated the safety of the process, several U.S. coal mining companies began using the technique to remove methane from coal seams before mining. This has four main benefits: (1) methane content in the coal seams is significantly reduced, resulting in lower methane concentrations in the mine during mining, which improves both mine safety and productivity as well as reducing ventilation requirements; (2) a valuable resource that would otherwise escape to the atmosphere is captured and can be utilized for profit; (3) produced gas is very high quality; and (4) emissions of methane - a powerful greenhouse gas (GHG) - from the mine are greatly reduced.

Several underground U.S. mines currently use vertical and horizontal wells to drain methane before mining. Drilling vertical wells and hydraulically fracturing the coal seam has been the standard completion method, but developments in drilling technology over the last decade have allowed the cost-effective drilling of horizontal wells. These wells have multiple lateral boreholes, drilled in specific patterns, allowing

the drainage of a large area of coal from one well-site. Operators report recovery rates of 80-90% of in-situ gas in a two to three year time period.

Vertical, hydraulically fractured wells and horizontally drilled wells have been used in coalbed methane (CBM) projects outside the U.S., mainly in Australia and Canada. Recent projects in China and India have yet to emulate U.S. production rates. Lower coal permeability values, more complex coal geology, a lack of service companies, regulatory issues and limited land availability increase technical risks and costs when compared to U.S. operations.

Most coal mines outside of the U.S. use in-mine drainage methods to degas their coals. In talks with USEPA, several of these coal mining companies have expressed interest in pre-mining drainage as an alternative degassing method. This paper will review the main pre-mining methane drainage techniques employed in the U.S. and will discuss the applicability of such technologies to methane drainage overseas, with particular focus on China, India and Kazakhstan.

#### **Methodology for the Economic Assessment of Enhanced Coal Mine Methane Drainage (ECMM) as a Fugitive Emissions Reduction Strategy**

Regina Sander, Luke Connell, CSIRO Earth Science and Resource Engineering,  
AUSTRALIA

A methodology for the assessment of the economic feasibility of strategies for reducing fugitive emissions from open cut mining is presented. This approach involves integrating reservoir simulation of gas drainage for various operational and reservoir conditions with economic analysis involving a range of financial parameters. The feasibility of conventional and enhanced coal mine methane drainage (CMM and ECMM) is evaluated relative to the business-as-usual scenario, where the methane is allowed to become fugitive. The methodology is demonstrated through a case study evaluating the economic merit of ECMM and CMM at open cut mines representative of the Hunter Coalfields, NSW, Australia. The results of the case study indicate that a positive business case exists for ECMM above a CO<sub>2</sub> penalty of A\$20/tCO<sub>2</sub> (electricity price A\$60/MWh) (US\$17/tCO<sub>2</sub> and US\$51/MWh using a long term exchange rate of A\$1 = US\$ 0.85). CMM did not appear economic under the considered conditions (CO<sub>2</sub> penalty: A\$10-\$60/tCO<sub>2</sub>, electricity price: A\$35-85/MWh) due to slow recovery rates and high residual gas content. Less favourable reservoir properties such as lower reservoir permeability and gas content can be compensated by higher CO<sub>2</sub> penalties and/or electricity prices.

#### **Effectiveness of Coal Mine Methane Drainage in Polish Mines**

Dariusz Obracaj, Nikodem Szlazak, Marek Borowski, Marek Korzec, Justyna Swolkien, AGH University of Science and Technology, POLAND

A longwall mining system is used in Polish coal mines. Ventilation systems and coal seams' degasification lead to a smaller methane emission to mining air and dislocation of high methane concentration from longwall face to gob. Effective methane drainage is the best way to improve safety in longwalls, but it can also increase coal output from one longwall.

The mines mine deeper and deeper seams. Natural content of methane increases with depth and that is one of the reasons why there is an increase in methane hazard in Polish coal mines. Improved coal productivity from one longwall is the second reason. Methane drainage which is the most effective way of reducing methane hazard in Polish geological conditions is presented in the paper. CMM is recovery in the most possible ways but ensuring the safety for mining is the principal aim.

To ensure the required effectiveness of methane drainage during designing longwall panel development, proper ventilation system and drainage system should be selected. The effectiveness of methane capture for different drainage and ventilation systems in Polish mines is presented in this paper.

The highest drainage effectiveness is obtained in ventilation systems with double tail entries. Usually in longwall faces with "Y" ventilation system drainage boreholes drilled from upper tail entry become leaky in some distance behind the face. In this kind of system higher concentration of methane was obtained from drainage boreholes. The aims of improving the effectiveness of CMM drainage systems in Polish coal mines are presented at the end of the paper.

#### **Numerical Modeling of Nitrogen Injection in Longwall Gob Area to Prevent Spontaneous Heating**

Liming Yuan, Alex C. Smith, Office of Mine Safety and Health Research, National Institute of Occupational Safety and Health, USA

Spontaneous combustion is a serious fire hazard for U.S. underground coal mines, especially for western mines where the coal is generally of lower rank. The spontaneous heating of coal in mines often occurs in a gob area and may not be easily detected. The amount of coal that accumulates in these areas and the degree of ventilation can combine to give optimum conditions for spontaneous combustion. Although there were no reported fatalities directly attributed to spontaneous combustion in U.S. coal mines in last decade, the potential for a spontaneous combustion event leading to an explosion still exists, especially in mines with substantial amounts of methane. Nitrogen (N<sub>2</sub>) injection is commonly utilized to prevent and control spontaneous heating in longwall gob area. However, its practical

application to a particular face configuration is still fairly empirical in terms of choice of the number and location of nitrogen injection points and injection flow rates. The effectiveness of nitrogen injection on preventing or suppressing spontaneous heating is often complicated by the ventilation flow near the face.

In this study, computational fluid dynamics (CFD) modeling was conducted to investigate the effectiveness of N<sub>2</sub> injection in an active longwall gob area to prevent spontaneous heating. A single longwall panel with a bleederless ventilation system was simulated, and typical ventilation data for a longwall mine was used in the simulations. N<sub>2</sub> is injected into the gob through pipes on the headgate side and boreholes on the surface. The N<sub>2</sub> injection rate at each location varies between 250 to 1000 cfm. The calibrated CFD model was used to simulate spontaneous heating of coal left in the gob with various N<sub>2</sub> injection rates. Parametric study was conducted to determine the optimum number and location of N<sub>2</sub> injection and injection rates for different coal sources. The effect of gob methane emission on the effectiveness of N<sub>2</sub> injection was also investigated. The results of this study may help mine ventilation engineers better prevent and control spontaneous heating of coal in underground coal mines.

#### **Reducing Explosion Based Shocks in Open Mines Through Parameter Optimization Using Taguchi Methods**

Bahadır Uygur, Ahmet Albayrak, İffet Ugur Kombe, Seçil Çolpan, Ümit Çepni,  
Turkish Coal Enterprises, TURKEY

In open and underground mine establishment, since it is an economical solution, drilling and exploding excavation methods that are still commonly used in excavating and relaxation of ore and the cover of ore, is the main source of environmental negativness. The most attractive of the environmental negativness recently, are the earthquakes because of the physical damages to the residential areas, people's reactions and the negative technical and economical affects of these reactions on the enterprises. Nowadays, minimizing these environmental problems from the view of enterprises is as important an aim as the securing of the explosion, reducing the cost and the providing of the ideal (required) relaxation or particle size. In the solutions of the explosion based technical and environmental problems; the importance of a explosion design that optimizes the factors that takes role in the disintegration mechanism according to the aim, is indisputable. That is why, for a healthy explosion design, it is necessary to considerate and investigate many factors taking role in this mechanism. That a healthy design is a critical subject in the solution of the explosion based problems increases the importance of using the design techniques in this area. One of these techniques is statistical experiment design. By using the experimental design methods in an enterprise, designing of the process parameters perfectly are done before starting the production, and by this way affective solutions can be developed during design period against the problems seen during the process. And this provides serious cost and time advantage in the enterprises and increases the productivity. Among SED methods, Taguchi experimental design that gives successful results by using it in many branches of production industry is seen to be the most rational method that can be used in solving the problems in drilling, explosion and other mining processes. Because this method when compared with other experimental design methods, gives the same result whereas need less experiment. When the difficulties and restrictions in making experiments are taken into consideration this case will provide easier solution with less cost and time in researches made in the areas where the site work is inevitable as in mining. That is why, Taguchi experimental design that gives more accuracy by doing less experiment, is a method that can be used affectively in solving mining problems in a short time with less cost. In (SLI) Seyitömer Linyitleri İşletmesi (Seyitömer Lignite Coal Enterprise) that is the area of this work, experiences problems caused by the right or wrong effects and complaints of the people living there because of the results of the earthquakes caused by explosions. The reduction of shocks caused by these explosions has much importance from the point of preventing the disturbance of these problems and their bad affects. In this research it is aimed to reduce the explosion based shocks through factor optimization by using Taguchi experimental design method that is experimental design method and investigating the affects of some hole geometry factors" (parameters) that can be controlled Under SLI conditions on the explosion based shocks. With this aim, 4 factor (distance between the holes , total amount of explosives , measure distance , Delay time) that can be controlled under SLI conditions are applied to 3 times repeated 8 experiment combination in 2 stages and by using L8(2)7 orthogonal series. The levels of these controllable factors are taken as; 8-12 m for the distance between the holes, 450-600 kg for the total amount of explosives, 75-150 m for the measure distance, 0-42 ms for the delay period. The shock values obtained after the experiments are read to the measurement device as particular speed (mm/sn) and recorded, and these experimental results are analyzed according to both average and S/N statistics. All experimental explosions are done on 22 m marn formation on the coal by preparing holes with 90° angle, 9 inc diameter, and by exploding them in series in triple groups in one part of Aslanlı area Dragline panel. In analyzing stage, essential effects and interactions are determined. In the other stage, variance analysis is done to determine the meaningfulness and effect rate of the effects of factor and interaction for both statistics. According to the variance analysis, final optimum conditions are determined and the reliability of this optimum conditions are found out by doing approving experiments. After the works, under SLI conditions it is found out that according to their bigness sequence, distance from the explosion point and the delay time in explosion are the



primary factors that are effective in reducing the explosion based shocks; the secondary factor is the in between holes distance-explosives transaction, the minimum shocking optimum conditions are 8 m between the holes and 600 kg total explosive, 150 m measure distance, 42 ms delay time. Besides this, it is seen that the shock amount of 62 mm/sn before the design work has been reduced to 34.56 mm/sn after the design work. With the approving experiments it has been understood that the design is reliable.

**SESSION 8**  
**Sustainability and Environment: General – 2**

**SESSION 7**  
**Clean Coal Demonstration and Commercial Projects: Financial Risk Management**

**EPA and Coal-Fired Power Plant Emission Regulation**

Peter B. Trick, Victoria I. Adams, David S. Wilson, Booz Allen Hamilton, Inc., USA

In this presentation we provide an overview of recent trends in the regulation of emissions from coal-fired power plants and related material streams, and suggest how these might affect major demonstration projects. We begin by reviewing actions that EPA has taken or proposed in the recent past, comparing this with the regulatory "train wreck" timeline described by EEI in 2010. We then discuss potential future trends in regulation and their implication for the coal industry under different natural gas price scenarios. We tie these implications to major demonstration projects, describing how the regulations might affect both the value and the cost of different types of projects.

**Carbon Capture and Storage – How to Manage Your Risks**

Patrick Maguire, McGriff Seibels & Williams, Inc., USA

Reducing CO emissions in the coming decades, without suffocating economic growth, is a growing concern for the coal industry. The presence of new and broader regulation will present new challenges to the Coal industry and its customers. The Carbon Capture and Storage (CCS) process continues to develop in order to provide a platform for new coal-fired power generation.

In a CCS-embracing future, power generators and other point-source generators of large CO will be faced with a number of new and challenging risks when dealing with CO. These include regulatory and credit risks, directors and officers liability, third party liability risks and more. It is key that all stakeholders in the CCS process carefully review their risk exposures. This presentation will provide a primer of the key issues associate with CCS.

**Building an Organizational Risk Management Framework**

Michael Sell, Global Association of Risk Professionals, USA

The Global Association of Risk professionals (GARP) is a professional membership association whose principal mission is to help educate the global risk management community primarily through professional risk management certification programs, education and training, media and events. In the areas of financial and energy risk management, GARP sets the global standard with the Financial Risk Manager (FRM®) and Energy Risk Professional (ERP®) designations.

Over the past several years we have observed several crises in global markets that demonstrate the importance of sound risk management practices. Regulation designed to solve structural weaknesses and market imbalances will likely only go so far. Of equal or greater importance is the implementation of a proper risk culture that addresses the unique risks inherent in every organization. We will discuss broad processes to help identify, evaluate and manage risk inherent in all organizations.

**Toward a Common Method of Cost Estimation for Power Plants with CO<sub>2</sub> Capture and Storage**

Edward S. Rubin, Carnegie Mellon University, USA

Organizations such as the U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), the International Energy Agency Greenhouse Gas Programme (IEAGHG) and others have each developed their own "standard" method and assumptions for power plant cost analysis. However, a comparison of these methods reveals significant differences in way various organizations estimate and report the cost of coal-based power plants with carbon capture and storage (CCS) systems. Such differences often are not apparent in publicly reported cost estimates for CCS or an overall power plant. As a consequence, there is significant misunderstanding, confusion, and mis-representation of CCS cost information, especially among audiences not familiar with the details of CCS costing. Given the international importance of coal-based power with CCS as an option for climate change mitigation, efforts to improve and systematize the methodology and communication of power plant costs are especially urgent and timely. This paper recommends a path forward to achieve that goal based on recommendations of an international Task Force on CCS Costing Methods, which will be presented.

**The Pittsburgh Aerosol Research and Inhalation Epidemiology Study (PARIES): A Retrospective Evaluation of Fine Particulate Matter, its Chemical Components, and Human Health in Southwestern Pennsylvania**

Daniel P. Connell, CONSOL Energy Inc.; Richard A. Bilonick, Evelyn O. Talbott, Judith R. Rager, University of Pittsburgh, USA

In 1997 and 2006, the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for fine particulate matter (PM<sub>2.5</sub>), based largely upon epidemiological evidence that suggests an association between total ambient mass concentrations of PM<sub>2.5</sub> and adverse human health effects. The NAAQS are the basis for EPA's Cross-State Air Pollution Rule, and coincidental reductions in PM<sub>2.5</sub> mass account for most of the health benefits claimed under EPA's Mercury and Air Toxics Standards. However, fine particulate matter is a complex mixture of many diverse chemical constituents, and it is still unclear whether a subset of these constituents, rather than total particle mass, is responsible for the observed health effects. In fact, EPA's Clean Air Scientific Advisory Committee recommends that "... future assessments more fully consider evidence on the compositional differences in PM effects in relation to both health and welfare, especially given the emerging view that metals and carbonaceous aerosols, typically referred to as elemental and organic carbon, are of greater concern for many endpoints."

The Pittsburgh Aerosol Research and Inhalation Epidemiology Study (PARIES) is being conducted to elucidate the health effects of individual chemical constituents of PM<sub>2.5</sub> by utilizing sophisticated statistical techniques to leverage millions of dollars of air monitoring and health data that have already been collected in the Pittsburgh, PA, region, thereby providing a cost-effective way to address a PM<sub>2.5</sub> research need with major public policy implications. Specifically, PARIES is focused on mortality, hospital admissions, and emergency department visits associated with respiratory and cardiovascular illness in Allegheny, Washington, and Westmoreland counties, which have a combined population of ~1.8 million. Associations of PM<sub>2.5</sub> mass and co-pollutant concentrations with human health are being studied over a ten-year period (1999-2008), and associations of PM<sub>2.5</sub> chemical components with human health are being studied over a five-year period (1999-2004). PM<sub>2.5</sub> chemical composition information is being obtained both from existing datasets and by chemically analyzing archived PM<sub>2.5</sub> samples that were collected at two monitoring sites in Allegheny County. In addition to providing the first-ever large-scale characterization of the health effects of PM<sub>2.5</sub> and its chemical components in the Pittsburgh region, PARIES will advance the state of PM<sub>2.5</sub> epidemiology by incorporating a number of advanced statistical techniques that are designed to overcome the limitations of conventional methods used in air pollution epidemiology. These advanced techniques, which include structural equation modeling for calibrating measurements from different monitoring sites, geostatistical approaches for providing spatially resolved daily exposure estimates, and generalized linear autoregressive moving average modeling for time series analysis, are expected to improve the robustness of exposure and health effect estimates. PARIES has been underway since 2008, and the project team has made substantial progress with constructing the expansive air monitoring and health effect databases required for the study, analyzing archived PM<sub>2.5</sub> samples, and developing statistical methods. Epidemiological modeling is just now beginning. This presentation provides an overview of the science and policy issues motivating PARIES, describes the design of this unique study, and summarizes the results obtained to date.

**Comparison and Recommendations Between Thermal Power Plants in Türkiye by Carbon Emissions and Coal Quality**

İffet Ugur Kombe, Ahmet Albayrak, Seçil Çolpan, Bahadır Uygur, Ümit Çepni, Turkish Coal Enterprises; Mahmut Yavuz, Eskisehir Osmangazi University, TURKEY

Producing electricity continues to attract interest by means of Coal-fired Thermal Plant in the world. However, this situation threat by degradation of the world's ecological balance, environmental health and environmental security. Thermal power plants that are running with coal are considered among the causes of global warming and carbon emissions and global climate change and carbon dioxide emissions. According to Protocol Kyoto an intensive worldwide carbon oscillations caused by an increase in and carbon dioxide emissions reduction, restriction, limitation, control are major hurdles for the development of coal-fired thermal power plants.

Therefore, in this study, it is made a comparison in coal-fired Thermal Power Plants by considering the difference between the supplied coal and what can be done to reduce the non-effective restorative agent of greenhouse gases for those power plants that haven't got FGD (Desulphurization of fuel gas) system. This situation how will be affected in coal preparation process was investigated.

In addition, environmental issues and the integration of energy policies for sustainable development "of energy supply security", "providing a competitive edge" and "environmental protection" solution suggestions were made about the responsibilities of Turkey in terms of Kyoto Protocol.

## Life Cycle Analysis of Electricity From Coal Fired Thermal Power Plants and a Comparative Study of the Efficient Combustion Technologies in India

Binita Shah, Seema Unnikrishnan, Neelima Naik, National Institute of Industrial Engineering, INDIA

It has been anticipated that in the coming decades the use of coal as a fuel to generate electricity will continue to increase in India. Coal is the most abundant fossil fuel resource. The aim of this paper is to assess the current emerging advanced efficient combustion technologies. We will assess the emerging advanced power generation technologies for the Indian scenario. In order to rate the Indian coal power sector. As we know India is one of the fastest growing economy in the world today, and energy is the most important factor which fuels in this growth. While the development and expansion of the nation is a crucial factor, we cannot neglect the fact that every step toward should be technologically advanced but also sustainably sound. Considering the quality of coal and the type of technologies available in India for the generation of electricity this is a very crucial study. Also it has an effect on the climate change factor.x

Here, Life cycle Analysis (LCA) is used as a tool to assess the environmental impacts of coal fired power plant. LCA considers the full process from Cradle to grave; it carefully investigates a variety of environmental impacts, in the whole process. Each combustion technology will be covered considering its pollution control add-ons, operational performance etc..

In order to assess whether or to what extent the introduction of these efficient combustion technologies to coal fired power plants will contribute to reducing these other environmental impacts.

## Mechanism, Kinetics and Thermodynamics of Adsorption of Aqueous Chromic Ion on HNO<sub>3</sub> Treated Mesoporous Activated Carbon

Shitang Tong, Lei Mao, Liu Wan, Mingxia Fan, Wuhan University of Science and Technology, CHINA; Charles Q. Jia, University of Toronto, CANADA

Mesoporous activated carbons (MACs) were prepared and modified with post-oxidation in HNO<sub>3</sub>. The resulting carbons were elaborately characterized for pore structural and surface chemical properties. The obtained mesoporous carbons possess the typical honey-comb-like pore structure with widely average pore size (77 ~ 91 nm), and richness in surface oxygen/nitrogen functionalities. These samples were subsequently applied in the removal of chromic ion, Cr(III) from the simulated or industrial wastewater to understand the roles of pore structural and surface chemical properties in adsorption of Cr(III) from acidic waste water. Mechanism, kinetics and thermodynamics of adsorption of Cr(III) on these carbons were virtually studied based on the experimental observation. The results indicated that adsorption of Cr(III) on the mesoporous activated carbons involves formation of carboxylate chelate of the hydrolyzed Cr(III) ion with endothermic nature and follows the ion exchange mechanism. The pseudo second order kinetic model with respect to the vacant surface binding sites was found to be the best suitable for representing the adsorption kinetic data. The maximum adsorption capacity on the examined carbon samples increased from 107.10 mg/g to 117.00 mg/g with increased temperature from 30 °C to 50 °C. The complexity of the industrial wastewater was found with no influence on Cr(III) adsorption performance of the acid treated MAC.

### SESSION 9 Gasification: General – 2

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

Mike Bockelie, Kevin Davis, Andrew Fry, Martin Denison, Randy Pummill, Tim Shurtz, Huafeng “Dave” Wang, Reaction Engineering International; Kevin Whitty, Mustafa Can Celebi, Cristina Jaramillo, University of Utah; Jost Wendt, Reaction Engineering International and University of Utah, USA

To improve cost competitiveness 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. Downtime events associated with the syngas cooler are often due to ash deposits. In this paper we provide an overview of our research into deposit formation in the syngas cooler and techniques to mitigate the plugging and fouling of the syngas cooler.

#### Application of Tunable Diode Laser Absorption Diagnostics and Gas Composition Analysis towards Quantification of Reaction Progress in a Fixed-Bed Gasifier

Anup Sane, Indraneel Sircar, Weichao Wang, Robert P. Lucht, Jay P. Gore, Purdue University, USA

An experimental investigation is reported on the use of tunable diode laser absorption spectroscopy (TDLAS) and gas composition analysis to quantify reaction progress in a fixed-bed gasifier. Many past studies on gasification have been conducted in batch-reactors and fixed-bed reactors in which reaction progress is tracked by sample mass measurements and downstream gas composition analysis. However, *in-situ* concentration measurements are rarely reported [1]. This paper reports the use tunable diode laser absorption spectroscopy (TDLAS) for *in-situ* gas concentration and temperature measurements. Comparisons of measurements from TDLAS with the downstream gas composition analysis are reported. An optically accessible fixed-bed high pressure capable reactor arrangement for studies of biomass and coal gasification is described. The reactor features gasification of coal and biomass in CO<sub>2</sub> environment at nearly isothermal conditions. Diagnostics include microbalance mass measurements, strain gauge pressure and thermocouple temperature measurements, and infrared absorption spectroscopy. Radiant heaters surrounding the reactor provide isothermal boundary conditions for gasification. The effluent gas compositions are analyzed using gas chromatography (GC). Structural and elemental changes in the biomass samples are analyzed using Scanning Electron Microscopy (SEM). The reactor is equipped with an optically-accessible window section that is located 2 cm downstream of the fixed-bed. This permits TDLAS measurements of temperature and carbon monoxide (CO) mole fractions at various times during the gasification process. It is expected that the measured evolution of CO concentration with time will provide quantification of reaction progress. The TDLAS measurements show good qualitative agreement with the GC product gas analysis. The char conversion behavior can be explained through the structural changes that occur during the gasification reaction. Structural changes are found to have significant impact on CO release.

#### Coal Ash Behavior in Reducing Environments (CABRE) III

Joshua J. Stanislawski, Donald P. McCollor, Alexander Azenkeng, Robert R. Jensen, University of North Dakota Energy & Environmental Research Center, USA

The goal of the CABRE III project is to produce a computer-based model that predicts slag flow behavior, ash partitioning, and deposition potential in gasification systems. The CABRE III Program is scheduled to be completed in March 2012. This program is cofunded by the U.S. Department of Energy through the EERC's National Center for Hydrogen Technology<sup>®</sup> and a consortium of industrial sponsors. The CABRE III Program is focused on developing models that accurately predict the fate and transformation of inorganic material from coal and petroleum coke in reducing environments. The computer-based model will enable commercial gasification facilities to be able to predict and control ash deposition in all areas of a gasification system. Specific areas of interest include elemental partitioning and advanced slag viscosity predictions.

The EERC utilized laboratory-scale measurements in conjunction with small pilot-scale gasifier runs to determine and ultimately predict the partitioning of ash components in a gasification system. A small pilot-scale entrained-flow gasifier and a fluid-bed gasifier were both used to develop the data on sponsor fuels. The project has taken place over three phases, with the first phase focused on the development of detailed laboratory data on the sponsor fuels of choice. The fuels were gasified in the second phase, and the final model has been developed in the third phase. This paper describes the basic focus of the model and demonstrates the utilization of the Windows-based user interface for predicting ash behavior in a gasification system.

#### Effect of Operating Conditions on Gas Composition in Atmospheric and Bubbling Fluidized Bed Gasification of Coal

Emir Aydar, Serhat Gul, Namik Unlu, Fehmi Akgun, Haydar Livatyali, TUBITAK Marmara Research Center, TURKEY

It is commonly accepted that gasification of coal has a high potential for a more sustainable and clean way of coal utilization. In recent years, research and development in coal gasification areas are mainly focused on the synthetic raw gas production, raw gas cleaning and, utilization of synthesis gas for different areas such as electricity, liquid fuels and chemicals productions within the concept of poly-generation applications. The most important parameter in the design phase of the gasification process is the quality of the synthetic raw gas that depends on various parameters such as gasifier reactor itself, type of gasification agent and operational conditions. In this work, coal gasification has been investigated in a laboratory scale atmospheric pressure bubbling fluidized bed reactor, with a focus on the influence of the gasification agents on the gas composition in the synthesis raw gas. Several tests were performed at continuous coal feeding of several kg/h. Gas quality (contents in H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>) was analyzed by using online gas analyzer through experiments. Coal was crushed to a size below 1 mm. It was found that the gas produced through experiments had a maximum energy content of 5.28 MJ/Nm<sup>3</sup> at a bed temperature of approximately 800°C, with the equivalence ratio at 0.23 based on air as a gasification agent for the coal feedstock. Furthermore, with the addition of steam, the yield of hydrogen increases in the synthesis gas with respect to the water-gas shift reaction. It was also found that the gas produced through experiments had a maximum energy content of 9.21 MJ/Nm<sup>3</sup> at a bed temperature range of approximately 800-950°C, with the equivalence ratio at 0.21 based on steam and oxygen mixtures as gasification agents for the coal feedstock. The influence of gasification agents, operational

conditions of gasifier, particle size of coal, etc. on the quality of synthetic raw gas, gas production efficiency of gasifier and coal conversion ratio are discussed in details.

### **Palladium Sorbents for High Temperature Capture of Mercury, Arsenic, Selenium and Phosphorus from Fuel Gas**

Evan J. Granite, Henry W. Pennline, Erik Rupp, Dennis C. Stanko, John P. Baltrus, DOE/NETL; Wilson Chu, Johnson Matthey; Tony Wu, Subhash Datta, Bob Lambrecht, John Wheelton, National Carbon Capture Center, USA; Hugh Hamilton, Liz Rowsell, Stephen Poulston, Andrew Smith, Johnson Matthey Technology Centre, UNITED KINGDOM

In gasification for power generation, the removal of mercury by sorbents at elevated temperatures preserves the high thermal efficiency of the integrated gasification combined cycle system. Unfortunately, most sorbents will display poor capacity for elemental mercury at elevated temperatures. Previous experience with sorbents in flue gas has allowed for judicious selection of potential high temperature candidate sorbents. The capacities of many sorbents for elemental mercury from nitrogen, as well as from different simulated fuel gases at temperatures from 400 - 700°F, were determined. The simulated fuel gas compositions contain varying concentrations of mercury, arsine, hydrogen selenide, phosphine, carbon monoxide, hydrogen, carbon dioxide, moisture, and hydrogen sulfide.

Palladium is an attractive sorbent candidate for the removal of mercury from fuel gases at elevated temperatures. Recent results suggest that palladium has excellent potential for arsenic, phosphorus and selenium capture from fuel gases, making it capable of multi-pollutant capture. A license agreement has been signed by the United States Department of Energy and Johnson Matthey for further development of the sorbents. The sorbents have recently removed nearly 100% of the mercury, arsenic and selenium from slipstreams of dirty syngas at 500oF during several extended exposures at a pilot gasification facility. Future research areas and sorbent development for trace metal capture from fuel gases will be discussed.

## **SESSION 10**

### **Combustion: Chemical Looping and Oxy-Combustion – 2**

#### **Three-Dimensional Calculation of a Chemically Reacting Coal Particle Agglomerate Moving in a Hot O<sub>2</sub>/CO<sub>2</sub> Atmosphere**

Andreas Richter, Petr A. Nikrityuk, TU Bergakademie Freiberg, GERMANY

This work is devoted to the numerical investigation of dense carbon-particle clusters (agglomerates) that are moving in hot O<sub>2</sub>/CO<sub>2</sub> environments. Such kind of agglomerates can be found in different applications such as fluidized-bed reactors, where they feature a different heat transfer and fluid flow compared to single particles. In the last decades, mainly the cluster formation was examined experimentally and numerically, and only a few works in literature focused on the fluid flow and heat transfer inside and around clusters. It is known from two-dimensional investigations (A. Nicolle and I. Eames, *J. Fluid Mech.* 679, 2011) that below a critical particle void fraction a distinct flow around each individual particle exists. Beyond this critical value, the cluster behaves similar to a solid particle with the equivalent diameter. In the literature, most works were devoted to clusters with only low void fractions. Contrary to these works, neither no information about heat and fluid flow in and around dense clusters or agglomerates, nor the impact of void fraction value on the heat transfer coefficient between a cluster and the ambient gas are given. For example it is not clear, how the flow field inside the cluster influences the overall mass and heat transfer. The next not well-studied feature is the interaction between bulk flow and the so-called Stefan flow appearing due to heterogeneous chemical reactions.

In order to clarify these physical effects, we numerically investigate particle agglomerates that are moving in hot environments. Since the oxy-combustion of coal with flue gas recirculation and carbon sequestration is one of the promising advances in the filtering and storage of CO<sub>2</sub>, we focus our investigations on agglomerates that are placed in hot O<sub>2</sub>/CO<sub>2</sub> atmospheres. To solve the three-dimensional Navier-Stokes equations for the flow field coupled with the energy and species conservation equations, a finite volume solver was applied. In addition to the solid carbon the model incorporates six gaseous chemical species (O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>). The reaction mechanism includes the forward and backward water-gas-shift reaction, one reaction for CO combustion and four heterogeneous reactions. The ambient medium is assumed to be nearly dry (Y<sub>H<sub>2</sub>O</sub>=0.001). The numerical model is validated carefully against analytical solutions and measurements published in the literature (M. Rodriguez and R. Raiko, *Finnish-Swedish Flame Days*, 2009). The agglomerate considered in this work consists of 185 spherical carbon particles in circular arrangement. The particle fraction is equal to 0.68. Due to the high void fraction most particles are connected to their neighbors.

The main motivation of the present work is to study the following questions: the influence of the cluster velocity (Re number) on the temperature and species concentration distribution inside the cluster; the role of Stefan flow in the balance of species; the influence of the cluster size on the processes inside and around the cluster.

To answer these questions, we consider agglomerates with outer diameters between 200 microns and 2cm. The temperature of the surrounding gas was varied between 1000K and 2500K. The cluster velocity corresponds to Reynolds numbers equal to 1, 10 and 100. Additional calculations for the partial oxidation of solid spheres with similar outer diameters are carried out and compared against the results achieved for the particle agglomerate.

#### **Evaluation of Reduction Kinetics of Copper Oxide on Various Supports for Chemical-Looping with Oxygen Uncoupling**

Christopher K. Clayton, Kevin J. Whitty, University of Utah, USA

In order to scale up a CLOU (Chemical-looping with Oxygen Uncoupling) reaction system using copper oxide as the oxygen carrier, the reaction kinetics of CuO/Cu<sub>2</sub>O must be better understood. In an effort to better understand the kinetics of the CuO/Cu<sub>2</sub>O system the University of Utah conducted a set of experiments on 3 different copper-based oxygen carriers. The kinetics of the reduction reaction of 50wt% CuO on TiO<sub>2</sub>, 20 wt% CuO on SiO<sub>2</sub> and 45wt% CuO on MgO-stabilized ZrO<sub>2</sub> measured under an inert atmosphere (CLOU conditions) in a thermogravimetric analyzer (TGA) and lab-scale fixed and fluidized beds are presented.

#### **Chemical Looping Combustion of Syngas Derived from Steam Gasification of Coal with Iron and Copper Oxygen Carriers**

Ewelina Ksepko, Marek Sciazko, Institute for Chemical Processing of Coal, POLAND; Ranjani V. Siriwardane, DOE/NETL; Hanjing Tian, Thomas Simonyi, DOE/NETL/URS, USA

The paper contains the results of research work on Chemical-looping combustion (CLC) that has been suggested as an energetically efficient approach for coal combustion without any energy penalty for CO<sub>2</sub> separation. The objective of this work was to prepare supported bimetallic Fe<sub>2</sub>O<sub>3</sub>-CuO oxygen carriers (oc) and to evaluate the performance of these for the CLC process with simulated synthesis gas derived from steam gasification of coal. Our previous work has shown that bi-metallic oxygen carriers such as Fe-Mn/support are promising candidates for synthesis gas CLC as compared to mono-metallic oxygen carriers. Therefore, mixed metal oxide oxygen carriers based on iron-copper were investigated in this study. Both Fe and Cu oxides have interesting characteristics. The iron oxide based oc is receiving attention due to both low cost and low environmental impact, while the copper oxide based ocs are promising candidates due to high reactivity and efficiency.

Ten cycle CLC tests were conducted with the Fe-Cu oxygen carriers in an atmospheric TGA utilizing simulated synthesis gas derived from steam gasification of Polish and American hard coal as a fuel. Effect of temperature on the reaction rates, chemical stability and oxygen transport capacity were determined. The fractional conversions and global reaction rates were calculated using the TGA data. It was observed, that support had a great effect on the reaction performance. The data showed that the reaction rates and oxygen capacities were stable during the 10-cycle TGA tests for most of Fe-Cu/support oxygen carriers. Bimetallic Fe-Cu/support oxygen carriers showed higher reduction rates than the monometallic supported Fe oxygen carriers. Oxidation reaction was significantly faster than the reduction reaction for all supported Fe-Cu oxygen carriers. The increase in temperature from 800 °C to 900 °C did not have a significant effect on the oxygen capacity and the reduction rates with synthesis gas derived from coal.

The promising results from the TGA tests indicated that Fe-Cu oxygen carriers may be successfully utilized up to 900 °C for CLC of synthesis gas derived from steam gasification of coal.

Acknowledgement: This study was financed by the Polish Ministry of Higher Education and Science, project No. 685/N-USA/2010/0 and the research work was conducted at U.S. Department of Energy/National Energy Technology Center.

#### **Development of the Coal Direct Chemical Looping Process at Ohio State**

Samuel Bayham, Ray Kim, Liang Zeng, Siwei Luo, Dawei Wang, Liang-Shih Fan, The Ohio State University, USA

The iron-based Coal Direct Chemical Looping (CDCL) process at Ohio State has undergone significant development from its initial concept as a process to directly convert coal without the need for an external gasifier. The uniqueness of Ohio State's CDCL process is in the design of the reduction reactor, which utilizes the concept of the countercurrent moving bed reactor to allow for a greater conversion of the oxygen carrier while allowing for near-complete conversion of the solid fuel. Furthermore, the countercurrent moving bed reducer requires less volume than a fluidized bed of similar fuel conversion capability, translating into a lower capital cost and lower solids circulation and attrition rates. A recent techno-economic evaluation of a potential 550 MW<sub>e</sub> commercial plant using ASPEN Plus software has shown that the CDCL process can produce 90% carbon capture with an increase in the levelized cost of electricity of only 33% above a subcritical PC-power plant of the same electric output, meeting the National Energy Technology Laboratory's CO<sub>2</sub> emissions control program target. Extensive work has been performed on a suitable iron-based oxygen carrier initially using thermogravimetric analysis (TGA) and fixed bed studies to determine the oxygen

carrier reduction-oxidation capabilities with solid fuels, leading to studies on a 2.5 kW<sub>th</sub> bench-scale reactor to prove the concept of the countercurrent moving bed reducer for solid fuels. Tests from the 2.5 kW<sub>th</sub> bench-scale reducer reactor have revealed to be promising, with some runs showing near-complete fuel conversion and with a higher oxygen carrier conversion than a fluidized bed reducer. The most recent process development is the construction and testing of a fully integrated 25 kW<sub>th</sub> CDCL sub-pilot demonstration reactor at Ohio State, which emulates the design of a circulating fluidized bed, with the downcomer acting as the moving-bed reducer reactor and the combustor as a fluidized bed. After the preliminary component shakedown, several types of solid fuels have been tested in the demonstration unit with reasonable fuel conversions and CO<sub>2</sub> capture.

**SESSION 11**  
**Carbon Management: CO<sub>2</sub> Capture – 1**

**Validation of Proposed Mechanism Towards In-Situ CO<sub>2</sub> Capture During Gasification by Simulating a High Si/Al and Low Ca Content Coal Source**

JC van Dyk, Sasol Technology; FB Waanders, North West-University, SOUTH AFRICA

The mechanistic behaviour of Ca-containing mineral species towards the in-situ capture of CO<sub>2</sub> during gasification, as well as understanding the chemistry and the interpretation of the mechanism involved, as measured by means of high temperature X-ray diffraction (HT-XRD), in combination with FACTSAGE™ modelling, is known. The CaO content of a South African and another coal source investigated previously ranged from 6 mass % to 30 mass % respectively. The basic components present in the coal, or specifically CaO, only act as a fluxing component (lowering of the melting temperature) up to a specific percentage, where after the AFT of the coal starts to increase again. At this turning point the (Si+Al):Ca ratio is 2.75, which is the stoichiometric chemical ratio for anorthite, which implies that after the turning point, the formation of anorthite is maximized and can thereafter only remain at the same level, or decrease with increasing temperature as the anorthite starts to become a slag-liquid.

The principle aim of this study was to validate the proposed mechanism by expanding the range of coal sources, specifically related to Si and Ca content, on which the mechanism was developed previously. A bituminous coal sample with a SiO<sub>2</sub> content of >60% and CaO content <2% were used for this investigation.

With the addition of the low CaO-content coal, for the validation of the mechanism towards CO<sub>2</sub> capture in-situ of the fixed bed gasification, it was re-confirmed that anorthite formed, when the Ca content increased, and followed the inverse trend of the ash flow temperature prediction curve with the coal containing higher amounts of CaO. The decrease in anorthite formation, with increasing Ca content, after the turning point in the graph, can be explained by the fact that more of the crystalline phase becomes a liquid (slag), and thus also the increase in the amount of CaO in the slag will be observed. At the turning point, it is also interesting to note the stabilization of the amount of other Ca-containing species. These are the minerals that are responsible and available for the mechanism where CO<sub>2</sub> can be captured on Ca to form CaCO<sub>3</sub>. The formation of CaCO<sub>3</sub> can also be observed from the turning point where the (Si+Al):Ca ratio is < 2.75, which corresponds with the formation of other Ca-containing species.

Thermodynamic modelling with FACTSAGE™ indicated that anorthite can only form to the point where the (Si+Al):Ca ratio is >2.75, with all non-reacted Ca utilized to react with CO<sub>2</sub> to form CaCO<sub>3</sub> further down in the combustion zone. With the low Ca-content coal used as validation for the mechanism, it was again confirmed that with high (Si+Al):Ca ratios, all Ca is captured in the form of anorthite (CaSi<sub>2</sub>Al<sub>2</sub>O<sub>8</sub>) and no free Ca is available to form any other minerals or to capture CO<sub>2</sub> as CaCO<sub>3</sub> within the combustion zone.

**Babcock & Wilcox Power Generation Group, Inc.'s RSAT™ Process and Field Demonstration of the OptiCap™ Advanced Solvent at the National Carbon Capture Center**

Christopher W. Poling, Jeb W. Gayheart, Ted R. Parsons, Stephen A. Moorman,  
Babcock & Wilcox Power Generation Group, USA

Southern Company manages and operates the U.S. Department of Energy's National Carbon Capture Center (NCCC), a focal point of national efforts to develop advanced technologies to reduce greenhouse gas emissions from coal-based power generation. The center, located in Alabama, works with scientists and technology developers from government, industry and universities who are creating the next generation of carbon capture technologies.

In the fall of 2011, Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) conducted a three-month test campaign at the NCCC to develop further commercially viable methods of reducing carbon dioxide (CO<sub>2</sub>) emissions from coal-fired power plants. The company tested its regenerable solvent absorption technology (RSAT™) process using its OptiCap™ advanced solvent.

This paper will provide general descriptions of results in the areas of regeneration energy, solvent degradation and corrosion, as well as non-quantitative results such as lessons learned and operating experience for a post-combustion carbon capture (PCC) pilot plant in a coal-fired utility power plant.

**Advanced Technology Testing at the National Carbon Capture Center**

John Northington, Frank Morton, Ruth Ann Yongue, Southern Company Services,  
USA

The US Department of Energy (DOE) established the National Carbon Capture Center (NCCC) as part of its strategy to address the need for cost-effective CO<sub>2</sub> capture technologies. The focus of the NCCC is to conduct research and development to advance emerging CO<sub>2</sub> control technologies to commercial scale for effective integration into coal-based Integrated Gasification Combined Cycle (IGCC) and combustion processes. To achieve this goal, the NCCC provides a test-bed for government, industrial, and university projects to conduct meaningful tests in an industrial setting.

The NCCC test plan includes both post-combustion and pre-combustion CO<sub>2</sub> capture development. A flexible post-combustion test facility, Post-combustion Carbon Capture Center (PC4), utilizes flue gas from Alabama Power's Plant E.C. Gaston, in Wilsonville, Alabama. The facility, which is managed by Southern Company Services, provides a platform for testing technologies at a wide-range of sizes and process conditions on coal-derived flue gas. Since completing commissioning and baseline testing in early 2011, several technologies have been tested.

The PC4 facility includes multiple slipstreams with a range of flue gas throughputs to allow the evaluation of post-combustion CO<sub>2</sub> capture technologies. It provides the capability to test modules from technology developers and to test solvents in an absorber/regenerator unit, the pilot solvent test unit (PSTU). In 2011, PSTU baseline tests were completed, using a reference solvent, monoethanol amine (MEA) to characterize its performance and verify the reliability of the data generated. The PSTU was later operated to test a potential commercial solvent developed by Babcock & Wilcox. Aker Carbon Solutions installed a mobile test unit at the site to test its commercial solvent, and Membrane Technology & Research installed and commissioned its 0.05-MW polymeric CO<sub>2</sub>-separation membrane, which will continue to be tested throughout 2012. Also in 2012, several other developers will test solvents in the PSTU and enzyme-based solvent systems in the bench scale area on coal-derived flue gas. Collaboration with additional developers for future test plans are on-going.

The NCCC also generates coal derived syngas which is available for testing technologies related to pre-combustion CO<sub>2</sub> capture. Several slipstreams are in place with a range of syngas throughputs. Technologies tested in 2011 include water gas shift catalysts, high-temperature mercury and CO<sub>2</sub> sorbents, a hydrocarbon removal system, physical and chemical solvents for CO<sub>2</sub> absorption, a polymeric CO<sub>2</sub>-separation membrane, and three hydrogen-separation membranes (carbon molecular sieve, polymeric, and palladium based). Several of these technologies will be tested further in 2012, and membranes and solvents from other developers will also be tested. Results from NCCC's testing have indicated the facility's usefulness in accelerating the commercialization of advanced CO<sub>2</sub> capture technologies. This paper will detail the NCCC's capabilities, test results, and future plans.

**Lab-Scale Assessment of a Post-Combustion Carbon Dioxide Capture Process Enabled by a Combination of Enzymes and Ultrasonics**

Sonja Salmon, Alan House, Novozymes North America, Inc.; Charles Freeman, Kayte Denslow, Pacific Northwest National Laboratory; Joe Remias, Balraj Ambedkar,

University of Kentucky, Center for Applied Energy Research, USA; Vinay Mulgundmath, Saravanan Swaminathan, Doosan Power Systems, UNITED KINGDOM

Methods and results for a laboratory scale assessment of a post-combustion carbon dioxide capture process enabled by a combination of enzymes and ultrasonics will be presented as the first stage on the path to constructing and operating an integrated bench-scale system. This solvent-based post-combustion carbon dioxide capture system integrates a low-enthalpy, aqueous potassium carbonate-based solvent with an absorption-enhancing carbonic anhydrase enzyme catalyst and an ultrasonic-enhanced regenerator in a re-circulating absorption-desorption process configuration. Whereas ultrasonics is used in a variety of industrial degassing applications, its use for solvent regeneration represents a novel approach for the CO<sub>2</sub> capture process. Carbonic anhydrase catalyzes the reversible hydration of carbon dioxide, helping to overcome kinetic limitations for use of K<sub>2</sub>CO<sub>3</sub>-based solvents for post-combustion capture, and allowing the capture system to operate at lower temperatures compared to benchmark MEA. Results from lab-scale evaluation of CO<sub>2</sub> absorption rates in the presence of enzyme, tolerance of enzyme to ultrasonics, and extent of degassing achievable by sonication in the presence of enzyme will be presented. The approach to integrating these components in a bench-scale system, performance goals, and anticipated energy requirements for the system will be described.

**SESSION 12**  
**Coal Mining and Coal Gas: General – 2**

**Local Geology and Hydrology Effects Promoting Methane Emissions in an Indiana Co., Pennsylvania, Coal Mine**

C. Özgen Karacan, Office of Mine Safety and Health Research, National Institute of Occupational Safety and Health, USA

In this study, local geological and hydrological effects that lead to methane emissions observed in a coal mine in Indiana Co., Pa are investigated. Within the course of the study, structural and depositional properties of the area were evaluated to assess the complexity and sealing capacity of roof rocks. Gas content of the Lower Kittanning coal and geochemistry of ground water obtained from observation boreholes were studied to understand in-place gas content and potential effects of abandoned mines within the same area.

Detailed analyses suggested that the source of methane was likely the overlying seams such as the Middle and Upper Kittanning coals and Freeport seams of the Allegheny Group. Simulated groundwater water elevations, gradients of ground water flow and presence of recharge and discharge locations at very close proximity to the mine indicated that methane was carried with groundwater towards the mine entries where emissions were observed.

**Henry Fayol Who is a Mining Engineer in Administration Science**

Ümit Çepni, Ahmet Albayrak, İffet Ugur Kombe, Seçil Çolpan, Bahadır Uygur,  
Turkish Coal Enterprises, TURKEY

The main purpose of this study is infact to analyze administration education for engineers. Basic question is how we can work more effective. So what we can do! Years and years ago Fayol layed on emphasis of administration for engineers. In this study examined the contribution of Fayol as an engineer to management sciences. It is pointed engineering is required to be integrated with management education.

**Thar Coal: Dig or Skip**

Farid A. Malik, EMR – Consult; Abid Aziz, Pak motors (Pvt.) Ltd., PAKISTAN

While coal has been the fastest growing fuel in the world, Pakistan – with the world's 2<sup>nd</sup> largest deposits in Thar – has been unable to develop this resource effectively to meet its energy requirements. Numerous studies have been carried out by national and international experts and consultants and sufficient data is now available to move ahead with a clear roadmap on Thar coal resources utilization. However, a bankable feasibility is considered essential to pave the way for future development and foreign investment by global mining and fuel companies.

UCG approach has been tried but with limited homework. Hydrology and modeling considerations have to be taken into account together with safety consideration.

According to an Asian Development Bank's report, 80 percent challenge is of mining the coal for which the development or test pit is the most appropriate approach. Once the coal mining modalities have been resolved and we are able to sit on top of the coal field all un-defined issues of costs and risks will be addressed.

**SESSION 13**  
**Clean Coal Demonstration and Commercial Projects: Path Forward for CCUS**

**Commercialization of Carbon Sequestration Projects; Scaling from Research to Reality**

The Honorable Sherwood L. Boehlert, The Accord Group, USA

The concept of carbon capture and sequestration (CCS) has been embraced by scientists and policymakers around the globe and across the ideological spectrum. However, absent a commercialization demonstration and deployment at scale now of the successful utilization of CCS technology this promising concept will remain just that – a promising concept.

We believe that initiating a large scale commercial CCS project in China, focused on the capture and sequestration of CO<sub>2</sub> emitted from coal combustion, makes eminent sense for China and ultimately the International Community. There are a number of compelling factors that have led us to the conclusion that the future of CCS as a climate management tool is directly linked to the timely demonstration and deployment of CCS technology in China.

First, China has the fastest growing demand for energy in the world and is projected to lead the world in energy demand by the end of the century. Second, China has one of the planets largest coal reserves and will likely draw upon these reserves for decades to come. Third, China has a geologic profile favorable for the large scale sequestration of carbon. Fourth, China is under increasing international pressure to reduce green house

gas emissions. Fifth, China has a unified energy and regulatory process that will allow a commercial scale CCS project to move forward years sooner than in western countries. And Finally, China has a proven ability to commit the engineering and manufacturing resources necessary to carryout large scale energy projects.

Ultimately, the CCS technologies proven in China will find their way to CCS projects around the globe and that is why we believe that initiating CCS projects in China today makes eminent sense for the international community.

**SESSION 14**  
**Gasification: General – 3**

**Raman Spectroscopic Investigations into Links between Intrinsic Reactivity and Char Chemical Structure**

Daniel Roberts, Mark Kochanek, David Harris, Meijun Wang, CSIRO; Chun-Zhu Li, Curtin University of Technology, AUSTRALIA; Liping Chang, Taiyuan University of Technology, CHINA

There are a large number of factors affecting the gasification reactivity of chars, including physical structure (e.g. surface area and pore structure), catalytically-active mineral matter, and chemical structure which includes the extent of crystallinity of the carbonaceous matrix and also the nature of the functional groups that comprise the char structure. This work focuses on the latter, using Raman spectroscopy to investigate the relationships between intrinsic reactivity and char chemical structure. An Australian bituminous coal char and a Chinese lignite char were characterised in terms of their intrinsic reactivities with CO<sub>2</sub> and H<sub>2</sub>O (separately), under conditions where chemical processes control the observed reaction rates (Regime I). Unreacted and partially-reacted chars were characterised using Raman spectroscopy and gas adsorption for determination of chemical structure indicators and surface area respectively. Raman spectra suggested that the ratio of small to large aromatic rings decreased with increasing carbon conversion, and for the bituminous coal char, this seemed to be linked to the reactivity behaviour of chars made from the bituminous coal. The intrinsic reactivity of chars made from the lignite seemed to have a less significant correlation with Raman features, possibly due to the relative influence of catalytic activity of inorganic species.

**Catalytic Coal Gasification with *In Situ* Capture of CO<sub>2</sub> and H<sub>2</sub>S**

Nicholas Siefert, Dushyant Shekhawat, David Berry, DOE/NETL; Shawn Litster, Carnegie Mellon University, USA

We present experimental results from a fixed bed, catalytic, steam-coal gasifier. The catalysts were alkali hydroxides, calcium oxide, and calcium silicate. These catalysts chosen for their potential to capture carbon dioxide inside of the gasifier. Molten alkali hydroxides were the best catalysts as well as acid gas capture agents, producing a syngas rich in hydrogen (~80 percent) and methane (~20 percent) at an intermediate range of gasifier temperatures (700°C to 900°C). Proceeding in the absence of oxygen, this process converts alkali hydroxides into alkali carbonates and alkali sulfides, and the alkali species remain in the molten phase as catalysts for steam-gasification and methanation reactions. Calcium oxide captured carbon dioxide and hydrogen sulfide; however, since calcium oxide remains in the solid phase, it was not as good a catalyst as molten alkali hydroxide. Finally, calcium silicate was not a good catalyst and did not capture significant amounts of hydrogen sulfide or carbon dioxide. Parametric studies were conducted to understand the effects of temperature, pressure, steam flow rate, and catalyst-to-carbon ratio of the syngas production rate of the molten catalytic gasifier. These experiments were performed using both Pittsburgh #8 bituminous coal and Wyodak-Anderson sub-bituminous coal. To measure the amount and the rate of coal conversion to syngas, we have developed a method termed the Reduction Charge Remaining, which is a measure of the chemical oxygen demand remaining in the coal. The chemical oxygen demand remaining provides a better definition of fuel conversion than does weight remaining or carbon remaining because the chemical oxygen demand accounts for all of the main elements in the coal, such as C, H, O, S, and N. This COD definition of coal conversion is crucial for gasifiers with *in situ* capture of carbon and sulfur species. While the low-carbon and low-sulfur syngas leaving the gasifier could be sent directly to a gas turbine to generate electricity, the driving force for this research was generating high methane content syngas for fuel cell applications. Endothermic steam-methane reforming in the anode flow channels of solid oxide fuel cells (SOFCs) can reduce the amount of parasitic losses due to high air flow cooling rates to maintain the fuel cell temperature. Integrating catalytic coal gasifiers with SOFCs has been shown to have fuel-to-electricity conversion efficiencies greater than 60% [1-3].

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[3] Li, M., Rao, A. D., Brouwer, J., and Samuelsen, G. S., *J Power Sources*, 2010, **195**, 5707.

## Technological and Economic Evaluation of Large-Scale Coal-Based Polygeneration Concepts for Load Flexible Electricity Generation

Robert Pardemann, Kristin Boblenz, Lars-Erik Gärtner, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

During the last years, evaluation and development of new technologies for electricity generation from coal at lowest CO<sub>2</sub> emissions was a major scientific and industrial research task. One promising option with respect to efficiency and environmental impact was integrated coal gasification combined cycle (IGCC) technology with carbon capture and storage (CCS). However, studies (e.g. German COORIVA project) indicated high process complexity resulting in complicated process integration, low flexibility, limited availability and high electricity generation costs (also because of high cost of investment for equipment).

Taking into account changed conditions on the electricity market, different polygeneration routes were investigated to identify the potential for lower costs and flexible power generation by coupling of syngas based chemicals syntheses with a combined cycle power block. Synthesis processes included in this study are the production of methanol, Fischer-Tropsch liquids, and the Methanol-to-Gasoline synthesis. The power block was assumed as an E-class combined cycle. Two different entrained flow coal gasification concepts were implied for syngas provision, considering three world market coals (incl. Pittsburgh#8 coal, Wyodak (PRB) coal and Kuzbass semi-anthracite).

A technological process analysis proves the feasibility of peak electricity generation with respect to load flexibility. The maximum thermal efficiency (LHV based) is 54.5 % being much higher than for conventional power plants, as well. CO<sub>2</sub>-emissions were calculated to be in range of 400–670 kg/MWh(chemicals (LHV) + electricity). However, net investment of the investigated concepts (Thermic capacity: 1,633–1,900 MW(th, coal capacity)) was calculated to range from 1,300–2,300 EUR/kW(th, coal input). Consequently, electricity generation costs were estimated to be at least as high as for IGCC-CCS power plants. In contrast, specific production costs of the chemicals showed economic advantages for higher value products like olefins or transportation fuels in comparison to methanol, which is not a recommend polygeneration route. The concept evaluation also included the investigation of different peak electricity generation scenarios (1 h/d, 3 h/d, 6 h/d peak electricity generation) and a sensitivity analysis to identify the most important factors influencing the economic performance.

### Cleaner-Coal Technology to Reduce Climate Change

Alex Wormser, Wormser Energy Solutions, Inc., USA

Third-generation technology will be needed if IGCCs are to become competitive. New technology is being developed that seeks to provide electricity as cheaply with 90% carbon capture as conventional power plants do without it. In principal, IGCCs have this potential insofar as they combine an inexpensive power plant (a gas plant) with an inexpensive fuel (coal). The trick is to make the gasifier – with carbon capture – inexpensively enough.

Wormser Energy Solutions (WES), a Massachusetts engineering company, has been developing such a design since 2006. Its main intended use is to repower existing coal plants, either to renew aging plants that would otherwise be retired, or to increase the generating capacity.

WES's design is an airblown IGCC that eliminates the char fines by burning them in a new type of fluidized-bed gasifier. This eliminates the efficiency losses and costs of oxygen gasification, while also avoiding the difficulties of gasifying char fines experienced in previous airblown gasifiers. Other sources of cost reduction include novel coal handling and carbon capture systems. Additional savings come from the use of the RTI warm-gas cleanup system, and savings brought on by repowering. The new systems are all improvements on previously-tested designs, including the gasifier, which was first developed with DOE funding in the 1970's.

Together, the cost reductions drop the cost of a repowered plant with carbon capture to under \$2,000/kW (at 2010 overnight costs, in 2007 dollars.) This is at least 10% cheaper than the cost of a new coal plant without carbon capture. The plant efficiency is also high – 48% HHV without carbon capture, and 38% without it. These costs are likely to make an IGCC competitive at replacing the U.S.'s aging fleet of coal plants over the coming decades. Its low cost of captured CO<sub>2</sub> – of \$15 per tonne – will enable the U.S.'s enhanced oil recovery market to expand. The technology remains to be demonstrated.

### The Pilot Trial of Air-Blown Entrained Flow Coal Gasification

Haifeng Liu, Qingfeng Liang, Xiaolei Guo, Xin Gong, Zhenghua Dai, Jianliang Xu, East China University of Science and Technology, CHINA

Coal is the source of energy in almost every area of everyday life in China. The entrained flow gasification is the key technology in coal utilization for its high efficiency and low pollutant emission. Developing advanced and efficient entrained-flow coal gasification technology have wide application prospect in China, and it attracts many attentions from society. The opposed multi-burner (OMB) entrained-flow coal gasification fed with coal water slurry or pulverized coal has been developed by Institute of Clean Coal Technology (ICCT), ECUST. Based on the development

experiences on the OMB gasification technology, the pilot trial about air-blown entrained flow coal gasification was carried out during 2009-2011, the object of this work is to obtain the rule of air-blown entrained flow coal gasification.

A air-blown two-stage gasifier with dry feed for a handling capacity 2-4 ton coal per day was employed in pilot trial, the syngas leaves from the top of gasifier, whereas the slag leaves through the bottom of the gasifier. The design on two-stage air feeding form appropriate temperature distribution and ensure molten slag discharge in gasifier, in addition the low thermal conductivity membrane wall lining made operating procedure convenient. The pneumatic conveying system was employed to feed coal to the gasifier using air as carrier gas, the data on performance of dilute-phase high moisture pulverized coal pneumatic conveying system under low pressure would be achieved. The gasifier was operated at atmospheric pressure and the syngas temperature at the top of gasifier was about 800°C. The effects of the operating conditions including oxygen/coal ratio and oxygen concentration in air on gasification results were investigated, and the concentration of (CO+H<sub>2</sub>+CH<sub>4</sub>) in syngas reached up to about 32.65% (vol., dry basis) when oxygen concentration in air was 33%. The typical operating results in this plant such as (CO+H<sub>2</sub>) concentration were almost as good as those of some well known air-blown entrained-flow coal gasification plants.

## SESSION 15 Gasification: Gas Cleaning

### State Estimation of an Acid Gas Removal (AGR) Plant as Part of an Integrated Gasification Combined Cycle (IGCC) Plant with CO<sub>2</sub> Capture

Prokash Paul, Debangsu Bhattacharyya, Richard Turton, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

An accurate estimation of process state variables not only can increase the effectiveness and reliability of process measurement technology, but can also enhance plant efficiency, improve control system performance, and increase plant availability. Future integrated gasification combined cycle (IGCC) power plants with CO<sub>2</sub> capture will have to satisfy stricter operational and environmental constraints. To operate the IGCC plant without violating stringent environmental emission standards requires accurate estimation of the relevant process state variables, outputs, and disturbances. Unfortunately, a number of these process variables cannot be measured at all, while some of them can be measured, but with low precision, low reliability, or low signal-to-noise ratio. As a result, accurate estimation of the process variables is of great importance to avoid the inherent difficulties associated with the inaccuracy of the data. Motivated by this, the current paper focuses on the state estimation of an acid gas removal (AGR) process as part of an IGCC plant with CO<sub>2</sub> capture. This process has extensive heat and mass integration and therefore is very suitable for testing the efficiency of the designed estimators in the presence of complex interactions between process variables. The traditional Kalman filter (KF) (Kalman, 1960) algorithm has been used as a state estimator which resembles that of a predictor-corrector algorithm for solving numerical problems. In traditional KF implementation, good guesses for the process noise covariance matrix (**Q**) and the measurement noise covariance matrix (**R**) are required to obtain satisfactory filter performance. However, in the real world, these matrices are unknown and it is difficult to generate good guesses for them. In this paper, use of an adaptive KF will be presented that adapts **Q** and **R** at every time step of the algorithm. Results show that very accurate estimations of the desired process states, outputs or disturbances can be achieved by using the adaptive KF.

### Poison Resistant Water-Gas-Shift Catalyst

Grish Srinivas, Steven C. Gebhard, William Spalding, 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. Unfortunately, the catalysts currently used to convert syngas from the coal-biomass gasifier are poisoned by compounds that originate in the biomass and coal. Thus, developing poison-resistant catalysts will advance coal/biomass-to-liquids (CBTL) technology and carbon-free integrated gasification combined cycle power generation (CF-IGCC).

The water gas shift reaction ( $CO + H_2O = CO_2 + H_2$ ) is used to convert CO in synthesis gas to hydrogen (CO<sub>2</sub> removal can be removed and sequestered if desired), and is an important step in all synthetic fuels processes. Hydrogen sulfide (H<sub>2</sub>S) is formed during coal gasification due to the presence of organic and inorganic sulfur compounds, and since H<sub>2</sub>S irreversibly poisons conventional low-temperature copper-based WGS catalysts, molybdenum-based, sulfur-tolerant, water gas shift (WGS) catalysts are widely used. Unfortunately, existing sulfur tolerant WGS catalysts must be operated at higher temperatures than conventional copper-based WGS catalysts, and this reduces the hydrogen yield because the WGS equilibrium is favored by lower temperatures. In addition, biomass gasification can produce contaminants that are not commonly found when using coal alone. Herbaceous biomass in particular, contains high levels of potassium and chlorine, and work at the National Renewable Energy Laboratory has shown that KOH, KCl and KOCN are released into the vapor phase at

high temperatures. Consequently synthesis gas derived from the co-feeding biomass and coal can contain a mixture of contaminants whose identities and concentrations depends on the amounts and types of coal and biomass in the feed.

TDA Research Inc. (TDA) has developed a sour WGS catalyst that is as active as conventional copper-based, low temperature water gas shift catalysts, and is not poisoned by sulfur, potassium compounds, or other contaminants present in syngas produced during the co-gasification of coal and biomass. Since our catalyst can operate at lower temperatures, it converts more CO to hydrogen, and improves the energy efficiency and economics of CBTL and IGCC plants. TDA's new low-temperature sour WGS catalyst is specifically designed to be used as a drop-in replacement for existing catalysts in sour service.

In this presentation and its accompanying paper, we report on recent work investigating the effects of potassium compounds and other poisons on the performance of our new low temperature, sulfur-tolerant WGS catalyst. In particular, we are investigating the effects of contaminants that can be present in syngas derived from mixtures of different types of coal and biomass on catalyst activity, selectivity and lifetime. Finally, our new WGS catalyst can be used in other gasification or partial oxidation applications that use coal, petcoke, tar-sand bitumen, heavy hydrocarbons, and similar feedstocks in petroleum refineries, petrochemical plants, methanol and ammonia plants, and stationary power plants.

#### **Advanced Acid Gas Separation Technology for the Utilization of Low Rank Coals**

Jeffrey R. Hufton, Robert Quinn, Amy Fabrice, Jeffrey W. Kloosterman, Ellen M. O'Connell, Air Products and Chemicals; Grant Dunham, Michael Swanson, University of North Dakota Energy and Environmental Research Center, USA

Air Products has developed a potentially ground-breaking technology – Sour PSA – to replace the solvent-based AGR systems currently employed to separate sulfur containing species, along with CO<sub>2</sub> and other impurities, from gasifier syngas streams. The Sour PSA technology is based on adsorption processes that utilize pressure swing or temperature swing regeneration methods. The performance of Air Products Sour PSA with feed gas generated from the gasification of lower rank PRB coal has been the focus of recent efforts. An experimental program has been conducted with the Energy and Environmental Research Center (EERC) to characterize the performance of a simple two-bed PSA/TSA system. It was operated with sour syngas generated from EERC's fluidized bed gasifier utilizing Montana Rosebud PRB coal under oxygen-blown conditions. The results of this testing were used to prepare a techno-economic assessment to predict the benefits of incorporating Sour PSA technology into a base 90% CO<sub>2</sub> capture IGCC power plant design utilizing low rank coal. The experimental and techno-economic results will be discussed.

#### **Advanced Gasification Process Demonstration: Fuel Upgrading, Warm-Gas Cleanup, and Hydrogen Separation Membranes**

Joshua J. Stanislawski, Michael L. Swanson, Tyler J. Curran, Scott G. Tolbert, University of North Dakota Energy & Environmental Research Center; Al Bland, University of Wyoming; Kumar Sellakumar, ETAA Energy, Inc., USA

Cost-effective CO<sub>2</sub> separation is a significant technical hurdle, with a potential increase of up to 84% in the cost of electricity produced for existing pulverized coal-fired power plants with retrofit carbon capture. Therefore, novel approaches to the problem are required, including fuel upgrading and hydrogen separation membranes. Fuel-upgrading technologies improve the efficiency of the plant and reduce the overall CO<sub>2</sub> footprint. Efficient and cost-effective membranes for the separation of hydrogen and CO<sub>2</sub> represent a potential cost-effective method for the coproduction of power, hydrogen, and/or fuels and chemicals while leaving CO<sub>2</sub> available for enhanced oil recovery. Significant progress has been made over the past decade in producing membranes that can effectively separate hydrogen from the syngas stream, leaving a relatively pure stream of CO<sub>2</sub> available at high pressure for sequestration.

The Western Research Institute's (WRI's) patent-pending heat treatment process for removing moisture and Hg from coal is a promising technology for applying higher-moisture coals to gasification technologies. WRI's process subjects the coal to heat in a two-stage process in a near-inert atmosphere. During the first stage, the coal is heated to 250°–280°F to remove moisture. The second stage involves heating the coal from 250° to 550°F to volatilize mercury and potentially other trace metals. Warm-gas cleanup techniques have been shown to improve the economics of coal gasification plants, and since mercury is challenging to remove from syngas at elevated temperatures, any technology that can remove it before gasification is beneficial.

Hydrogen separation membrane development to date has occurred mainly on simulated mixtures of syngas. Impurities from coal-derived syngas that could poison a hydrogen separation membrane include H<sub>2</sub>S, COS, NH<sub>3</sub>, CO, and HCl. Long-term success of hydrogen separation membranes will require long-term exposure to coal-derived syngas to understand the impact of the impurities. While the majority of the impurities will be removed in a gas cleanup process, concentrations to less than

1 ppmv may be required for long-term viability.

The Energy & Environmental Research Center (EERC) and WRI recently completed a project to evaluate the performance of upgraded subbituminous and lignite coals in the EERC's transport reactor demonstration unit (TRDU). This gasifier fires nominally 200–500 lb per hour of fuel and is the pilot-scale version of the full-scale gasifier currently being constructed in Kemper County, Mississippi. A slipstream of the syngas was used to demonstrate warm-gas cleanup and hydrogen separation using membrane technology. Two membranes were exposed to coal-derived syngas, and the impact of

coal-derived impurities was evaluated. This paper reviews the performance of WRI's upgraded coal in the EERC's TRDU and presents the results of the warm-gas cleanup and hydrogen separation tests. The potential efficiency improvements as compared to conventional technologies are also reviewed.

#### **On the Use of Zinc Oxide Absorbent for Sulfur Emissions Control in GTI's Pilot-Scale Gasification Facilities**

Rachid B. Slimane, Bruce G. Bryan, Andrew Kramer, James Aderhold, Patrick Bishop, Gas Technology Institute, USA

GTI, with over 50 years of gasification and related systems development history, has in the last several years developed state-of-the-art pilot-scale facilities with wide-ranging capabilities. This complex, in Des Plaines, Illinois (a suburb northwest of Chicago), started with the design, construction, and commissioning in 2004 of the Flex-Fuel Test Facility (FFTF), which houses a fluidized-bed gasifier (up to 6 MW<sub>th</sub> input) with associated syngas cleaning and conditioning systems prior to gas flaring. The FFTF was then expanded by the addition of the Advanced Gasification Test Facility (AGTF), which houses several gas treatment reactors including catalytic tar reforming, syngas cooling, and scrubbing, as well as separate bays dedicated to advanced gasification and syngas conversion technologies. FFTF expansion has also included the relocation and installation of a pilot-scale facility for acid gas removal (e.g., Morphosorb<sup>®</sup>) with associated sulfur scavengers, and the upgrading of support systems such as high-pressure oxygen supply and automated fines removal lockhoppers. Work is currently under way to add additional capability to condition the scrubbed syngas (compression and treatment in the AGR unit) and to purify it further such that it becomes suitable for processing in a liquid fuel synthesis process, Haldor-Topsøe's TIGAS for the production of gasoline. Test campaigns lasting for as long as 30 days are planned, which will utilize essentially all pilot-scale units in an integrated fashion, to produce approximately 22.5 barrels of gasoline per day from forest residues. GTI's facilities are also fitted with innovative sample extraction and conditioning systems and state-of-the-art instrumentation that enable comprehensive, real-time performance assessment of the various unit operations.

These facilities have been used successfully to evaluate feasibility of efficiently gasifying high-ash coals, to demonstrate operability and performance of advanced gasifier designs, to confirm large-scale performance of an innovative syngas ultra-cleaning process, and to develop commercial design data for several biomass conversion technologies into various end products including bio-diesel, synthetic natural gas (SNG), and gasoline. In each case testing was completed under conditions ensuring that environmental emissions compliance requirements were met. While sulfur control in some of these projects is embedded in the gas treatment section downstream of the gasifier, as part of the overall process scheme, in other cases sulfur control had to be developed separately as an add-on system. No more was this needed than in the PWR Advanced Gasifier development project, which used high-sulfur fuels and at significantly higher throughputs. As part of this project GTI evaluated several approaches and decided on the implementation of a high-temperature desulfurization approach relying on the use of commercially-available zinc oxide absorbent as a sulfur scavenger material capable of handling the limitations imposed by the expected raw product gas composition (high CO and moisture content) and providing the flexibility required for the planned tests.

This paper reports on GTI's ZnO-based sulfur emissions control approach and the experience gained from several test campaigns completed over approximately 18 months of Advanced Gasifier testing with Illinois coal and petroleum coke. We will describe the technical basis for selecting the ZnO absorbent used (Süd-Chemie's Actisorb S2, 4.5 mm diameter extrudates) and integration of the sulfur removal unit operation in the overall test configuration, material performance, operating experience including efforts to maximize utilization of the material for sulfur removal, and interactions with the manufacturer to further understand and resolve some of the challenges encountered in tailoring their product for this demanding application. Non-proprietary examples of test results will be provided to support these evaluations.

#### **Integrated Hot and Cold Synthesis Gas Clean-Up**

Parvana Aksoy, Isil Isik-Gulsac, Orcun Er, Alper Sarioglan, Siringul Ay, Ersin Uresin, Aykut Argonul, Yeliz Cetin, Fehmi Akgun, TUBITAK Marmara Research Center; Husnu Atakul, Istanbul Technical University, TURKEY

It is generally accepted that gasification of coal is the most promising route for clean utilization of coal for different applications. The gasification process converts coal and other feedstocks into synthetic raw gas suitable for different utilization areas such as production of electricity, value-added chemicals and liquid fuels. However, coal-derived synthesis gas contains harmful contaminants which need to be removed. The sulfur removal is a must prior to utilization of the gasification products either as a fuel for gas turbines, gas engines or fuel cells or as a synthesis gas for Fischer-Tropsch synthesis, ammonia or methanol productions. Hydrogen sulfide and other sulfur compounds can cause corrosion in pipelines thus limit the plant lifetime. Hydrogen sulfide is also a well-known catalyst poison. For these reasons, it is necessary to reduce the H<sub>2</sub>S concentration around one ppmv level.

A semi-pilot scale bubbling bed gasification system equipped with hot and cold synthesis gas (syngas) clean-up units has been installed at Energy Institute of

TUBITAK MAM. This system has been used for coal derived syngas clean-up purposes. A pilot scale pressurized bubbling fluidized bed gasification system is also current being developed by TUBITAK MAM. By using a combination of various techniques, we have already been able to we reduced the H<sub>2</sub>S content of syngas below 1 ppmv level. The ongoing research efforts will be described in this paper with a particular focus on sulfur compounds removal.

High temperature desulfurization performance of dolomite for coal derived syngas was investigated in this study. The results indicated that dolomite can be active in sulfur removal at the temperatures higher than 750°C. However, due to the thermodynamic equilibrium conditions, H<sub>2</sub>S clean-up was limited to around 150-200 ppmv in presence of water vapor. The presence of water vapor in the dolomite bed seemed to inhibit sulfidation reactions. On the other hand, the presence of CO<sub>2</sub> in the gas stream did not have a suppressing effect on sulfidation reactions, whereas, it tended to depress the calcination of CaCO<sub>3</sub> to CaO.

## SESSION 16

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

#### Direct Power Extraction with Oxy-Combustion: An Overview of Magnetohydrodynamic Research Activities at the NETL-Regional University Alliance (RUA)

C. Rigel Woodside, Kent H. Casleton, E. David Huckaby, Thomas Ochs, Danylo Oryshchyn, George Richards, Peter A. Strakey, Jeremy Pepper, DOE/NETL; Ismail B. Celik, Jose Escobar-Vargas, West Virginia University; Daniel C. Haworth, NETL-RUA and The Pennsylvania State University; Osama A. Marzouk, DOE/NETL and WVURC; Xinyu Zhao, The Pennsylvania State University, USA

In conventional oxy-fuel power generation scenarios, oxy-fuel combustion provides no significant advantage other than to simplify CO<sub>2</sub> capture. So in terms of power production and efficiency, the energy and costs required to produce that oxygen are a burden. However, the high temperatures possible with oxy-fuel combustion can enable direct electric power extraction from high-temperature electrically-conductive gases using magnetohydrodynamic (MHD) principles, which would then be followed by a steam cycle also producing electricity. The combined system would produce a high CO<sub>2</sub> exhaust stream - yet with efficiency that may exceed today's best coal power systems. The concept of adding an MHD topping unit to a coal fired power plant in order to directly extract electrical power is not new, and significant effort was made in this direction from about 1973 to 1993. During this time period, it was shown the MHD concept worked in the sense that power was generated, but ultimately development was discontinued due to the high cost of designing, constructing, and operating a complete MHD-steam plant. Additionally, there were a number of technical challenges associated with the technology. Some specific issues cited for coal MHD were slag removal problems, MHD channel operation problems, and cost effectiveness of seed utilization. In this paper, we revisit the use of MHD technology in the context of using it with oxy-combustion to enable cost effective carbon capture. Ongoing research activities within the National Energy Technology Laboratory – Regional University Alliance (NETL-RUA) to address legacy MHD power challenges, and apply new computational tools to MHD power systems are presented. Much has changed since earlier MHD studies: oxygen supplies have become less expensive (because of interest in oxy-fuel for CO<sub>2</sub> control). Superconducting magnets have improved substantially. Perhaps the most dramatic technological improvement since previous MHD efforts is in the area of computational modeling. Today, we have three dimensional multi-physics models that could be utilized to design a more effective system (combustor and generator). To begin addressing the combustion issue, current work applies transported probability density function methods to solve the high-temperature combustion problem. An MHD generator model, which considers fluid dynamics and heat transfer, as well as relevant MHD equations involved in the process, is presented. The modeling efforts also address issues in using wall functions to bridge the laminar sublayer to the fully turbulent boundary layer when Lorentz force is dominant or equally important as compared to other forces.

#### Challenges of Naturally-Occurring Ilmenite for Chemical Looping Processes

Elena Chung, Deepak Sridhar, Siwei Luo, Zhenchao Sun, Ankita Majumder, Liang Zeng, Liang-Shih Fan, The Ohio State University, USA

Chemical looping processes (CLP) have the potential to efficiently utilize the indigenous abundant carbonaceous fuels such as coal in an environment-friendly manner. The CLP utilize an oxygen carrier particle to indirectly convert carbonaceous fuels while capturing the CO<sub>2</sub> byproduct for sequestration. The oxygen carrier particles loop between two reactors, namely the reducer and the combustor, to accomplish complete fuel conversion and oxygen carrier regeneration, respectively. Over the past two decades, this transformative process has resulted in the global development of the chemical looping technology.

The CLP process can be widely categorized into two types of chemical looping systems based on the mode of operation of the reducer or fuel reactor. The widely practiced reactor configuration involves utilization of a fluidized bed reactor operation mode for the reducer. On the other hand, at the Ohio State University (OSU), CLP systems using a unique counter current moving bed reactor mode have been extensively demonstrated under various scales from bench-scale to sub-pilot scale units for gaseous and solid fuels. The Syngas Chemical Looping process developed for gaseous fuels and Coal Direct Chemical Looping process developed for solid fuels have been demonstrated in the sub-pilot scale that elucidate the increased extent of oxygen carrier conversion observed in moving bed reactors as compared to the extents for fluidized bed reactors. The mode of reducer reactor operation presents unique requirements on the oxygen carrier.

The demonstrations in both the modes of reducer operation have revealed the requirement of large quantities of oxygen carriers to be used in a commercial CLP system. Additionally, the attrition associated with the oxygen carrier looping within the system and the deactivation associated with using solid fuels is expected to increase the inventory of oxygen carriers required. For this purpose, the use of naturally-occurring minerals such as ilmenite, an iron titanium ore, present an attractive alternative for oxygen carrier particles for CLP as it is abundant and inexpensive as compared to synthetically-engineered iron oxide-based particles. Recent studies have demonstrated the potential for utilizing ilmenite in terms of reactivity, recyclability, and oxygen carrying capacity for CLP.

This presentation will discuss the challenges associated with naturally-occurring minerals such as ilmenite as oxygen carriers for CLP systems, with specific focus on the mode of operation of the reducer reactor. The reaction chemistry of the ilmenite during CLP will be presented in detail. Experimental results of ilmenite for CLP systems will be summarized and discussed. Finally, the potential of ilmenite for scale-up CLP units will be highlighted.

#### Near Field Aerodynamics Effects of Pure O<sub>2</sub> Injection in Co-Axial Oxy-Coal Turbulent Diffusion Flames

Dadmehr M. Rezaei, Eric G. Eddings, Kerry E. Kelly, Jost O.L. Wendt, University of Utah, USA

Oxy-coal combustion allows the concentration of oxygen in each burner stream to be controlled as an independent variable. Input concentrations of oxygen and the way it is injected can have significant impacts on the turbulent mixing and flame stability in coaxial turbulent jets. Whereas previous studies have quantified the effects on flame stability of partial pressure of oxygen in primary and secondary streams in coaxial oxy-coal burners, this research focuses on triple concentric coaxial oxy-coal burners, with a view to determining flame stability effects of adding as much oxygen as possible in a pure oxygen stream, located either in the middle annulus, with coal/CO<sub>2</sub> in the center and O<sub>2</sub>/CO<sub>2</sub> in the outside, or in the center tube, surrounded by annular coal/CO<sub>2</sub>, and O<sub>2</sub>/CO<sub>2</sub> streams. Flame stability was quantified by flame probability density functions (PDF) of the stand-off distance, which were determined using photo-imaging techniques developed in previous work. PDF's of flame length were also obtained. Experiments were conducted in a systematic way so that differences caused by stream composition changes alone could be explored, keeping velocities constant. The PDF's obtained from these simplified prototype configurations can be used for simulation validations, and also lead to physical insight into flame stabilization mechanisms. For example, flame stand-off distances for flames with pure oxygen in the center annulus are more attached than those with oxygen in the center pipe. This result is consistent with a physical picture of coal jet attachment mechanisms in which fine particles that are the key to ignition, are transported radially outward by large turbulent eddies, passing through the pure oxygen stream when that is in the middle annular position, but away from the pure oxygen stream when that is at the center pipe.

#### Effect of SO<sub>2</sub> and Steam on Chemical Looping Combustion of Coal with Iron and Copper Oxygen Carriers

Hanjing Tian, Tom Simonyi, URS/DOE/NETL; Ranjani Siriwardane, DOE/NETL, USA

Chemical-looping combustion (CLC) is a novel combustion technology that utilizes an oxygen carrier, such as metal oxide, to transport oxygen from the air to the fuel, thereby avoiding direct contact between fuel and air. The significant advantage of CLC over conventional combustion is that CLC can produce a sequestration-ready carbon dioxide (CO<sub>2</sub>) stream—not diluted by nitrogen (N<sub>2</sub>)—without expending any major energy required for the separation of CO<sub>2</sub>. The objective of this work was to investigate the effect of SO<sub>2</sub> and steam on the reaction performance of direct coal CLC with copper and iron oxide as oxygen carriers.

Thermogravimetric analysis (TGA) was conducted to investigate the effect of SO<sub>2</sub> on coal CLC with CuO and Fe<sub>2</sub>O<sub>3</sub> as oxygen carriers. Combustion performances of every sample were evaluated in the presence of SO<sub>2</sub> at three different concentrations in N<sub>2</sub>: 0%, 1.5% and 3% SO<sub>2</sub>. In the absence of SO<sub>2</sub>, coal and CuO reacted at 790 °C. When the reaction was conducted at similar conditions but in the presence of 3% SO<sub>2</sub>, the reactions were observed at 793 and 873 °C indicating that there are two types of combustion reactions. It was also observed that the presence of SO<sub>2</sub> during the reduction also contributed to the increase in oxidation reaction rate during the



subsequent oxidation step, but did not change total oxygen uptake. The reaction profile changes due to SO<sub>2</sub> with the oxygen carriers will be discussed in this paper.

Bench scale fixed bed reactor tests were conducted to investigate the effect of steam on coal CLC reaction with Fe<sub>2</sub>O<sub>3</sub> and 60% CuO-20% Fe<sub>2</sub>O<sub>3</sub>/20% Al<sub>2</sub>O<sub>3</sub> oxygen carriers. The reduction performance of every sample was evaluated under three different steam concentrations in N<sub>2</sub>: 0%, 15%, and 20% steam. Without steam, the combustion temperature of coal and Fe<sub>2</sub>O<sub>3</sub> was at 997 °C but the addition of steam decreased the peak reaction temperature significantly: The reaction temperatures were 771 °C with 15% steam and 760 °C with 20% steam.

**SESSION 17**  
**Carbon Management: CO<sub>2</sub> Capture – 2**

**Pre-Combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process**

S. James Zhou, Howard Meyer, Gas Technology Institute; Ben Bikson, Yong Ding,  
PoroGen Corporation, USA

This paper summarizes the membrane contactor technology development status for pre-combustion carbon capture. Our objective is to develop a practical and cost effective technology for CO<sub>2</sub> separation and capture for pre-combustion coal-based gasification plants using a membrane contactor/solvent absorption process. The goals of this technology development work are to separate and capture at least 90% of the CO<sub>2</sub> from Integrated Gasification Combined Cycle (IGCC) power plants with less than 10% increase in the cost of energy services.

Gas Technology Institute (GTI) and PoroGen Corporation (PGC) have developed a novel hollow fiber membrane technology that is based on chemically and thermally resistant commercial engineered polymer poly(ether ether ketone) or PEEK. The PEEK membrane material used in the membrane contactor during this technology development program is a high temperature engineered plastic that is virtually non-destructible under the operating conditions encountered in typical gas absorption applications. It can withstand contact with most of the common treating solvents. GTI and PGC have developed a nanoporous and superhydrophobic PEEK-based hollow fiber membrane contactor tailored for the membrane contactor/solvent absorption application for syngas cleanup. The membrane contactor modules were scaled up to 8-inch-diameter commercial-size modules. We have performing extensive laboratory and bench testing using pure gases, simulated water-gas-shifted (WGS) syngas stream, and a slipstream from a gasification-derived syngas from GTI's Flex-Fuel Test Facility (FFTF) gasification plant under commercially relevant conditions. The team have also carried out an engineering and economic analysis of the membrane contactor process to evaluate the economics of this technology and its commercial potential.

Our test results have shown that 90% CO<sub>2</sub> capture can be achieved with several physical solvents such as water and chilled methanol. The rate of CO<sub>2</sub> removal by the membrane contactor is in the range of 1.5 to 2.0 kg/m<sup>2</sup>/hr depending on the operating pressures and temperatures and depending on the solvents used. The final economic analysis has shown that the membrane contactor process will cause the leveled cost of electricity (LCOE) to increase by 21% from the base plant without CO<sub>2</sub> capture. The 21% increase in LCOE is a substantial improvement as compared with the 31.6% increase in LCOE as in DOE Case 2 (state of art capture technology using two stages of Selexol™).

**Separation Work and the Thermodynamics of CO<sub>2</sub> Capture**

Hugo S. Caram, Lehigh University and ExxonMobil Research and Engineering; Hans Thomann, Ramesh Gupta, Walt Weissman, ExxonMobil Research and Engineering,  
USA

The work presented here applies to processes where the separation process involves a first step of capturing the gas to be separated followed by stripping in a second step. The concept can be applied to absorption, chemical reaction, or a combination of them. Of specific interest are the processes used for the separation of CO<sub>2</sub> from flue gases. Among the many possibilities these will include liquid absorption cycles, mostly amine based and chemical looping using calcium oxide or sodium carbonate-bicarbonate. While the capture process occurs spontaneously, stripping and regeneration of the solvent that releases the purified gas requires energy addition. Given the large scale of these processes it is of interest to minimize the energy requirements. For liquid processes the heat provided to the stripper reboiler may be responsible for up to 80% energy requirements of the gas capture operations. It is then important to develop a conceptual understanding of the factors affecting its energy consumption. They include, among others, rich and lean loadings, stripper pressure, energy losses in cross flow heat exchangers and the type of solvent. It is expected that this model will do that and provide at lower bound for the energy consumption. The analysis will address the minimum separation work from a liquid solvent and its relation to the minimum separation from an ideal gas mixture. It will provide a clear criteria for liquid solvent selection and will be used in a simplified model to predict reboiler duties in a stripper. The results will be compared with reported experimental and industrial results.

**Performance and Cost Analysis of Post-Combustion CO<sub>2</sub> Capture Using Calcium Looping Process for Coal-Fired Power Plants**

Hari Chandan Mantripragada, Edward S. Rubin, Carnegie Mellon University, USA

Ca-looping (CaL) process utilizes the reversible chemical reaction between CaO and CO<sub>2</sub> in order to capture CO<sub>2</sub> from gaseous streams. CO<sub>2</sub> in a gas stream reacts with CaO in an exothermic carbonation reaction to form CaCO<sub>3</sub>, at a temperature close to 650°C. The product CaCO<sub>3</sub> from the carbonator is then sent to a separate vessel called calciner where the calcination reaction takes place, releasing high purity CO<sub>2</sub>, which can be sent to sequestration. CaO is sent back to carbonator to complete the loop. This approach has been widely proposed and tested by various researchers for post-combustion CO<sub>2</sub>-capture from the flue gas of a coal-fired boiler. The CaL technology for CO<sub>2</sub>-capture has the potential to be less energy intensive and more economical than a conventional post-combustion CO<sub>2</sub>-capture process using amines.

Most of the studies dealing with CaL CO<sub>2</sub> capture assume the use of pressurized fluidized bed combustors (PFBC) as the boiler technology of the base plant. However, since a majority of the boilers in the US use pulverized coal (PC) technology, a CO<sub>2</sub>-capture system which can be retrofitted to existing power plants is of more relevance. In this paper, the performance and cost characteristics of retrofitting a CaL process for post-combustion CO<sub>2</sub> capture from existing PC power plants is studied.

Performance models are developed to conduct a detailed thermodynamic analysis of a PC power plant with a CaL CO<sub>2</sub>-capture process. Oxy-combustion of coal within the calciner is proposed in many studies as a source of heat for the calcination reaction which needs a high temperature of close to 900°C. Different plant configurations will be developed with different heat integration schemes within the plant that can reduce the heat supply from the expensive oxy-combustion process in the calciner. Since limestone is also used in a flue gas desulfurization (FGD) system to capture SO<sub>2</sub> from the flue gases, the synergy between FGD and the CaL processes will also be studied. The possibility of co-capturing CO<sub>2</sub> and SO<sub>2</sub> in the same system will also be analyzed, from a thermodynamic perspective. The effects of varying operating parameters such as temperature and CO<sub>2</sub> partial pressure and sorbent properties such as loss of reactivity due to repeated cycling, on plant efficiency are studied for each of the plant configurations. Results from the performance models will be used to calculate the capital cost (\$/kW) and operating costs (\$/MWh) of the power plant. Sensitivity and probabilistic uncertainty analysis are also performed in order to understand the effect of uncertainties in process and cost parameters. The results from this techno-economic analysis are compared to a power plant with amine-based (MEA or advanced amines) CO<sub>2</sub>-capture technology, using the Integrated Environmental Control Model (IECM) developed at Carnegie Mellon University.

This work is supported under a contract from the U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL).

**Advanced CO<sub>2</sub> Capture Technology for IGCC Systems**

Gökhan Alptekin, Ambalavanan Jayaraman, Michael Cesario, Amanda Parker, TDA Research, Inc., USA

TDA is developing a novel sorbent that removes CO<sub>2</sub> via physical adsorption from synthesis gas; the relatively strong affinity of the sorbent to CO<sub>2</sub> enables effective operation at temperatures up to 300°C (well above the dew point of synthesis gas stream generated by most commercial gasifiers). However, because the sorbent and the CO<sub>2</sub> do not form a true covalent bond, the energy needed to regenerate our sorbent (4.9 kcal per mol of CO<sub>2</sub>) is much lower than that observed for either chemical absorbents (e.g., 29.9 kcal/mol CO<sub>2</sub> for sodium carbonate) or amine-based solvents (e.g., 14.2 kcal/mol CO<sub>2</sub> for monoethanolamine). Our sorbent can be regenerated isothermally and that CO<sub>2</sub> can be recovered at pressure (~150 psia). Thus, the energy needed to regenerate the sorbent and compress the CO<sub>2</sub> for sequestration is significantly lower than that for any technology reported to date. TDA's CO<sub>2</sub> sorbent could be used to capture CO<sub>2</sub> in an Integrated Gasification Combined Cycle (IGCC) power plant after the water-gas-shift (WGS) reaction or could also be used in combination with the WGS catalyst to replace the second and/or the third stage WGS. This integrated Water Gas Shift (WGS) catalyst/CO<sub>2</sub> sorbent can capture over 90% capture of the CO<sub>2</sub> emissions with much lower increase in the cost of electricity (COE) than Selexol based systems.

We carried out bench-scale evaluations of the integrated WGS catalyst/CO<sub>2</sub> sorbent in a fixed-bed adsorber. The sorbent achieved a high CO<sub>2</sub> working capacity of 6 to 8% wt. CO<sub>2</sub> and while converting the entire CO into CO<sub>2</sub>. We are optimizing the catalyst to sorbent ratio and will carry out a 1,000 cycle durability test. The sorbent has been previously shown to have excellent durability (over 10,000+ cycles) in the bench scale testing and demonstrated in a slipstream of coal-derived synthesis gas at the National Carbon Capture Center (NCCC) in Wilsonville, AL. We are scheduled to carry out the demonstration of the integrated WGS catalyst/CO<sub>2</sub> sorbent in July-September 2012. Our results will feed into a techno-economic analysis that is consistent with DOE/NETL Cost Estimation Guidelines. We will use Aspen Plus™ software to estimate the impact of the integrated WGS catalyst/CO<sub>2</sub> capture system on the thermal efficiency of the plant and COE. The results from this DOE sponsored work will be presented at the meeting.

## Development of ReaxFF Force Field for Carbon Dioxide Capture with Ionic Liquids: A Combined First Principles and Classical Simulation

Bo Zhang, J. Karl Johnson, University of Pittsburgh/DOE/NETL, USA

Ionic liquid (IL) are salts in the liquid state below 100°C. The number of ions that can form IL is well over tens of thousands. ILs are considered as promising materials for CO<sub>2</sub> capture due to their wide liquid range, negligible vapor pressure, thermal and chemical stability, and the ability to tailor the interaction with CO<sub>2</sub> through choosing appropriate ions. We are exploring ILs that can capture CO<sub>2</sub> through chemical reactions and physical interactions via first principles and classical simulation techniques. Our goals are to understand the mechanism of IL and CO<sub>2</sub> interaction, to develop a new force field that will capture both the physical interactions and chemical reactions, and to calculate the thermodynamic and transport properties of bulk and confined IL with CO<sub>2</sub> via large-scale simulations. These simulations will be used to accelerate the design of new ILs that have tailored interactions and acceptable viscosities for pre-combustion CO<sub>2</sub> capture processes. We use the ReaxFF formalism for describing the physical and chemical interactions in the IL-CO<sub>2</sub> system. ReaxFF has been proven to be a very successful formalism for modeling chemical as well as physical interactions with an empirical approach. [P(C<sub>4</sub>)<sub>4</sub>][Gly] is chosen as a model IL to elucidate the interactions between ILs and CO<sub>2</sub>. Two possible interaction sites have been identified with first principles molecular dynamics (MD) simulations. One is the -NH<sub>2</sub> center and the other one is the -CO<sub>2</sub><sup>-</sup> center, both on the [Gly] anion. The calculated binding energy and CO<sub>2</sub> angle distribution indicate that the interaction with the amine center is a chemical type interaction and the interaction with carboxylic group appears to be a complicated weak chemical interaction. The reaction between CO<sub>2</sub> and -NH<sub>2</sub> has been identified as a two-step reaction mechanism. The first step involves a proton transfer with barrier height of about 1 kcal/mol, and the second step is mainly a libration motion, also leading to a proton transfer, with barrier height around 2.3 kcal/mol. The reaction pathways along with other data, including bond-energies, angle-energies, torsion angle-energies have been compiled into a training set to parameterize the ReaxFF force field. The force field is optimized against the calculated structure-energy relationships. With the optimized force field, the model IL [P(C<sub>4</sub>)<sub>4</sub>][Gly] interacting with CO<sub>2</sub> has been studied through large scale MD simulations. The thermodynamic and transport properties have been computed.

## Mg-CaCO<sub>3</sub> Double Salt Absorbents for CO<sub>2</sub> Removal at 300-500°C

Xiaohong Shari Li, David King, Liyu Li, Pacific Northwest National Laboratory;  
Haobo Chen, Arizona State University; Keling Zhang, Prabhakar Singh, University of Connecticut; Yuhua Duan, DOE/NETL, USA

CO<sub>2</sub> absorbents with high capacity and high stability, which can be used at a temperature range of 300 to 500 °C for CO<sub>2</sub> removal, are highly desired because the cooling/heating treatments of the syngas stream can be eliminated, and the thermal efficiency is expected to be improved; also CO<sub>2</sub> removal at this temperature range can be used to facilitate equilibrium-restricted processes, e.g. water-gas-shift reaction. When integrated with water-gas-shift reactions, it is possible to directly produce high purity hydrogen from coal. However, no practical regenerable absorbents have been developed yet in 300~500°C range.

In this talk, we will report our recent progress on the development of Mg-CaCO<sub>3</sub> double salt absorbents for CO<sub>2</sub> removal at 300-500 °C. We carefully studied the effects of several synthesis parameters, including Ca/Mg ratio, solution salt concentration, method of mixing, synthesis temperature, drying and activation temperature and duration. The properties of the intermediate products and the final absorbents were thoroughly characterized by SEM, XRD, and BET. The performance of the absorbent was evaluated in both a TGA-DSC unit and a fixed bed reactor. Mg-CaCO<sub>3</sub> double salt absorbents with a high CO<sub>2</sub> capacity of over 4 mmol/g were produced and the capacity was confirmed to have good repeatability. These absorbents can be easily regenerated through pressure swing or temperature swing. The mechanism of the CO<sub>2</sub> adsorption on these Mg-CaCO<sub>3</sub> double salt absorbents have been investigated. The results will also be discussed.

### SESSION 18 Coal-Derived Products: General – 1

#### A Truly Green and Achievable Energy Policy

Scott Montgomery, Catholic University of America; Robert L. Freerks, Rentech, Inc., USA

In the United States of America, there is an ongoing debate about our future energy policy regarding both fueling our passenger vehicles as well as powering the electric grid. As a result, many options have been offered to mitigate this need for fuel. Some of the most popular solutions offered today are bio-fuels using a variety of vegetation, debris from forests and other natural sources, plant life from oceans, wind, and solar. Other options discuss conservation and drawing down high-energy usage. Still other solutions involve hydrogen, battery generation, and even more reliance on imported

fuels and natural resources. The problem with these solutions is that they have not been proven a viable option to replace our energy reliance on coal, oil, and natural gas. The best use of our current resources is to clean up the use of coal and put it to work providing electricity to our electric grid while simultaneously producing liquid fuel that provides our passenger cars a sufficient fuel source that alleviates our need importing more oil from abroad. This option is also a cleaner source of fuel than petroleum, some 33% cleaner by some estimates. It is also essential that natural gas be used in this same process to produce as much clean fuel as possible. These operations are known as Coal to Liquids (CTL) and Gas to Liquids (GTL) plant operations. They would be combined with pollutant scrubbing operations known as Carbon Capture and Storage (CCS). When operations are combined to create both fuel for passenger car use and fuel to provide energy for the electric grid, this is known as a Combined Production Plant (CPP). This is because CTL or GTL is produced to provide liquid fuel for passenger vehicles and the byproduct of this production can be converted into steam, which in turn provides electricity for the power grid at a very affordable price. This production process is 98% effective in getting rid CO<sub>2</sub> emissions deemed harmful by the EPA and the burning of these fuels will be combined with bio-fuels (8% blend) so that they may burn even cleaner than E 85. The fuel produced would have to be diesel fuel or jet fuel, but that is a more efficient fuel to burn in passenger vehicles and reduces emissions from aircraft (a very difficult emissions source to control). For example, an eight-cylinder car that gets 17 mpg burning gasoline will get 35-40 mpg in an equivalent diesel engine. That would mean that less fuel would be used over the course of a year which is one reason this type of engine is 33% cleaner than a conventional gas engine. An operation like this would require a large capital investment of approximately \$5-7 bn. This amount of money would be very difficult to finance by a single energy company but a combined effort would be a better solution. In particular, a combined effort between the Federal Government and a private enterprise would be ideal. The Federal Government has control of an organization, The Tennessee Valley Authority, which is in the process of shutting down coal fired power units in many of its existing plants. One particular plant, Widows Creek, in Stevenson, AL, is shutting down six of its eight power units in the next couple of years and there has been no announcement as to how these units or the power that they produce are to be replaced. The best possible solution would be to convert this plant into a CTL/GTL plant with the possibility of CCS and produce liquid fuel for automobile use and energy that can be sent into the power grid. A CTL/GTL plant would make the plant cleaner environmentally, domestic fuel production units that would save jobs from being outsourced, lower fuel costs for all consumers, lower the costs of a new CTL/GTL plants as the infrastructure is already in place, improve the balance of payments, increase revenue from taxes, and provide a profitable source of income for the producers of this type of energy. A CTL plant would also alleviate the potential demand of natural gas the power grid would need to use if coal were to be completely replaced as an energy source. Furthermore, there are suitable locations for CCS nearby the Widows Creek Power Plant, as there are many depleted coal and oil fields within a short distance from the plant. The possibility of putting a 50,000 Bl/Day fuel production capability with the possibility of an equivalent 550 MW power unit that could provide the amount of energy lost with the closure of the six power units with a cost savings of 20% over the cost of a new CTL plant would be preferable to any other energy solution.

#### Two-Stage Conversion of Low-Rank Coal and Biomass into Liquid Fuel Under Mild Condition

Xian Li, Dedy Eka Priyanto, Ryuichi Ashida, Kouichi Miura, Kyoto University, JAPAN

With the rapid depletion of petroleum, some substitutes, such as coal and biomass, are expected to be economically competitive as sources for liquid fuels. But this substituting coal and biomass for petroleum have not been realized commercially. One of the main reasons is that the severe reaction conditions of the conventional conversion processes of coal or biomass to liquid fuels cause rather high capital cost and operation and management costs for the factory development. Economical conversion routes of coal or biomass to liquid fuel will surely be realized under rather mild conversion conditions. In our previous work, we have presented a degradative solvent extraction method to convert low-rank coals and biomasses into residue and extracts at lower than 350 °C in N<sub>2</sub>. The residue can be used as solid fuels because they were almost free from moisture and had rather higher heating value. The extracts were free from moisture and ash. The carbon content and oxygen content of extracts were respectively higher than 80 % and lower than 13%, similar to bituminous coal. The extracts had molecular weight of around 300 and can melt completely at lower than 100 °C. Several promising routes of converting the extracts into liquid fuels were expected. If some cheap solvents, such as coal derived oil and biodiesel, are used as extraction solvent, the mixture of extracts and solvent can be used directly as liquid fuel without separation for some purposes. The extracts might be also used as liquid fuel alone for some special equipments, because they can become liquid at lower than 100 °C. Furthermore, the extracts can be easily liquefied to produce light oil under relatively mild condition compared with the conditions of direct coal liquefaction. Preliminary results of extracts liquefaction showed that the oil (hexane soluble excluding water) yields reached to higher than 60 % at 400 °C under the H<sub>2</sub> pressure of only 2 MPa (room temperature). The oil obtained from extracts liquefaction had rather

higher carbon content and lower oxygen content than the oil obtained from their parent materials liquefaction had. Furthermore, H<sub>2</sub> consumptions of extracts liquefaction were rather lower than those of their parent materials liquefaction. Thus, the proposed degradative solvent extraction method might be a promising method for producing liquid fuel or producing precursors for light oil production. The combination of this proposed extraction method and direct liquefaction of extracts at mild condition maybe have a promising feasibility for liquid fuel production.

#### **Adding Value to Coke Oven Gas**

Christian Wix, Martin Skov Skjøth-Rasmussen, Berit Hinnemann, Thoa Thi Minh Nguyen, Casper Funk Jacobsen, Haldor Topsøe A/S, DENMARK; Niels Richard Udengaard, Haldor Topsoe Inc, USA

The main product from a coke oven plant is naturally the coke itself. However, all coke oven plants also produce coke oven gas, which represents a value that is highly dependent on local conditions.

The main components of a coke oven gas are CO (5-10%), CO<sub>2</sub> (1-5%) and H<sub>2</sub> (55-60%). The value of hydrogen is in general lower when hydrogen is used as a fuel rather than as a feedstock for synthesis of other valuable products, and this is the main driver for the technology presented in this paper.

A number of products, including ammonia and methanol, may be produced from coke oven gas. This paper focuses on Haldor Topsøe's new technology for conversion of coke oven gas into substitute natural gas (SNG). The SNG can be distributed either directly to a pipeline or as liquefied natural gas (LNG).

The paper describes the highly efficient methanation process developed by Haldor Topsøe for production of SNG. The paper explains the special features of the technology and discusses the influence of feed gas composition, feed gas impurities, such as higher hydrocarbons and BTX, as well as operating parameters on process performance and economics.

The conversion of coke oven gas to SNG takes place in three steps: coke oven gas purification, methanation synthesis and drying or liquefaction. The purification of coke oven gas includes compression, removal of tars, sulphur, ammonia and BTX.

SNG will normally be produced for distribution in natural gas pipelines and will therefore have to comply with pipeline gas specifications. These differ from case to case but will typically define limits for heating value, Wobbe index, dew point and content of carbon dioxide, carbon monoxide, hydrogen and contaminants such as sulphur and mercury. If the SNG is liquefied to LNG, then the requirements are different.

The methanation process features a series of adiabatic methanation reactors containing proprietary Ni-based methanation catalysts. In the first reactor a special high-temperature catalyst is used, and in the last reactor a catalyst optimized for high activity at low temperature is used. Catalyst choice for intermediate reactors depends on the specific case.

The outlet temperature of the first reactor is controlled via a recycle of partially converted coke oven gas over this reactor. The inlet temperature must be high enough to avoid formation of gum on the catalyst, and the outlet temperature is limited by the risk of catalyst deactivation by sintering and carbon formation. The specific features of the high-temperature catalyst allow a relatively high temperature increase over the reactor, minimizing the recycle gas flow and addition of water to avoid carbon formation. This of course represents both an OPEX and a CAPEX saving when compared to other solutions.

Furthermore, the relatively high outlet temperature from the first reactor optimizes the recovery of process heat by production of superheated high-pressure steam (up to 140 bar g, 540°C). The paper illustrates the benefits of the Topsøe methanation process in terms of energy efficiency, investment cost and environmental performance.

Finally, the paper discusses the specific feature of where CO<sub>2</sub> from another source, e.g. by extraction of CO<sub>2</sub> from a blast furnace, can be added to the coke oven gas and thus be converted into SNG and at the same time remove any excess of hydrogen.

#### **Impact of Co-Gasifying Coal and Agricultural Wastes on Condensate Production in Updraft Gasifiers**

Akinwale Aboyade, University of Cape Town; Marion Carrier, Johannes Knoetze, Johann Görgens, Stellenbosch University; JC van Dyk, Sasol Technology R&D, SOUTH AFRICA

Co-utilizing of coal and agricultural waste in existing coal based gasification/synthesis installations potentially presents a realistic starting scenario for the production of second generation biofuels. Updraft, fixed bed dry bottom gasifiers are currently the most commercially successful gasifiers used for coal gasification and produce significant quantities of tar along with syngas. In some coal gasification applications, the tar is processed separately from syngas into valuable by-products. This study aims to evaluate the impact of co-gasifying coal and agricultural waste (sugarcane bagasse and corncobs) on the quantity and quality of tar produced within a typical updraft gasifier. An atmospheric thermogravimetric analyser was employed in studying pyrolysis weight loss behaviour and devolatilization kinetics. Pyrolysis experiments using a pressurized packed-bed reactor were employed in studying the influence of coal-biomass mix ratio on condensate production. It was determined that co-feeding had a strong influence on pyrolysis behaviour as characterized by reaction kinetics and

condensate quality. It was also observed that synergistic or non-additive interactions between biomass and coal impacted on the ability to predict the yields of specific liquid condensate products.

#### **The Effect of Particle Size and Pressure on Coal-Tar Quality for a Typical Permian-Aged South African Inertinite-Rich Coal**

Daniel van Niekerk, Rudi Coetzer, Sasol Technology, SOUTH AFRICA

Pyrolysis is a potential process that can be utilized to produce hydrocarbon liquids directly from coal and other carbonaceous materials. During typical pyrolysis, coal is heated to high temperatures (e.g. 600 °C) resulting in the release of gaseous and liquid hydrocarbons. In this study the effect of coal particle size and pressure on coal-tar quality was investigated using a typical South African inertinite-rich coal. The aim of this study was to determine the potential operating conditions that can be changed to manipulate the quality of pyrolysis tars. All experiments were conducted in an inert atmosphere using a pressurized pyrolysis reactor. Various analyses were conducted on the generated tars: Simulated distillation (simdis), gas chromatography mass spectrometry (GCMS) and size-exclusion chromatography (SEC-UV).

Coal-tar formed at high-pressures was lighter in boiling point distribution than coal-tars produced at low-pressures (atmospheric to 28 bar). GCMS results showed that a change in pressure will affect coal-tar composition (similar molecular components, but with different ratio's). Coal-tars produced at low-pressures were significantly different than coal-tar produced at high-pressures in regards to molecular weight distribution: High-pressure coal-tar was significantly lighter than low-pressure coal-tar. Coal-tar generated from small coal particles (+1.7-2.35 mm) was slightly lighter in boiling point distribution than tars produced from large coal particles (+13-19 mm). GCMS results showed that a change in coal particle size will affect coal-tar composition (similar molecular components, but with different ratio's). Slight differences between coal-tars produced from small coal particles and large coal particles were observed: Coal-tar from large coal particles was slightly lighter than coal-tar produced from small coal particles. This study concluded that pyrolysis coal-tar composition of a typical inertinite coal will change if pressure or particle size is changed. However, the effect of pressure on coal-tar quality is more significant than particle size.

#### **Effect of Mineral Distribution on the Coking Properties of Coal**

Yong-Jian Bai, Shu Zhang, De-Ping Xu, Yong-Gang Wang, China University of Mining and Technology (Beijing), CHINA

Based on petrographic analyses, the macerals and microlithotype were analyzed to obtain the contents of carbominerite and minerite of several coal samples with similar ash contents. The microstructure of cokes which were produced from a 40 kg coking furnace was characterized to explain the effect of status and distribution of minerals on coking properties. The results show that coking coal and fat coal featured good coking properties due to the high-ratio carbominerite and low-ratio minerite and thus could be used as blend. Comparatively, gas coal and lean coal showed poor coking properties although they also had high-ratio carbominerite. This indicates that besides the petrology index such as the reflectance of vitrinite and the activity and inertia ratio, mineral distribution had a great influence on the coking properties. Well dispersed minerals in organic matrix were playing positive roles for the coking properties, while clusters and large particles of minerals had adverse effects.

#### **SESSION 19**

#### **Clean Coal Demonstration and Commercial Projects: Technical - 1 (Commercial Projects)**

#### **Prairie State Energy Campus: Next Generation of Coal-Fueled Power**

Peter DeQuattro, Ashlie Keener Kuehn, Prairie State Generating Company, LLC, USA

Prairie State Energy Campus represents an important step in helping to create a sustainable and secure energy future for this country. It utilizes domestic coal resources and deploys clean generation technologies to produce electricity in a more efficient and environmentally friendly manner.

Located in Washington County, Illinois, Prairie State Energy Campus includes a coal-fired generating plant and adjacent coal mine. The facility generates 1600 MWs of power, with 95 percent of the output already dedicated to eight (8) Midwestern-based public power utilities.

The Prairie State Energy Campus is a technologically advanced electric generation facility, 95-percent owned by eight non-profit utilities that are committed to providing clean, reliable and affordable base-load power to hundreds of local communities in the Midwest and Mid-Atlantic regions. Its combined design efficiencies mean Prairie State will significantly improve our industry's environmental profile by replacing existing, less-efficient power plants.

## **Dominion's New Virginia City Hybrid Energy Center: How State Incentives and Clean Coal Technology Combine for a Successful Project**

Mark D. Mitchell, Herbert Wheary, Dominion Resources Services, Inc., USA

Over the past decade, tightening environmental restrictions have posed increasing challenges to siting, designing and permitting of coal-fired power stations. Many planned power stations have been abandoned as the hurdles became seemingly insurmountable and projected costs were deemed prohibitive. In 2004, to "ensure an adequate and reliable supply of electricity and to promote economic development", The Commonwealth of Virginia began providing incentives for siting and development of coal-fired electric generating facilities by investor-owned utilities. Qualifying utilities would be eligible for additional basis points on cost recovery for construction of a "carbon capture compatible, clean-coal powered" facility. Dominion Resources worked within that structure to develop and move forward with a 668 MW (585 MW net) coal-fired facility located at Virginia City in Wise County, Virginia. This facility has recently been completed and is expected to be in commercial operation by the time this presentation is given.

An overview of the successful completion of The Virginia City Hybrid Energy Center will be presented, covering significant incentives and challenges and how they guided site selection, choice of technology and environmental impact mitigation. The selection of a brown field site, the use of air-cooling and the capability to fire biomass contributed to the acceptability of the proposed facility. In addition a commitment was made to convert one of the older coal stations in the fleet to natural gas. The need to accommodate a diversity of fuels and other factors, including cost and reliability favored the selection of fluidized bed combustion. Proximity to coal bed methane seams provides an opportunity for carbon sequestration, and the feasibility of this has been demonstrated by work conducted by The Virginia Center for Coal & Energy Research at VirginiaTech and supported by the U.S. Department of Energy and other sponsors including Dominion. The major factors that have aided in the permitting of the facility will be reviewed. Examination of the story behind the successful development of this facility may provide valuable insight into incentives and compliance strategies that could be transferred to other states to encourage construction of clean coal facilities.

### **GE Technology Update - Duke Edwardsport IGCC**

Norman Shilling, Larry Duke, Jeffrey Goldmeier, GE Power & Water, USA

Duke Edwardsport represents the realization of commercial scale IGCC and the value proposition that cleaner coal technology will have on our environment and on meeting world energy demands. When commissioned, the proposed 618-megawatt IGCC facility will be the largest, one of the cleanest, and one of the most efficient coal-fired power plants in the world. Based heavily on GE technology, it will emit significantly less sulfur dioxide, nitrogen oxides and particulates than the plant it replaces – while providing more than 4 times the electric power.

During 2012, the Duke Edwardsport IGCC facility will be in the validation phase of the startup where GE tests the performance of the power block, the Gasification Island including the radiant syngas cooler, and the overall system performance. An important element to the validation of the power block is the performance of the 7F Syngas Gas Turbines. These turbines were tested at full speed no load (FSNL) conditions at GE's Greenville, SC facility before being shipped.

In addition, GE's IGCC full plant simulation was used to evaluate a number of operation scenarios as well as to develop contingency plans for potential operating upsets during start up, thus allowing and GE and Duke to achieve 85 % plant availability as fast as possible.

The presentation will provide plant updates and highlight GE's advancements in gasification and turbine technology.

### **Update on the Kemper County IGCC Project Using Transport Integrated Gasification (TRIG™)**

Randall E. Rush, Tim Pinkston, Matt Nelson, Guohai Liu, Southern Company; Diane Revay Madden, DOE/NETL, USA

Mississippi Power Company is building a 2 x 1 Integrated Gasification Combined Cycle (IGCC) facility in Kemper County, Mississippi. The plant—based on the Transport Integrated Gasification (TRIG™) technology developed by Southern Company, KBR, and the U. S. Department of Energy (DOE)—will use local Mississippi lignite and produce 582 MW of electricity at peak power production with 524 MW from syngas. 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. In addition to carbon dioxide, the plant will also produce ammonia and sulfuric acid as byproducts. The Kemper County project team is currently completing the last phase of detailed engineering for the plant. All major equipment is under order, and above-ground construction is underway. The facility Commercial Operation Date (COD) is set for May 2014.

This paper will outline the TRIG™ technology and provide an update on the status of the project.

## **SESSION 20 Coal-Derived Products: General – 2**

### **Tar and Gas Evolution From the Devolatilization of Large South African Coal Particles**

Burgert B. Hattingh, Raymond C. Everson, Hein W.J.P Neomagus, North West University; John R. Bunt, Daniel van Niekerk, Sasol Technology (Pty) Ltd., SOUTH AFRICA

Tar, gas and char evolution potential was assessed for four different South African coals differing in maceral content and seam origin. Devolatilization studies were performed at two temperatures i.e.; 450°C and 750°C on large coal particles (5 mm and 20 mm) with the aid of a self-fabricated reactor system enabling for the capture of tar and online measurement of gaseous products. Tar yield was found to be the largest for the vitrinite-rich coals, while lower yields were obtained for the inertinite-rich species. The large tar yield of coal G#5 was found to be directly correlated to its larger liptinite yield, while the lower tar yield for coal TSH was confined to its slightly higher rank. Gas- and volatile yield increased significantly with increasing temperature. The influence of particle size was however less prominent. Evolved gasses mainly constituted of H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and light olefinic and –paraffinic species.

### **Analysis of Low-Temperature Pyrolysis Oil of Low Rank Coal**

Yinhua Long, Xiaofen Guo, Li Wang, National Institute of Clean-and-Low-Carbon Energy; Quan Shi, China University of Petroleum, CHINA

Pyrolysis oil is one of important products of low-temperature coal pyrolysis, and usually composed of thousands of compounds. Coal pyrolysis oil can be further processed to chemicals, or upgraded to more valuable transportation fuels or lubricants. Therefore, research to obtain knowledge of physical properties and chemical composition of pyrolysis oil is essential for better selection of oil processing technology. Due to high heteroatom content in low rank coal pyrolysis oil, the conventional standard test methods for petroleum products are not applicable, and new analytical methods need to be developed. In this study, pre-distillation, acid/base extraction, and extrography were employed for fractionation of pyrolysis oils. Chemical composition study and quantification were investigated by Gas Chromatography-Mass Spectrometry (GC/MS) and Fourier Transform Ion Cyclotron Resonance-Mass Spectrometry (FTICRMS). In a typical coal low-temperature pyrolysis oil, paraffin with C4-C30 and similar distribution of  $\alpha$ -olefins were detected. Acidic fraction makes up ~ 30 wt% of pyrolysis oil with phenols and dihydroxyl benzenes as major components. Additional oxygenated components were also detected in pyrolysis oil, including a lot of aliphatic and aromatic ketones with similar structure and distribution to their parent hydrocarbons. Pyridine, indoles and carbazoles are found to be major N-containing components, while benzothiophene and dibenzothiophene dominate trace S-containing compounds in low-temperature coal pyrolysis oils.

### **Liquid Transportation Fuels from Coal and Natural Gas**

Harold A. Rosen, National Academy of Engineering, USA

Gasoline, diesel and aviation fuels can be synthesized at low cost and low environmental impact by using a synergistic combination of our abundant coal and natural gas resources as feedstocks, with modern techniques that so far have only been used separately on industrial scales. There are major advantages to this approach. First, our reserves are sufficient to allow not only the achievement of our long sought energy independence but also significant export of synthetic petroleum. Second, unlike the proposals to use hydrogen, methanol or natural gas as transportation fuels, the use of these synthesized fuels would require no changes to our extensive distribution system or the vehicles using them.

The classic Fischer-Tropsch synthesis of liquid fuels from syngas derived from coal generates so much carbon dioxide in the process, and the carbon available for the liquid product is so diminished, that twice as much coal is needed as a result. This carbon dioxide is an unwanted byproduct of the reaction that creates the hydrogen required to augment the syngas obtained from the hydrogen poor coal gasifier. By using reformed natural gas having hydrogen rich syngas as a parallel source with the raw coal gasifier output, a stoichiometrically optimum combination for liquid synthesis can be obtained when equal amounts of carbon are supplied by each source. This combination allows four times as much liquid transportation fuel to be produced for each ton of coal feedstock as the classic method. At current prices, the total feedstock cost with this process is \$16 per barrel of oil, assuming the conversion facilities are located at Powder River Basin coal or North Dakota lignite mines, near which adequate supplies of natural gas and water are available.

Negligible amounts of carbon dioxide are produced in this chemical process, although the heat and electrical power needed to drive the conversion will emit carbon dioxide if supplied by burning fossil fuel. Even so, the carbon dioxide produced is a small fraction of that produced in the classic Fischer-Tropsch process. The blending of biomass with coal to reduce the carbon footprint of the synthesis is very expensive, of

limited scope and questionable value, since much lower cost alternatives to mitigating climate change exist should such steps ever become desirable.

The capital costs of the conversion process are rate dependent, on the order of \$100,000 per barrel per day. These high costs can be reduced by using the syngas to methanol to gasoline process for gasoline and optimizing the Fischer-Tropsch reactor for the higher carbon number diesel and aviation fuels, which are not yet available via the methanol route. The pressure vessels, piping, and heat exchangers for the synthesizers can be produced in our underemployed rust belt. The total cost of the product would be under \$60 per barrel, or \$1.50 for a gallon for gasoline.

The creation of reliable and efficient 100,000 barrel a day syncrude plants will be a formidable undertaking, but no more so than the creation of the transcontinental railroad, the Panama Canal, the interstate highway system, and geostationary communication satellites. Our coal reserves are adequate to produce at least a trillion barrels of syncrude when we replace coal fired power plants with nuclear power sources. When our natural gas sources become exhausted, the needed hydrogen can be provided by nuclear powered water electrolysis plants.

#### **Coal-To-Liquids: Viability as a Peak Oil Mitigation Strategy**

Mikael Höök, Uppsala University, SWEDEN; Dean Fantazzini, Lomonosov Moscow State University, RUSSIA; Simon Snowden, University of Liverpool, UNITED KINGDOM; André Angelantoni, Post Peak Living, USA

Converting coal to a liquid, commonly known as coal-to-liquids (CTL), can supply liquid fuels and has been successfully used in several countries, particularly in South Africa. However, it has not become a major contributor to the global oil supply. Increasing awareness of the scarcity of oil and rising oil prices has increased the interest in coal liquefaction. This paper surveys CTL technology, economics and environmental performance. Understanding the fundamental aspects of coal liquefaction technologies is vital for planning and policy-making since future CTL production will be integrated in a much larger global energy and liquid fuel production system.

The economic analysis shows that many CTL studies assume conditions that are optimistic at best. In addition, the strong risk for a CTL plant to become a financial black hole is highlighted. This helps to explain why China has recently slowed down the development of its CTL program.

The technical analysis investigates the coal consumption of CTL. Generally, a yield of between 1–2 barrels/ton coal can be achieved while the technical limit seems to be 3 barrels/ton coal. This puts a strict limit on future CTL capacity imposed by future coal production, regardless of other factors such as economic viability, emissions or environmental concern. For example, assuming that 10% of world coal production can be diverted to CTL, the contribution to the liquid fuel supply will be limited to only a few million barrels per day (Mb/d). This prevents CTL from becoming a viable mitigation plan for liquid fuel shortage on a global scale.

However, it is still possible for individual nations to derive a significant share of their fuel supply from CTL but those nations must also have access to equally significant coal production capacity. It is unrealistic to claim that CTL provides a feasible solution to liquid fuels shortages created by peak oil. At best, it can be only a minor contributor and must be combined with other strategies to ensure future liquid fuel supply.

#### **Upgrading of Oils Derived from Thermal Processing of Coal**

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

Indirect and Direct Coal Liquefaction Technologies can be used to produce high-quality transportation fuels. The characteristics of these products are well defined and documented. There are, however, other sources of coal-derived liquids produced from thermal processing of coal including coke ovens, pyrolysis, solvent refining and low temperature gasification processes. These thermally produced coal liquids are highly unsaturated, with high aromatic, nitrogen and oxygen contents. Based on these characteristics upgrading using conventional refining technologies to produce high quality fuels and petrochemicals provides some unique challenges. Extensive experimental and development work has been done by Axens to characterize the raw coal liquids and to define secondary processing of raw coal liquids required to produce high quality fuels and petrochemicals. This presentation will describe quality of these coal-derived oils, define the processing requirements and show that high quality liquid fuels and petrochemicals be produced.

### **SESSION 21 Gasification: Modeling – 1**

#### **Investigation of Two-Stage Oxygen Feeding in a Downdraft Entrained-Flow Coal Gasifier**

Ting Wang, Xijia Lu, University of New Orleans, USA; Heng-Wen Hsu, Cheng-Hsien Shen, Industrial Technology Research Institute, TAIWAN

The traditional practice of employing a two-stage coal-fed gasification process is to feed all of the oxygen in the first stage to provide a vigorous amount of combustion in the first stage, but only feed the coal without oxygen in the second stage to allow the endothermic gasification process to occur downstream of the second stage. One of the merits of this 2-stage practice is to keep the gasifier temperature low downstream from the 2<sup>nd</sup> stage and, thus, to extend the life of refractory bricks, decrease gasifier shut-down frequency for scheduled maintenance, and reduce the maintenance costs. In this traditional 2-stage practice, the temperature reduction in the second stage is exchanged for a higher than normal gasification temperature in the first stage. This study investigates a concept totally opposite to traditional two-stage coal feeding practices in which the injected oxygen is split between the two stages, while all the coal is fed into the first stage. The hypothesis of this two-stage oxygen injection is that a distributed oxygen injection scheme can also distribute the release of heat to a larger gasifier volume and, hence, reduce the peak temperature distribution in the gasifier. The increased life expectancy and reduced maintenance of the refractory bricks can prevail in the entire gasifier, not just downstream from the second stage.

In this study, both experiments and a computational simulation have been performed. A series of experiments, performed by the Industrial Technology Research Institute (ITRI), shows that the peak temperature and temperature range in the gasifier do decrease from 600-1550°C with one stage oxygen injection to 950-1230°C with a 60-40 oxygen split-injection. Since experiments are expensive, and data is usually limited and difficult to measure with certainty, a computational fluid dynamics (CFD) scheme is employed to assist in expanding the operating conditions to broader variations. The CFD result shows that (a) the carbon conversion rates for different oxygen injection schemes are all above 95%, (b) H<sub>2</sub> (about 70% vol.) dominates the syngas composition at the exit, (c) the 80-20% case yields the most uniform temperature distribution along the gasifier, and (d) the 40-60% case produces the syngas with the highest HHV.

#### **Dynamic Maximization of Oxygen Yield in an Elevated-Pressure Air Separation Unit Using Linear Multiple Model Predictive Control (MMPC) Framework**

Priyadarshi Mahapatra, Stephen E. Zitney, AVESTAR<sup>TM</sup> Center/DOE/NETL, USA

In a typical air separation unit (ASU) utilizing either a simple gaseous oxygen (GOX) cycle or a pumped liquid oxygen (PLOX) cycle, the flowrate of liquid nitrogen (LN2) stream connecting high-pressure and low-pressure ASU columns plays an important role in the total oxygen yield. It has been observed that this yield reaches a maximum at a certain optimal flowrate of LN2 stream. At nominal full-load operation, the flowrate of LN2 stream is maintained near this optimum value, whereas at part-load conditions this flowrate is typically modified in proportion with the load-change (oxygen demand) through a ratio/feed-forward controller. Due to nonlinearity in the entire ASU process, the ratio-modified LN2 flowrate does not guarantee an optimal oxygen yield at part-load conditions. This is further exacerbated when process disturbances in form of “cold-box” heat-leaks enter the system. To address this problem of dynamically maximizing the oxygen yield while the ASU undergoes a load-change and/or a process disturbance, a multiple model predictive control (MMPC) algorithm is proposed. This algorithm uses linear step-response “blackbox” models surrounding the operating points corresponding to maximum oxygen yield points at different loads. It has been shown that at any operating point of the ASU, the MMPC algorithm, through model-weight calculation based on plant measurements, naturally and continuously selects the dominant model(s) corresponding to the current plant state, while making control-move decisions that approach the maximum oxygen yield point. This dynamically facilitates less energy consumption in form of compressed feed-air compared to a simple ratio control during load-swings. In addition, since a linear optimization problem is solved at each time step, the approach involves much less computational cost compared to a first-principle based nonlinear MPC.

#### **On the Dynamic Modeling of an Entrained Gasifier Using Aspen Custom Modeler**

Job Kasule, Richard Turton, Debansu Bhattacharyya, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

The gasifier is the heart of the integrated gasification combined cycle (IGCC), a technology that has emerged as an attractive alternative to conventional coal-fired power plant technology due to its higher efficiency and cleaner environmental performance especially with the option of CO<sub>2</sub> capture and sequestration. Understanding the optimal performance of the gasifier is therefore paramount for the efficient operation of IGCC power plants.

Numerous gasifier models of varying complexity have been developed to study the various aspects of gasifier performance. These range from simple one-dimensional (1D) process-type models to rigorous higher order 2-3D models based on computational fluid dynamics (CFD). Whereas high-fidelity CFD models can accurately predict most key aspects of gasifier performance, they are computationally expensive and typically take hours to days to execute on high-performance computers. Therefore, faster 1D partial differential equation (PDE)-based models are required for use in dynamic simulation studies, control system analysis, and training applications. A number of 1D gasifier models can be found in the literature, but most are steady-state models that have limited application in the practical operation of the gasifier. As a

result, 1D PDE-based dynamic models are needed to further study and predict gasifier performance under a wide variety of process conditions and disturbances.

In the current study, a 1D transient model of a single-stage downward-fired GE/Texaco-type entrained-flow gasifier has been developed. The model comprises mass, momentum and energy balances for the gas and solid phases. The model considers the initial gasification processes of water evaporation and coal devolatilization. In addition, the key heterogeneous and homogeneous chemical reactions have been modeled. The resulting time-dependent PDE model is solved using the well-known method of lines approach in Aspen Custom Modeler®, whereby the PDEs in the spatial domain are discretized and the resulting differential algebraic equations (DAEs) are then integrated over time using a dynamic integrator. The dynamic response results of the gasifier performance parameters to certain disturbances commonly encountered during practical operation are presented. These disturbances include ramp and step changes to input variables such as coal flow rate, oxygen-to-coal ratio and water-to-coal ratio among others. Comparison of model predictions to available dynamic data will also be discussed.

#### **CFD Simulation of Brazilian Coal Gasification on a Circulating Fluidized Bed Reactor**

Daniel Augusto Kesterling, Thiago Fernandes de Aquino, Júlio Cesar Spillere Ronchi, Beneficent Association of the Santa Catarina Coal Industry – SATC, BRAZIL; Ronald W. Breault, DOE/NETL, USA

The Brazilian Coal Association (BCA) and the U.S. Department of Energy's National Energy Technology Laboratory (NETL) signed a Memorandum of Understanding (MOU) that reflects a mutual interest of the parts to pursue collaborative work to advance the technical, environmental, and cost performance of fossil energy technologies including gasification. The Brazilian coal is a specific coal that has a very high, non-cleanable, ash content. One of the possible applications for this fuel is produce fuel gas through the circulating fluidized bed (CFB) technology. To verify the behavior of Brazilian coal in a gasification system at atmospheric pressure, 2D simulations were performed with different reactor configurations and geometry where air has been used as oxidizing agent. The tests were done using a Brazilian bituminous coal called "Bonito", which is situated at Criciúma, Santa Catarina state. The Two-Fluid (or Eulerian-Eulerian) Method was used to describe governing equations. The particle diameter, coal and air flow rates, and coal feeding position were the main parameters varied in this study. The software C3M was used to provide the reaction constants through the Chemical Percolation Model for Coal Devolatilization (CPD) Model and C3M's default kinetics. The results from C3M were incorporated in a Computational Fluid Dynamics (CFD) code the Multiphase Flow with Interphase Exchanges (MFIEX), developed at NETL. In this work the CFD simulation utilized the default models in MFIEX, namely the Syamlal-O'Brien correlation for the gas-solid drag force. The model takes accounts nine gas species, which are O<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, Tar and soot, and four pseudo-species of solids, that are Fixed Carbon, Volatile Matter, Moisture and Ash. The results indicated that the gasification process using a CFB technology can be very useful to produce fuel gas from Brazilian coal.

#### **CFD Results of Siemens Gasifier During Commissioning at Shenhua Ningxia Coal Industry**

Achim Moser, Frank Hannemann, Tino Just, Siemens Fuel Gasification Technology GmbH, GERMANY

Five of the largest Siemens SFG® gasifiers finished commissioning in 2011 at Shenhua Ningxia Coal Industry, NCPP I Project located near Yinchuan, China. The commissioning of these five Siemens SFG-500 gasifiers was supported by CFD simulations at Siemens gasification headquarters in Freiberg, Germany. Due to the axial symmetric design of the Siemens 500 MW<sup>th</sup> gasifier, a two dimensional CFD model was applied during the CFD simulations. The mesh was generated with a CENTAUR™ mesh generator and the simulations were carried out using ANSYS® Fluent®. Main features of the numerical setup were a 2-D pressure-based solver, steady simulation, a SSTKW turbulence model, a discrete particle model, a multiple-surface-reaction model, and a discrete ordinates radiation model. Actual plant operating conditions were used as boundary conditions for CFD simulations.

This paper will review two cases that show the effect of loading,  $\lambda$  and slagging on heat flux during gasifier operation. One simulation covers the situation at the beginning of the commissioning using the startup burner while the second case covers the situation after few months of operation.

The first start up of a SFG gasifier was characterized by part load operation, low  $\lambda$  and a high heat flux. During this operational period the burner was operated with small O<sub>2</sub> outlet cross section and low O<sub>2</sub> swirl was installed to keep the hot reactions zone close to the centerline of the gasifier. Under these conditions the slagging of the interior walls of the gasifier's cooling screen takes place. As the slagging of the reactor wall increases, the heat flux drops while the load and  $\lambda$  increases. After all the gasifier's systems were in stable operation with nominal loading, the gasifier was shut down and the burner adjusted to a larger O<sub>2</sub> outlet cross section and increased O<sub>2</sub> swirl, which is more appropriate for nominal to maximum loading.

In addition to confirming integral measurement values like heat flux, the CFD simulations reveal details about the environment inside the reactor including temperature distribution, wall temperatures and slag deposition on the cooling screen walls. The CFD results give useful hints of the situation inside the reactor and for future gasifier performance improvement.

### **SESSION 22 Combustion: Ash and Combustion - 1**

#### **One Dimensional Simulation of the Reducer in Syngas Chemical Looping Process**

Qiang Zhou, Liang Zeng, Liang-Shih Fan, The Ohio State University, USA

The syngas chemical looping (SCL) process co-produces hydrogen and electricity from coal derived syngas through the cyclic reduction and regeneration of an iron oxide based oxygen carrier. In this paper, a one-dimensional (1-D) dynamic reactive flow model is developed to simulate the countercurrent gas-solid flow pattern within a moving bed reducer, which reduces the oxygen carrier with syngas. A three-interface shrinking core model is used to represent the overall reaction kinetics of individual oxygen carrier pellet. The individual particle model is validated by TGA experiments. The 1-D moving bed code is validated by comparing the modeling results with previous experimental data from the iron ore reduction industry and also by performing the simulation of the bench-scale SCL experiment. The 1-D model is used to investigate the flow and reaction progress of the SCL gasification process. First, the whole progress of the composition evolution in the moving bed reducer is obtained through explicit temporal integration. Second, the model can be used for optimizing reactor design and operation conditions, which saves significant amount of capital and operation costs. Third, the converging time before the reducer reaches the steady state is analyzed by varying the ratio between gases and solids flow rates. It is found minor change of the feed-rate ratio at a critical point might cause significant difference of the time to reach steady state. The mechanism behind this difference is explored, based on which, some proper feed-rate ratios are recommended for the actual reducer operations.

#### **Ash Deposition during Oxycoal Combustion under High Inlet O<sub>2</sub> Concentration Conditions**

Zhonghua Zhan, Jost O.L. Wendt, University of Utah; Andrew Fry, Reaction Engineering International; Lawrence E. Bool, Praxair Inc., USA; Weidong Fan, Shanghai Jiaotong University, CHINA

Oxy-fuel combustion is one of more promising technology for CO<sub>2</sub> capture in a coal combustion power plant. For a newly designed oxycoal combustion power plant, using high O<sub>2</sub> concentrations and lower recycling ratios will decrease the size of the power plant thereby reducing the capital cost as well as increasing the overall efficiency. Ash deposition and fouling have always been troublesome problems for fuels containing mineral matter. These processes cause reduction of furnace wall heat transfer, corrosion and additional maintenance of the furnace. In order to determine the potential of oxy-firing for retrofit to existing units, it is necessary to determine the impacts of an oxy-combustion environment on fouling and ash deposition. Research described here is concerned with Powder River Basin coal combustion in a 100 kW down-fired Oxy-Fuel Combustor (OFC). The current paper describes initial tests with once through CO<sub>2</sub> to simulate fully cleaned flue gas recycle and an inlet O<sub>2</sub> concentration of 50%. Future experiments will involve recycled flue gas and lower oxygen contents at the burner. A novel stainless steel deposit sampling probe that allowed control of the deposit probe surface temperature was designed and fabricated and is described in detail. Deposit ash samples were obtained under various conditions: namely, 3 different sampling ports (different flue gas temperatures), 3 different sampling probe surface temperatures (723 K, 823 K and 923 K) and 3 different deposit holding times (1 hour, 4 hour and 7 hour). Current results are as follows: (1) the deposit ash from the vertical surface and inside layer of the horizontal surface contain more Na, S and Ca (about twice) and much less Si (about half) than that in the bulk deposit ash on the horizontal surface; (2) the deposit ash from the vertical surface and inside layer of the horizontal surface have much smaller particle sizes compared to the bulk deposit ash on the horizontal surface.

#### **Influence of Reactant Temperature on Coal-Particle Methane-Air Hybrid Flames**

Minkyu Lee, Ali S. Rangwala, Worcester Polytechnic Institute, USA

Laminar flame speeds of lean methane-air fuel mixtures mixed with micron-sized coal dust particles in the ranges of 53-63  $\mu\text{m}$ , 75-90  $\mu\text{m}$ , and 106-125  $\mu\text{m}$  are modeled over a range of equivalence ratios (0.7 – 0.95) and reactant preheat temperatures (up to 700 K). The Bunsen flame approach, based on imaging measurements of the reaction zone area, is shown to produce reasonable results when compared with previous data published in literature (Xie et al.). It is observed that the laminar flame speed is a function of two competing effects: a local increase in equivalence ratio (due to coal particle volatilization in the preheat zone) and reduction in flame temperature (due to

the heat sink effect induced by particle-flame interaction). The impact of these two processes is qualitatively analyzed using a simple mathematical model. The broader impact of the results on coal-mine explosions and safety is discussed.

### **Effect of Excess Air Ratio on Flue Gas Emissions for Co-Combustion of a Lignite Coal and Woodchips in a Circulating Fluidized Bed Combustor**

Murat Varol, Aysel T. Atimtay, Middle East Technical University; Hayati Olgun, TUBITAK-MRC; Hüsnü Atakül, Istanbul Technical University, TURKEY

In this study, combustion of coal and biomass was carried out in a circulating fluidized bed combustor. A Bursa-Orhaneli lignite was used as coal and woodchips was used as biomass in the tests. Woodchips refers to the Rhododendron genus of woody plants in Ericaceae family which is mainly cultivated in the Black Sea region of Turkey. In this study, co-combustion of lignite and woodchips mixtures containing 10%, 30% and 50% woodchips by weight was studied. The experimental setup consists of a circulating fluidized bed combustor column, a fuel feeding system, electrical heaters, two cyclones and a bag filter. The combustor column has an inside diameter of 108 mm and a height of 6 m. The temperatures along the column are observed with thermocouples located at specific heights. The temperature of the column is kept at 850 °C during the combustion tests. The pressure drops along the combustor column, cyclone, and downcomer are continuously measured and observed in order to determine the solid mass flux within the combustor. A series of co-combustion tests was performed in order to investigate the effect of excess air ratio on the flue gas emissions. During the combustion tests, CO<sub>2</sub>, CO, O<sub>2</sub>, NO, and SO<sub>2</sub> emissions in the flue gas was continuously measured and recorded by ABB-AO 2000 flue gas analyzer. The results of the tests showed that as the woodchips ratio in the fuel mixture increases for co-combustion, the combustion takes place more in the freeboard of the main column. Therefore, the maximum temperatures are seen in the freeboard rather than in the bed. It is possible to combust Orhaneli lignite and woodchips mixtures in a circulating fluidized bed combustor without any operational problems for a long time. In order to get minimum flue gas emissions, the best excess air ratios for the co-combustion tests of fuel mixture including 10%, 30% and 50% woodchips by weight were determined to be 1.37, 1.54 and 1.59, respectively. As the percentage of woodchips in the fuel mixture was increased, it was required to feed more air into the combustor to get minimum emissions, especially CO emission.

Woodchips addition to Orhaneli lignite made the CO emission worse and caused CO emission to exceed the Turkish emission limit. NO emissions were under the limits for all cases except for the case of co-combustion of Orhaneli lignite with 50% woodchips. SO<sub>2</sub> emissions were above the emission limits when the percentage of woodchips in the Orhaneli+woodchips fuel mixture was 10% by weight. For the other mixtures, SO<sub>2</sub> emissions were measured under the limit. Woodchips addition decreased the SO<sub>2</sub> emissions as the percentage of biomass increased in the fuel mixture since the biomass contained almost no sulfur. When the system was operated under the condition where NO emission was minimum, it was observed that more CO emission was produced. Therefore, it is necessary to make an optimization on excess air ratio according to CO and NO emissions. In this set of experiments, CO emission has the priority in order to determine the best excess air ratio because it is possible to reduce NO emission by giving secondary air to the combustor.

## **SESSION 23 Carbon Management: CO<sub>2</sub> Capture – 3**

### **Investigation of Sorbents for Warm CO<sub>2</sub> Capture by Pressure Swing Adsorption**

Zan Liu, William H. Green, Massachusetts Institute of Technology, USA

Integrated gasification combined cycle with CO<sub>2</sub> capture and sequestration (IGCC-CCS) emerges as a promising method for achieving higher energy efficiency and better emission control compared with the traditional pulverized coal plant. But the current CCS technology, especially the commercially-available solvent-based CO<sub>2</sub> capture process is energy intensive which makes the IGCC process unaffordable. To achieve DOE's goal concerning IGCC-CCS, which requires a 90% CO<sub>2</sub> capture with less than 10% increase in cost of electricity, some energy-efficient capture process needs to be developed. Recent research conducted in our group indicates that a warm CO<sub>2</sub> capture process based on solid sorbent can potentially improve the efficiency of IGCC compared with the solvent-based CO<sub>2</sub> capture process. This motivates our investigation of proper sorbent material for warm CO<sub>2</sub> capture.

In this work, we present a sorbent material which could be potentially used for warm CO<sub>2</sub> capture in IGCC process. The sorbent material was synthesized using incipient wetness impregnation method. Its sorption behavior under various temperature and pressure were studied in a high-pressure microbalance and a thermogravimetric analyzer. Long time cycle tests and comparisons with competitive sorbent materials were also conducted. The results indicate the sorbent has a stable working capacity when operating in the 180 ~ 240 °C temperature range. It has good working capacity, fast kinetics and low heat of adsorption. Compared with the widely studied mixed oxides and K<sub>2</sub>CO<sub>3</sub>-promoted hydrotalcite, the material has relative advantage in

capacity and kinetics. In addition, a pressure swing adsorption (PSA) process based on the real sorbent data is also established. The preliminary process simulation shows a 10-step PSA using the sorbent can capture 90% of CO<sub>2</sub> with a high H<sub>2</sub> recovery rate.

### **Thermodynamic Properties of CO<sub>2</sub> Capture Reaction by Solid Sorbents: Theoretical Predictions and Experimental Validations**

Yuhua Duan, David Luebke, Henry W. Pennline, DOE/NETL; Keling Zhang, David King, Xiaohong Shari Li, Liyu Li, Pacific Northwest National Laboratory, USA; Lifeng Zhao, Yunhan Xiao, Chinese Academy of Sciences, CHINA

It is generally accepted that current technologies for capturing CO<sub>2</sub> are still too energy intensive. Hence, there is a critical need for development of new materials that can capture CO<sub>2</sub> reversibly with acceptable energy costs. Accordingly, solid sorbents have been proposed to be used for CO<sub>2</sub> capture applications through a reversible chemical transformation. By combining thermodynamic database mining with first principles density functional theory and phonon lattice dynamics calculations, a theoretical screening methodology to identify the most promising CO<sub>2</sub> sorbent candidates from the vast array of possible solid materials has been proposed and validated. The calculated thermodynamic properties of different classes of solid materials versus temperature and pressure changes were further used to evaluate the equilibrium properties for the CO<sub>2</sub> adsorption/desorption cycles. According to the requirements imposed by the pre- and post-combustion technologies and based on our calculated thermodynamic properties for the CO<sub>2</sub> capture reactions by the solids of interest, we were able to screen only those solid materials for which lower capture energy costs are expected at the desired pressure and temperature conditions. These CO<sub>2</sub> sorbent candidates were further considered for experimental validations. In this presentation, we first introduce our screening methodology with validating by solid dataset of alkali and alkaline metal oxides, hydroxides and bicarbonates which thermodynamic properties are available. Then, by studying a series of lithium silicates, we found that by increasing the Li<sub>2</sub>O/SiO<sub>2</sub> ratio in the lithium silicates their corresponding turnover temperatures for CO<sub>2</sub> capture reactions can be increased. Compared to anhydrous K<sub>2</sub>CO<sub>3</sub>, the dehydrated K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O can only be applied for post-combustion CO<sub>2</sub> capture technology at temperatures lower than its phase transition (to anhydrous phase) temperature, which depends on the CO<sub>2</sub> pressure and the steam pressure with the best range being PH<sub>2</sub>O ≤ 1.0 bar. Above the phase-transition temperature, the sorbent will be regenerated into anhydrous K<sub>2</sub>CO<sub>3</sub>. Our theoretical investigations on Na-promoted MgO sorbents revealed that the sorption process takes place through formation of the Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> double carbonate with better reaction kinetics over porous MgO, that of pure MgO sorbent. The experimental sorption tests also indicated that the Na-promoted MgO sorbent has high reactivity and capacity towards CO<sub>2</sub> sorption and can be easily regenerated either through pressure or temperature swing processes.

### **Evaluation of Advanced Solvents and Other Technologies for CO<sub>2</sub> Capture from Fossil Fuel-Fired Systems**

Nathan J. Fiala, Brandon M. Pavlish, Joel G. Downs, John P. Kay, University of North Dakota Energy & Environmental Research Center, USA

The Energy & Environmental Research Center (EERC) is leading the Partnership for CO<sub>2</sub> Capture, the focus of which is to demonstrate CO<sub>2</sub> capture technologies at pilot scale for fossil fuel-fired systems. The program aims to identify challenges and benefits associated with the most commercially ready capture technologies. Pilot-scale results provide technical and economic information for multiple fuels and system configurations. ASPEN modeling software and EERC-developed models are used to extrapolate the pilot data to commercial-scale CO<sub>2</sub> capture applications. Both postcombustion and oxycombustion technologies are evaluated. Postcombustion capture technologies were tested on an absorber–stripper column system designed and built as part of a pulverized coal-fired pilot-scale facility at the EERC. Test results for advanced amine-based solvents are compared to those of monoethanolamine (MEA), the current industry standard, to determine economic and technical feasibility of each technology. Data from these tests show that for similar test conditions at pilot scale, some advanced solvents may require 10%–40% less regeneration energy input than MEA to achieve 90% CO<sub>2</sub> capture. Capabilities of the CO<sub>2</sub> capture equipment as well as the results of testing will be presented.

### **Novel Solvent–Gas Contactor for CO<sub>2</sub> Capture Cost Reductions**

Joel G. Downs, Brandon M. Pavlish, John P. Kay, Nathan J. Fiala, University of North Dakota Energy & Environmental Research Center, USA

The Energy & Environmental Research Center (EERC) along with Neumann Systems Group, Inc. (NSG), conducted a project to evaluate the NSG NeuStream™-C system, an advanced gas contactor, which has the potential to significantly reduce the cost of postcombustion solvent-based CO<sub>2</sub> capture. The system, which consists of a three-stage absorber and a four-stage stripper, was designed and built by NSG and installed at the EERC's combustion test facility. Technoeconomic analysis based on bench-scale testing has shown that the NeuStream™-C system has the potential to meet U.S. Department of Energy requirements of less than a 35% increase in cost of electricity. Testing was performed at the EERC using the pilot-scale NeuStream™-C system on a stream of coal-derived flue gas. The pilot-scale data include but are not limited to the

following: heat of regeneration required, solvent flow rates, temperatures, energy consumption (fans, pumps, regeneration), flue gas components (SO<sub>x</sub>, NO<sub>x</sub>, O<sub>2</sub>, CO<sub>2</sub>, Hg), final CO<sub>2</sub> purity, flue gas flow rates, CO<sub>2</sub> capture efficiencies, corrosion rate, foaming, and several other operating parameters. The capabilities of the solvent system, pilot-scale test results, and economic analysis using pilot-scale data will be presented.

### **Process Simulation of Iron-Based Chemical Looping Schemes with CO<sub>2</sub> Capture for Hydrogen and Electricity Production from Coal**

Daniel P. Connell, CONSOL Energy Inc.; Liang Zeng, Liang-Shih Fan, The Ohio State University; David A. Lewandowski, Robert M. Statnick, Clean Energy Engineering, USA

Chemical looping combustion is a potentially transformational technology, because it shows promise for substantially reducing the cost and energy penalty associated with carbon dioxide (CO<sub>2</sub>) capture from coal- and other fossil fuel-based energy systems. The technology, which is a next-generation form of oxycombustion, uses metal oxide particles to carry oxygen from the combustion air to the fuel, avoiding the need for a cryogenic air separation unit and its associated large capital and energy requirements. The Ohio State University (OSU) is working to develop chemical looping processes that use iron-based oxygen carrier particles. A key feature of the OSU technology is its use of an innovative two-stage moving bed reducer (fuel reactor), which is capable of achieving high conversions (i.e., >95%) for the reaction of oxygen carrier particles with either gaseous or solid fuels. In the standard configuration, the chemical looping process includes two main reactors: the reducer, where the oxygen carrier particles are reduced as they react with fuel to form CO<sub>2</sub> and H<sub>2</sub>O, and the combustor, where the carrier particles are re-oxidized by reaction with air. However, a third reactor also can be added between these reactors to partially oxidize the iron particles with steam, producing hydrogen. The process is well suited for CO<sub>2</sub> capture in either configuration, because the fuel carbon is concentrated as CO<sub>2</sub> in the gaseous effluent from the reducer, which requires only simple dehydration, polishing, and compression to prepare it for sequestration.

OSU is developing several variations of the iron-based chemical looping technology, including the Syngas Chemical Looping (SCL) process, in which the coal is first gasified and the syngas is fed to the reducer, and the Coal Direct Chemical Looping (CDCL) process, in which the coal is fed directly to the reducer. Both processes have been tested at the sub-pilot (25 kW) scale, and a 250 kW, pilot SCL unit will be constructed at the National Carbon Capture Center in Wilsonville, AL, this year. This paper explores the future application of iron-based chemical looping technology at commercial scale and presents process simulation results for several potential plant configurations, including plants designed for syngas and direct coal feed, and plants configured to produce electricity and hydrogen as products. The performance of these configurations, including efficiency, is compared, and the implications for development and commercialization of the chemical looping technology are discussed. Results show that iron-based chemical looping has the potential to afford substantial performance improvements relative to conventional CO<sub>2</sub> capture technologies. For example, the projected net efficiency (higher heating value basis) for a 550 MW<sub>e</sub> supercritical coal-fired CDCL power plant with >90% CO<sub>2</sub> capture and compression is 35.2%, whereas the projected efficiency for a comparable plant equipped with a monoethanolamine scrubbing system for 90% CO<sub>2</sub> capture and compression is 28.5%. Key economic and commercial design considerations for the SCL and CDCL processes are also discussed.

### **SESSION 24 Coal Science: General – 1**

#### **Evaluation of the Performance of a Two-Stage, Warm Air Dryer for Fine Coal Particles**

Steven Rowan, Eric Johnson, Bruce Kang, West Virginia University, USA

De-watering of coal fines is an important concern in the processing, transportation, handling and combustion of coal. The weight of the moisture in coal leads to higher transportation costs, and the adhesive nature of wet coal leads to numerous materials handling issues. Among these issues is clogging in silos, bunkers and crushing/grinding equipment. In addition, many pulverized coal power plants operate with coal feed stocks that can contain upwards of 40% moisture, which is a major contributing factor to power plant inefficiencies. In many instances, the economic costs of drying the coal prior to combustion are prohibitive.

In an effort to address the difficulties associated with wet coal, a two-stage fluidized bed system has been designed and constructed at West Virginia University. This Warm Air Dryer for Fine Particles (WADFP) consists of a steam-jacketed, two-stage fluidized bed with secondary air injection.

Preliminary tests have been carried out using a low-rank lignite coal from Texas. These initial tests resulted in reductions of moisture content ranging from 31% to 74%,

and an overall increase in the higher heating value (HHV) of the coal ranging from 9% to 23%.

### **Thermal and Mechanical Analysis of Briquetted Coal Fines Using Municipal Solid Waste (MSW) Plastics**

Matthew Massaro, Lori Groven, Steven Son, Purdue University, USA

Significant ecological concerns and attractive financial opportunities are raised by growing deposits of waste coal fines in the United States. Roughly two billion tons of waste coal fines are stored in impoundments in the United States and approximately 50 million additional tons are generated annually [1]. These fines can be utilized by extrusion or roller press briquetting along with a binder to impart mechanical strength and water resistance to the briquettes. In this study, a variety of materials were considered for use as a binder and were evaluated on seven criteria: cost, availability, binding ability, processability, water resistance, heating value, and toxicity/environmental impact. Municipal solid waste (MSW) plastic binders are our primary focus in this study due to their superior performance in all areas. The goal of this study was to characterize a briquetted coal product, using waste plastics, which may be an economically and ecologically viable substitute for conventional stoker coal. High density polyethylene (HDPE) and low density polyethylene (LDPE) provide water resistance to the coal briquettes, and since they do not contain chlorine will not yield dioxin or furan formation when combusted. In addition, the heating value of LDPE is 46.4 MJ/kg — over double that of the 21.9 MJ/kg waste coal fines used in this study. For example, a 10 wt% LDPE-90 wt% coal mixture was found to have an 11% higher heating value over the neat waste coal fines. A number of coal/LDPE mixtures were briquetted with varying coal particle size distributions, moisture content, and LDPE concentrations using a laboratory-scale roller press. To examine mechanical robustness, briquettes were exposed to simulated rain and then subjected to compressive testing and tumbler testing according to ASTM D 441-07. Thermal analysis of the briquetted fuels using thermogravimetric analysis/simultaneous differential scanning calorimetry (TGA/DSC) in air revealed a significant interaction between coal and LDPE. Laboratory-scale combustion tests revealed a dependence of combustion efficiency on LDPE concentration in the briquetted fuel. The results of this work indicate that HDPE and LDPE can serve as excellent waste coal binders due to their high energy density, water resistance, binding ability, and relatively low cost.

### **SESSION 25 Clean Coal Demonstration and Commercial Projects: Technical - 2 (Polygeneration)**

#### **Progress Update of the Air Blown IGCC and Gasification Plant**

Koichi Sakamoto, Hiromi Ishii, Mitsubishi Heavy Industries, Ltd.; Tetsuya Fujino, Yasunori Ishizu, Mitsubishi Power Systems Americas, Inc., JAPAN

From the viewpoint of energy security and global warming issues, highly efficient coal utilization system, such as the integrated coal gasification combined cycle (IGCC) power systems and chemical synthesis processes using coal gasification are regarded as an effective clean coal technology that is close to commercialization.

As one of the leading company in the field of IGCC and coal gasification, Mitsubishi Heavy Industries, Ltd. (MHI) is now in a position of actively undertaking its realization with an integration of two stage entrained bed air-blown coal gasifier, which achieves the highest net plant efficiency by using air as the gasification agent, and G-class high temperature combustion turbines for the U.S. market.

In addition, as for the field of coal gasification-based chemical synthesis plant and poly-generation, MHI offers two stage entrained bed oxygen-blown gasifier with highly efficient gasification performance.

This paper will discuss the latest activities MHI have been taking for the commercial plants of air-blown IGCC including the updated project status of the 250MW Nakoso IGCC demonstration project which has been successfully operating since 2007 and oxygen-blown based projects.

Furthermore future vision to achieve higher efficiency currently we are striving for are also discussed.

MHI believes that our technologies will contribute to energy or fuel resource security and global environmental needs.

#### **Compact Gasification System Demonstration Program Status**

Alan Darby, Pratt & Whitney Rocketdyne, USA

Pratt & Whitney Rocketdyne (PWR) is developing a gasification system consisting of a Compact Gasifier and Dry Solids Pump that will provide significant improvements for future gasification plants. Commercial plants using PWR's technology can expect capital cost reductions of 20%, increased availability up to 95% and Cold Gas Efficiencies 2-3% greater than existing entrained flow gasifiers. Based on the results of our pilot plant gasifier and prototype dry solids pump test programs, PWR initiated a 400 TPD Demonstration Plant program as the next step to commercialization. Located



in China, the demonstration plant will operate for at least one year, with three different feed stocks, to provide performance and reliability data needed for commercial sales. The presentation will summarize PWR gasification technology and review PWR's demonstration plant configuration, test goals, schedule, project status, and the partners supporting the project.

#### **Coal-Water Slurry Gasification Technology of Opposed Multi-Burner and Its Application Progress**

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

Entrained-flow coal gasification is a type of clean and efficient technology of coal utilization, representing the direction of development of coal gasification. Coal-Water Slurry (CWS) gasification technology of Opposed Multi-Burner(OMB) is a typical entrained-flow gasification technology, which is suitable for large-scale. The process of OMB gasification includes CWS preparation section, OMB gasification and "step by step" primary syngas purification section and slag water treatment section of direct heat exchange. OMB gasification technology is applied widely in China. There are 9 users (22 gasifiers) in commercial operation. In addition, there are more than 19 users (more than 56 gasifiers) in design or construction phase. The total capacity is over 100 thousand tons coal per day. The products include methanol, ammonia, acetic acid, oil, olefin, hydrogen, electricity and so on. OMB gasification technology has also been licensed to a project in the United States. OMB gasifier with capacity of 2000 TPD (tons coal per day) in Jiangsu Linggu Chemical Co., Ltd. passed the online 72-hour performance test during Nov. 25 – 28, 2011 organized by China Petroleum and Chemical Industry Federation. More than 2 years operating experience of the plant shows that the gasification unit runs in a stable manner and the performance achieves a world-advanced level. With Shenhua coal as raw material typically used in China, specific oxygen consumption of OMB gasification unit is  $352\text{Nm}^3 \text{O}_2/1000\text{Nm}^3 (\text{CO} + \text{H}_2)$ , specific coal consumption  $568\text{kg coal} / 1000\text{Nm}^3 (\text{CO} + \text{H}_2)$ , the effective gas ( $\text{CO} + \text{H}_2$ ) content 82.9% (v), the combustible matter content of crude slag less than 2% (wt), and the carbon conversion is higher than 99%. In addition, OMB gasifier with capacity of 3000 TPD is under construction.

#### **RTI Warm Syngas Clean-Up and Carbon Capture Sequestration Project**

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

Currently, coal is used to generate 48.5% of the electricity used within the United States and is a dominant fuel for power generation worldwide. Furthermore, coal, because of existing infrastructure, abundant resources, and commercially available technologies, should remain a dominant fuel for electric power generation for the foreseeable future. But coal's dominance is being threatened by cheap natural gas supplies in the U.S. and by global efforts to reduce greenhouse gas emissions. Although coal has a legacy of being a "dirty" fuel, technology advances, particularly integrated gasification combined cycle (IGCC) plants, have been shown to provide near zero emissions from coal-based plants. However, commercial deployment of new more efficient and cleaner coal-based gasification plants has been constrained due to lack of demonstrating significant technology advancements that have great potential to improve overall plant efficiency, availability, and costs (both capital and O&M).

RTI has developed a warm syngas desulfurization process that has been demonstrated at both the lab and pilot scale. Results from the lab and pilot tests have shown that RTI's technology can improve both efficiency and costs on IGCC plants. But a larger scale demonstration of the process is required to mitigate the technical and scale up risk associated with commercial deployment. RTI has negotiated a cooperative agreement with the U.S. Department of Energy for a 50 MW demonstration of this warm syngas clean-up technology platform with the goal of being ready for commercial deployment by 2015. RTI will locate the project at Tampa Electric's IGCC plant at Polk Power Station outside of Tampa, Florida. A 20% slip stream of Tampa Electric's syngas will be treated in RTI's warm gas desulfurization process. The project scope also includes a sweet water gas shift (90% carbon capture conversion) coupled with downstream carbon capture via an advanced activated amine system provided by BASF. This advanced activated amine system has enhanced capabilities for  $\text{CO}_2$  capture, but has previously been excluded from use in coal- or petcoke-based applications because of its sensitivity to high-level sulfur exposure. Because of the selective upstream sulfur removal by RTI's warm syngas desulfurization process, the  $\text{CO}_2$  capture target can be achieved by this amine process without the detrimental effects of higher sulfur exposure. Because the amine process does provide some additional non-selective sulfur removal at low levels, the integration of these two processes is expected to reduce overall sulfur in the treated syngas to very low (<100 ppb) concentrations, suitable for the most rigorous syngas applications. These integrated processes are also expected to achieve syngas cleanup at costs substantially below that of conventional processes, thus expanding the application of RTI's warm syngas cleanup technology beyond power generation to applications such as chemicals, fertilizers, fuels, and hydrogen.

The goals of this project are to demonstrate that the warm gas desulfurization technology can remove >99.9% of  $\text{H}_2\text{S}$  and COS from coal derived syngas, operate for 5,000 to 8,000 hours, and capture up to 90% of any  $\text{CO}_2$ . The results from this project

will be used to establish performance criteria for stable commercial operation including reliability, availability, and maintenance (RAM) and provide extensive operating experience including startup/shutdown and operator training. The results from the demonstration project will be utilized to validate the current performance and economic models. This presentation will provide an overview of these syngas cleanup technologies and their expected performance, the status of the pre-commercial demonstration project, and economic comparisons with conventional syngas cleanup technologies.

#### **SESSION 26 Coal-Derived Products: General – 3**

#### **Structural Features of Chars and Tars Derived from South African Large Coal Particles**

Burgert B. Hattingh, Raymond C. Everson, Hein W.J.P Neomagus, Johan H.L. Jordaan, Andre Joubert, North West University; John R. Bunt, Daniel van Niekerk, Sasol Technology (Pty) Ltd., SOUTH AFRICA

Tars and chars derived from four typical South African coals (confined to the large particle regime) at 450°C and 750°C respectively were subjected to different advanced analytical techniques in order to evaluate respective structural features. GC/MS, GC/FID, SEC, SIMDIST and NMR analyses were performed on all generated tars, while chars generated were subjected to XRD,  $^{13}\text{C}$  NMR and HRTEM analyses. Low temperature tars were characterised by the presence of aliphatic material and some simple aromatic hydrocarbons (such as phenol), while tars generated at the higher temperature were progressively more aromatic (containing higher order aromatics such as anthracenes, naphthalenes and PAH). Furthermore, a subsequent shift in molecular mass distribution to lower molecular masses was observed for all tar samples at the higher temperature.  $^{13}\text{C}$  NMR and XRD performed on the generated chars revealed the subsequent removal of the aliphatic band leading to more aromatic, poly-condensed solid residues. In addition, a subsequent shift in molecular mass distribution to higher molecular fringes with increasing charring temperature was also observed for all four coal samples.

#### **Importance of the Ni/W Ratio in Ni/W/Alumina Catalysts for Hydrotreating of Model Compounds and Low Temperature Coal Tar**

Hai-Yong Zhang, Shu Zhang, Pei-Zhong Zhang, Yong-Gang Wang, De-Ping Xu, China University of Mining & Technology(Beijing), CHINA

Low temperature coal tar is a potentially abundant feedstock for the oil refineries and can be catalytically hydrotreated to obtain jet fuel. Alumina supported Ni-W catalysts with different Ni/W atom ratios were prepared and characterized by BET, SEM, XRD and  $\text{H}_2$ -TPR. Their catalytic activities were investigated on a trickle bed reactor by hydrotreating cresol-naphthalene model compounds in *n*-heptane solution. The results show that all the catalysts had excellent hydrodeoxygenation and hydrogenation activities while the promotion of Ni on  $\text{WS}_2$  exhibited a plateau for naphthalene hydrogenation. The most active catalyst was selected for hydroprocessing a low temperature coal tar fraction; the product and the kerosene fraction were analyzed by GC-MS and elementary analyser. Phenols and di-aromatics in the tar were almost converted while percentages of cycloalkanes and hydro-aromatics increased significantly. In the meantime, heteroatoms, especially O atoms, reduced remarkably.

#### **Study on the Preparation of Activated Carbon from Macerals in Shenfu Coals Separated by Flotation**

Wei Zhao, Zhen Li, Anning Zhou, Xian University of Science and Technology, CHINA

This paper focus on the study of methods for the separation and effective utilization of coal macerals, using froth flotation to separate and concentrate the vitrinite and inertinite, and utilizing them to prepare activated carbon. The influence of pH value of coal slurry on flotation tests was investigated. And the relationship of the properties of activated carbon with the content of macerals was explored. The results showed that the enrichment ratio of vitrinite and inertinite could be controlled by the pH value of coal slurry; the inertinite rich coal samples were benefit to make mesoporous activated carbon, and vitrinite rich samples could be used to make microporous activated carbon.

**SESSION 27**  
**Gasification: General – 4**

**Production of Substitute Natural Gas Using Steam Hydrogasification Configured with a Water Gas Shift Reaction**

Yoothana Thanmongkhon, Chan S. Park, Joseph Norbeck, University of California, Riverside, USA

The steam hydrogasification reaction (SHR) process has been developed by the Bourns College of Engineering - Center for Environmental Research and Technology (CE-CERT). The SHR process has been shown to produce methane, enriched synthesis gas from various carbonaceous materials with steam in a hydrogen environment. Carbon monoxide, one of the products in the output gas of the SHR, can be further reacted with steam via the water gas shift (WGS) reaction to generate H<sub>2</sub>. This process configuration, using the SHR process and a WGS reactor has the potential to generate Substitute Natural Gas (SNG). This process can use carbonaceous feedstock including coal, biomass and carbon-based waste. Additionally, hydrogen, a product from the WGS reaction, can be internally recycled as a feed into SHR to maintain a self-sustainable process. A mixture gas (CO, H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>) with steam, which simulates the producer gas of the SHR process, was fed into a laboratory scale continuous WGS reaction system using a high temperature shift catalyst. The optimum catalyst temperature was 350°C with the space velocity about 4500 hr<sup>-1</sup>. CO conversion was observed to be 85% at typical process conditions. Under these conditions there was sufficient H<sub>2</sub> to recycle to the SHR process.

**Coal Char-CO<sub>2</sub> Gasification Measurements and Modeling in a Pressurized Flat-Flame Burner**

Thomas H. Fletcher, Randy C. Shurtz, Brigham Young University, USA

The effects of elevated pressure and high heating rates on coal pyrolysis and gasification were investigated. A high-pressure flat-flame burner (PFFB) was designed and built to conduct these studies. The PFFB was designed to provide an environment with laminar, dispersed entrained flow, with particle heating rates of ~105 K/s, pressures of up to 15 atm, and gas temperatures of up to 2000 K. Residence times were varied from 30 to 700 ms in this study.

Char gasification studies by CO<sub>2</sub> were conducted on a subbituminous coal and 4 bituminous coals in the PFFB. Pressures of 5, 10, and 15 atmospheres were used with gas compositions of 20, 40, and 90 mole % CO<sub>2</sub>. Gas conditions with peak temperatures of 1700 K to 2000 K were used, which resulted in char particle temperatures of 1000 K to 1800 K. Three gasification models were developed to fit and analyze the gasification data. A simple 1st-order model was used to show that the measured gasification rates were far below the film-diffusion limit. The other two models, designated CCK and CCKN, were based on three versions of the CBK models. CCKN used an *n*th-order kinetic mechanism and CCK used a semi-global Langmuir-Hinshelwood kinetic mechanism. The two CCK models fit the PFFB gasification data better than the 1st-order model. The fits of the gasification data with CCK and CCKN were comparable to each other. The fit of the data in CCK suggests that Knudsen diffusion may have influenced the gasification rates in the PFFB experiments. The gasification rate parameters in each of the three models were correlated with coal rank. 13C-NMR parameters were used to estimate a structural parameter of the coal char. Char-CO<sub>2</sub> gasification rate coefficients correlated better with this NMR-based char structure index than it did with the carbon and oxygen content of the parent coal.

**Investigation of Low Rank Coal Gasification in a Two-Stage Downdraft Entrained-Flow Gasifier**

Ting Wang, Xjia Lu, University of New Orleans, USA

Low-rank coal contains more volatiles, more inherent moisture, high alkali metals (Na, K, Ca), high oxygen content and low sulfur than high-rank coal. Low-rank coal gasification usually has lower efficiency than high-rank coal, since more energy has been used to drive out the moisture and volatile matters and vaporize them. Nevertheless, Low-rank coal comprises about half of both the current utilization and the reserves in the United States and is the largest energy resource in the United States, so it is worthwhile and important to investigate the low-rank coal gasification process. Among the existing commercial coal gasifiers, two-stage fuel feeding has been employed only in updraft gasifiers, such as the E-gasifier. In this study, the two-stage fuel feeding scheme is investigated in a downdraft, entrained-flow, and refractory-lined reactor. The two-stage coal feeding gasification process injects all of the oxygen in the first stage and provides a certain amount of coal slurry without oxygen in the second stage. The endothermic gasification process downstream of the second stage could keep the gasifier at a lower temperature; and hence, the life of the refractory bricks can be extended and maintenance costs reduced. However, this benefit gained at the second stage is obtained at the cost of a higher peak combustion temperature in the first stage than a typical one-stage gasifier. Since the combustion temperature of low-rank coal is lower than the high rank coal, it is hypothesized that low-rank coal can help reduce the peak temperature at the first stage. Therefore, hypothetically, it seems that it is more

advantageous for utilizing low-rank coals to in a two-stage coal gasification process. This study aims to investigate these hypotheses.

Both high-rank coal and low-rank coal have been used for comparison. Considering that the high-moisture content in the low-rank coal cannot help reduce the amount of water needed for making an appropriate recipe of coal slurry, dry coal feeding seems to be more energy efficient than slurry coal feeding. Hence, both dry coal and slurry coal feeding methods are studied, and the results are compared.

**Development of a Slag Submodel for an Entrained-Flow Gasifier**

Pratik Pednekar, Debansu Bhattacharyya, Richard Turton, West Virginia University; Raghunathan Rengaswamy, Texas Tech University, USA

In slagging gasifiers with hot wall configurations, a portion of the molten slag flows along the inner walls of the gasifier. The slag can penetrate into the gasifier refractory causing degradation. However, due to the harsh operating conditions inside such a gasifier, it is impossible to measure the refractory degradation with current measurement technology. Therefore, a mathematical model can be useful in understanding the effects of various operating conditions and physicochemical properties on the degradation characteristics.

With this incentive, a slag sub-model is being developed. This sub-model will be eventually integrated with a 1D steady-state model of a single-stage, downward-firing, oxygen-blown, slurry-fed, entrained-flow gasifier previously developed at WVU using Aspen Custom Modeler® (ACM). In this paper, we have presented a model for calculating the deposition rate of the detached slag droplets considering Illinois#6 coal as the gasifier feed. The model is then used to investigate the effect of the droplet size distribution on the deposition rate.

**SESSION 28**  
**Combustion: Ash and Combustion – 2**

**Kinetic Study on Combustion of Pulverized Coal Blended with Bottom Ash Using Thermo-gravimetric Analysis (TGA) Reactor**

Sang Shin Park, Hyo Jae Jeong, Jungho Hwang, Yonsei University; Myung-chul Shin, Korea Institute of Industrial Technology, KOREA

Coal thermoelectric power plant emits bottom ash as by-product. The bottom ash causes environmental problem and lack of landfill. Combustion technology for pulverized coal blended with the bottom ash has been an issue. In this study, in order to understand the kinetic characteristic for the combustion, thermo-gravimetric analysis (TGA) was carried out under air atmosphere and isothermal condition at temperatures of 800°C, 900°C, 1000°C, and 1100°C. The blending ratios of coal and bottom ash were 1, 0.9, and 0.8. The kinetic parameters (*A*, *E<sub>a</sub>*) were obtained by Volume Reaction Model (VRM), Shrinking Core Model (SCM), and Random Pore Model (RPM) from the TGA experimental data. The activation energy (*E<sub>a</sub>*) and frequency factor (*A*) of coal and bottom ash-air reaction were determined using the Arrhenius equation.

**Investigation of the Effect of Biomass-Limestone Interaction on the Ash Compositon for Co-Combustion of a Lignite Coal and Olive Cake in a Circulating Fluidized Bed Combustor**

Murat Varol, Aysel T. Atimtay, Middle East Technical University, TURKEY

In this study, it is aimed to investigate the effect of biomass+limestone mixtures on ash composition. Olive cake was used as a biomass resource because of its high alkali metal (Na and K) content (K<sub>2</sub>O content of olive cake ash was about 50% by wt.). Bursa- Orhaneli lignite and Can limestone was used in the tests. The Ca/S ratio was kept at 2. The tests included co-combustion of Bursa- Orhaneli lignite and olive cake mixture containing 50% by wt. olive cake with and without limestone addition. Co-combustion tests were conducted in a circulating fluidized bed combustor at 850°C. The combustor column has an inside diameter of 108 mm and a height of 6 m. A Deposit Sampling Probe (DSP) was designed and used in the upper part of the combustor column during the tests to simulate a heat exchanger tube. The probe was cooled to 550°C with air. The particles accumulated on the surface of the probe were collected at the end of the combustion test. After the probe was taken out of the combustor column, the particles collected on the probe were very slowly and carefully scraped from the surface into a sampling pot. Then, they were sent for XRD and SEM-EDS analysis. At the end of the combustion test, bottom ash (BA) was also collected. Bottom ash samples were taken for XRF, XRD and SEM-EDS analyses. Ash deposition rate was calculated. Ash balance was done. In order to compare the results from co-combustion tests in the CFBC, Bursa-Orhaneli lignite and olive cake samples were combusted alone in a furnace according to the ASTM standards (ASTM D1374-04 Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal for coal samples, ASTM E1755-01 Standard Test Method for Ash in Biomass for olive cake). The ash samples obtained were subjected to XRF and XRD analyses. The results of fuel ash analyses were compared with the analysis results of ashes obtained

from the co-combustion tests (both the bottom ash and the ash collected on the deposit probe).

The results of this study showed that although SiO<sub>2</sub>, MgO, and CaO are the major oxides in the bottom ash for the co-combustion test without limestone, CaO, SO<sub>3</sub>, SiO<sub>2</sub>, and MgO are also the major oxides in the bottom ash from the tests with the addition of limestone. However, the CaO content in bottom ash has increased due to limestone addition. Quartz (SiO<sub>2</sub>), Lime (CaO), Anhydrite (CaSO<sub>4</sub>), Arcanite (K<sub>2</sub>SO<sub>4</sub>) and Forsterite (Mg<sub>2</sub>(SiO<sub>4</sub>)) are the phases encountered in the bottom ash for the co-combustion test without limestone. The Quartz (sand) which is used as bed material is the dominant phase in the bottom ash. Quartz (SiO<sub>2</sub>), Calcite (CaCO<sub>3</sub>), Lime (CaO), Anhydrite (CaSO<sub>4</sub>), Arcanite (K<sub>2</sub>SO<sub>4</sub>) Potassium Calcium Sulfate (K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) and Forsterite (Mg<sub>2</sub>(SiO<sub>4</sub>)) are the phases encountered in the bottom ash for the co-combustion test with limestone. Limestone addition to the fuel mixture might transfer K element from Arcanite to Potassium Calcium Sulfate in the bottom ash. While K was in the form of Arcanite for the co-combustion test without limestone, it mostly appears in the form of Potassium Calcium Sulfate in the bottom ash for the co-combustion test with limestone. The main phase determined in the deposits obtained from the Deposit Sampling Probe is also Potassium Calcium Sulfate. Since the surface of the deposit sampling probe is at 550°C, it is expected that the K oxides in the fuel mixture condenses on the surface of the probe and transforms into the phase of Potassium Calcium Sulfate. SEM-EDS results are strongly consistent with XRF and XRD results for the bottom ash samples and the ash from the Deposit Sampling Probe.

#### Analysis of Turbulent Hybrid Methane-Air-Coal Dust Flames

Ali S. Rangwala, Scott R. Rockwell, Worcester Polytechnic Institute, USA

Initiation and propagation of dust deflagrations are extremely complex phenomena due to the interaction between solid particles and the gaseous flame front. In comparison with premixed gas deflagration, a dust-oxidizer deflagration depends on the rate of evolution of volatiles, the mixing of these volatiles with the oxidizer surrounding the particles, coupling of the particles and gas phase oxidation as well as radiative energy exchange between the flame and its surroundings. Due to these complications, a comprehensive mathematical theory to predict deflagration mechanisms of dust clouds is at present beyond reach. Although vast amount of testing, both small scale (20 liter explosion vessel) and large scale tests have been done over the last 50 years, most theories that connect the data to models are heavily empirical and the problem has never been analyzed from a fundamental viewpoint.

This study will identify the controlling parameters of turbulent hybrid dust deflagration mechanisms. To study flame propagation in dust clouds a novel premixed-dust-air burner is designed to measure the burning velocity of a hybrid mixture of Pittsburgh seam coal dust, with typical particle sizes in the range of 75 to 90 μm and methane-air. Figure 1 depicts shadowgraph images of a sample of flames tested. The results show that the addition of coal dust in a laminar methane-air premixed flame (Fig. 1 (b)) reduces the burning velocity. An opposite trend of an increase in the burning velocity is observed in a turbulent flame (Fig. 1 (d)). Two competing effects are considered to explain these trends. The first effect is due to volatile release, which increases the overall equivalence ratio and thus, the burning velocity. The second is the heat sink effect that the coal particles take up to release the volatiles. This process reduces the flame temperature and accordingly the burning velocity also. A mathematical model is developed considering these effects and it is seen to successfully predict the change of burning velocity for various cases with different dust concentrations and equivalence ratios of the gas mixture. Furthermore, the implication of this study to coal mine safety is discussed.

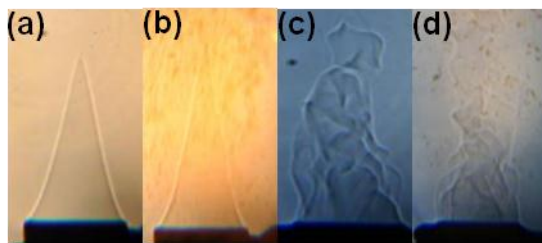


Figure 1: Shadowgraph images of: (a) laminar methane-air flame (b) laminar methane-air-dust flame (c) turbulent methane-air flame, (d) turbulent methane-air-dust flame. Methane-air equivalence ratio,  $\Phi = 0.9$  for all cases. Coal-dust particle size = 75 – 90 μm in (b) and (d), and concentration = 70 g/m<sup>3</sup>. Turbulent intensity  $u' = 0.7$  m/s for (c) and (d).

#### Influence Factors on Particle Size of Fly Ash from Pulverized Coal Combustion

Kenji Tanno, Hiromi Shirai, Michitaka Ikeda, Central Research Institute of Electric Power Industry, JAPAN

The combustion of pulverized coal inevitably produces fly ash which causes some problem in plant operation (e.g. slugging, fouling, and erosion of boiler, and collection in bag filter or electrostatic precipitator (ESP)). There are many properties of fly ash particle, but one of the most important property is particle size, because transportation behavior in a boiler and collection efficiency in ESP are strongly affected by particle

size. Therefore, it is of great importance to evaluate fly ash particle size during pulverized coal combustion. In this study, as the first step of development of comprehensive predicting method, influence factors on fly ash particle size from pulverized coal combustion were investigated by using the Computer Controlled Scanning Electron Microscopy (CCSEM) and developing a CCSEM-based fly ash formation model. The fly ash formation model separately treat included mineral and excluded mineral in pulverized coal. Included minerals are randomly dispersed to individual coal based on coal and mineral particle size and assumed to be coalesced with other included minerals during combustion. Coalescence parameter was introduced to investigate the effect of coal properties and combustion condition on coalescence behavior. Fragmentation of excluded minerals was simulated using Poisson distribution. Furthermore, in order to compare CCSEM data and predicted results, 8 different brands of bituminous coal were combusted in our combustion test facility and 12 kinds of fly ash were sampled in actual coal-fired power plants. The results showed that fly ash size are strongly affected both mineral size and the ratio of excluded mineral. The ratio of excluded mineral depends on both coal property and pulverizing condition, hence this result indicates the necessity to clarify fundamental mechanism of coal pulverizing. The predicted particle size distribution was in good agreement with experimental data by choosing adequate coalescence parameter. The difference of adequate coalescence parameter indicates the difference of coalescence behavior of included minerals during combustion. Coalescence behavior was strongly affected by combustion temperature near the burner. Gaseous temperature became high, coalescence parameter took higher value, and consequently, fly ash particle size became large. This result may be due to the difference of char structure formed during devolatilization process.

#### SESSION 29

#### Carbon Management: CO<sub>2</sub> Capture – 4

#### Amine-Silica “Nanobubbles” for CO<sub>2</sub> Sorption

Karen Uffalussy, Götz Vesper, University of Pittsburgh/DOE/NETL; Craig Stevenson, University of Pittsburgh, USA

Recent efforts in the development of post-combustion CO<sub>2</sub> capture materials have focused on combining the advantages of solid capture materials with those of liquid amines by both grafting and embedding amine groups onto solids. Here, we report on the application of this sorbent design principle to the encapsulation of polyethylenimine and tetraethylenepentamine (PEI and TEPA, two liquid amines widely investigated for CO<sub>2</sub> capture) in silica “nanobubbles”, as nanoencapsulation may result in unique properties for CO<sub>2</sub> sorption.

Porous silica shells were prepared in a reverse microemulsion using a straightforward one-pot synthesis method developed in our laboratory. The resulting “nanobubbles” consist of a microporous silica shell with wall thickness which can be tailored between ~4-30nm encapsulating a pronounced cavity of ~15 nm diameter. Liquid amines were introduced into these porous silica nanobubbles by a simple wet impregnation approach, resulting in controllable liquid amine loadings of ~25 – 75wt%. The CO<sub>2</sub> sorption kinetics were then measured via isothermal thermogravimetric analysis (TGA) over a temperature range of 60 – 105°C during alternating exposure to a high purity CO<sub>2</sub> stream ( $P_{CO_2} = 1$  bar), followed by desorption into a pure inert gas stream (He) at the same temperature.

Results show distinct contributions from kinetic and thermodynamic effects with increasing temperature, and, more importantly, a drastic acceleration of the sorption kinetics for the nanoencapsulated PEI in comparison to the free liquid PEI by about three orders of magnitude. Furthermore, the specific CO<sub>2</sub> sorption capacity (per mole of PEI) is twice as high for the nanoencapsulated PEI than for the unconfined liquid PEI (~125 mg-CO<sub>2</sub>/g-PEI vs ~250 mg-CO<sub>2</sub>/g-PEI, respectively). The strongly accelerated kinetics can be explained by the drastic reduction of the diffusion length for the nanoconfined material, and hence a complete removal of mass transfer limitations during CO<sub>2</sub> capture. The reason for the enhanced sorption capacity is still under investigation, but is likely due to configurational changes of PEI in the nanoconfinement.

The nanoencapsulated TEPA performed best at a 1:1 ratio for greater amounts of TEPA and silica (142 mg CO<sub>2</sub>/g sorbent), whereas the PEI embedded material performed best at a 1:1 ratio of PEI to silica. This suggests that the MeOH solvent plays a different role in entraining the material into the silica nanobubbles. The TEPA material is less stable than PEI under impregnation conditions, and it is likely that some TEPA volatilizes during the embedding procedure. This effect appears to increase with higher concentrations of MeOH. Furthermore, TEPA-nanobubble material is not stable under TGA operating conditions, as the weight of the material decreases past the initial weight even after the first cycle. This loss in mass is likely due to the high vapor pressure of TEPA at  $T > 60$  °C. In contrast, PEI@SiO<sub>2</sub> showed stable operation over multiple cycles at temperatures as high as 75 °C, suggesting that the PEI-nanobubble sorbent might constitute a feasible sorbent material with extremely fast sorption kinetics. Further investigations into the mechanism of PEI sorption into the nanobubbles are on-going. Overall, the nanoencapsulated PEI shows promise as a hybrid liquid-solid CO<sub>2</sub> sorbent material, and results to-date suggest that further

improvement of the performance will be possible based on appropriate nanostructuring of the “nanobubbles”.

### **Dynamic Modeling and Transient Studies of a Solid-sorbent Adsorber for CO<sub>2</sub> Capture**

Srinivasarao Modekurti, Debansu Bhattacharyya, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

The U.S. Department of Energy's *Carbon Capture Simulation Initiative* (CCSI) is dedicated to accelerating the commercialization of carbon capture technologies from discovery to development, demonstration, and ultimately the widespread deployment to hundreds of power plants. In this multi-lab initiative in partnership with academic and industrial institutions, the National Energy Technology Laboratory (NETL) leads the development of a multi-scale modeling and simulation toolset for rapid evaluation and deployment of carbon capture systems. One element of the CCSI is focused on optimizing the operation and control of carbon capture systems since this can have a significant impact on the extent and the rate at which commercial-scale capture processes will be scaled-up, deployed, and used in the years to come. Capture processes must be capable of operating over a wide range of transient events, malfunctions, and disturbances, as well as under uncertainties. As part of this work, dynamic simulation and control models, methods, and tools are being developed for CO<sub>2</sub> capture and compression processes and their integration with a baseline commercial-scale supercritical pulverized coal (SCPC) power plant.

Solid-sorbent-based post-combustion capture technology was chosen as the first industry challenge problem for CCSI because significant work remains to define and optimize the reactors and processes needed for successful sorbent capture systems. Sorbents offer an advantage because they can reduce the regeneration energy associated with CO<sub>2</sub> capture, thus reducing the parasitic load. In view of this, the current paper focuses on development of a dynamic model of a solid-sorbent CO<sub>2</sub> adsorber-reactor and an analysis of its transient performance with respect to several typical process disturbances.

A one-dimensional, non-isothermal, pressure-driven dynamic model of a two-stage bubbling fluidized bed (BFB) adsorber-reactor is developed in Aspen Custom Modeler (ACM). The BFB stages are of overflow-type configuration where the solids leave the stage by flowing over the overflow-weir. Each bed is divided into three regions, namely emulsion, bubble, and cloud-wake regions. In all three regions, the model considers mass and energy balances. Along with the models of the BFB stages, models of other associated hardware are developed and integrated in a single flowsheet. A valid pressure-flow network is developed and a lower-level control system is designed so that the overall CO<sub>2</sub> capture can be maintained at a desired level in face of the typical disturbances. The dynamic model is used for studying the transient responses of a number of important process variables as a result of the disturbances that are typical of post-combustion CO<sub>2</sub> capture processes.

### **Nanoclay-Based Solid-Amine Sorbents for Carbon Dioxide Capture**

Elliot Roth, Sushant Agarwal, Rakesh K. Gupta, West Virginia University, USA

The objective of the research project is to develop an efficient, low cost, highly recyclable solid sorbent for carbon dioxide capture from large point sources, such as coal-fired power plants. The sorbent developed here is composed of a nanoclay (montmorillonite), commonly used in the production of polymer nanocomposites, grafted with commercially available amines such as Aminopropyltrimethoxysilane (APTMS) and polyethylenimine (PEI). FTIR and TGA analysis were used to characterize the amine grafted nanoclays. CO<sub>2</sub> adsorption tests revealed that the optimal adsorption temperature was between 75 C and 85 C with maximum CO<sub>2</sub> adsorption capacity of 6.7 wt% for nanoclay treated with APTMS; with the additional grafting of PEI to the surface of the clay, the adsorption capacity increased to 9.7 wt% CO<sub>2</sub>. In a more realistic simulated flue gas of 10% CO<sub>2</sub> and 90% N<sub>2</sub>, the adsorbents had essentially the same adsorption capacity of 9.6% for clay treated with APTMS and PEI. Adsorption studies in pure CO<sub>2</sub> at room temperature under pressure of up to 300 psi showed capture capacity at 7.5 wt% with APTMS treated nanoclay, while the combination of APTMS and PEI treatment on the clay increased the average adsorption capacity to 11.4 wt% CO<sub>2</sub>. It is also shown that the nanoclay solid sorbent can be regenerated using pure N<sub>2</sub> at 100 C as a sweep gas and then reused. This small difference in adsorption and regeneration temperatures should result in considerable savings in energy penalties. This amine treated nanoclay solid sorbent shows comparable capture capacities to other emerging CO<sub>2</sub> adsorption technologies, but it has the benefit of being low cost and easily available and together with the use of commercially available amines should provide a more commercially realistic CO<sub>2</sub> adsorbent.

### **Carbon Capture-Promoted Syngas Utilization for Production of Fuels and Chemicals**

Keling Zhang, Prabhakar Singh, University of Connecticut; David King, Xiaohong Shari Li, Rob Dagle, Liyu Li, Pacific Northwest National Laboratory; Yuhua Duan, DOE/NETL, USA

Purified syngas from coal or biomass gasifiers can be utilized through subsequent catalyzed processes for the production of fuels and chemicals, as well as for fuel cell-based power generation. Capture of CO<sub>2</sub> during the process of syngas preparation provides benefits, both in reducing greenhouse gas emissions as well as facilitating the equilibrium conversion levels when CO<sub>2</sub> is co-produced. Current commercially available cleanup technologies provide capture of harmful impurities, along with CO<sub>2</sub>, at ambient or sub-ambient temperatures. Subsequent utilization of the syngas requires an inefficient re-heating of the gas to the appropriate temperature. Moreover, this CO<sub>2</sub> capture step does not facilitate subsequent syngas conversions that are equilibrium limited and can be facilitated by CO<sub>2</sub> by-product absorption. Warm gas cleanup has the potential to alleviate this energy efficiency, but also requires warm CO<sub>2</sub> capture to preserve the energy efficiency.

Preliminary research results have described the development and structure of MgO-based CO<sub>2</sub> capture materials, specifically Mg-Na double salts<sup>1</sup>, for warm CO<sub>2</sub> capture. In multiple CO<sub>2</sub> absorption-desorption cycle tests, the double salt material significantly outperformed MgO, even though, thermodynamically, MgO is expected to provide high CO<sub>2</sub> capacity through formation of MgCO<sub>3</sub>. We have identified an important role for NaNO<sub>3</sub>, a byproduct of the double salt synthesis, in facilitating CO<sub>2</sub> capture with these materials<sup>2</sup>. CO<sub>2</sub> adsorption characteristics for the double salt have been evaluated using both temperature and pressure swing processes using a TGA/DSC apparatus. A capture capacity of 3.7mmol/g of absorbent was achieved at ambient pressure. Pressure and thermal swing tests show excellent regenerability and structural stability of the sorbent. This capture capacity of the absorbent will be evaluated in a fixed bed reactor and the results will be discussed. Preliminary results combining CO<sub>2</sub> capture with water gas shift and natural gas production will also be described.

<sup>1</sup>Keling Zhang, Prabhakar Singh, Liyu Li, David L. King. Aggregated Role of Double Salt Structure and Formulations for Warm Temperature CO<sub>2</sub> Capture; presented at the 2011 Pittsburgh Coal Conference, Pittsburgh, PA, September 2011.

<sup>2</sup>David King, Keling Zhang, Liyu Li, Hao Chen, Yuhua Duan, Xiaohong Shari Li, Prabhakar Singh. Carbon Capture-Promoted Syngas Utilization for Production of Fuels and Chemicals, presented at the 11<sup>th</sup> Annual Conference on Carbon Capture, Utilization & Sequestration, Pittsburgh, PA, May 2012.

## **SESSION 30 Coal Science: General – 2**

### **Advances in Coal Analyses and Simulations 1989-2012**

Jonathan P. Mathews, The Pennsylvania State University; Randal Winans, Argonne National Laboratory; Ryan P. Rodgers, National High Magnetic Field Laboratory and Florida State University, USA; Atul Sharma, National Institute of Advanced Industrial Science and Technology, JAPAN

There are periodic publications that address advances in coal science. This continues that fine tradition and focuses on the author's views of the more significant advances in analytic techniques (chemical and physical) and molecular based simulation that has expanded our ability to quantify coal properties and explore behavior. During the last two decades (plus a few years) the rationalization of coal chemistry has been considerably expanded by: the additional quantification of solid state <sup>13</sup>C NMR, the quantification of the lattice fringe views from coal HRTEM micrographs, evaluation of molecular weight distribution by laser desorption ionization (LDI) mass spectroscopy (MS), and the inclusion of structural diversity via the Fourier transform ion cyclotron resonance (FT-ICR) MS approach for coal extracts. Specifically, the Solum et al. combined dipolar dephasing coupled with CPMAS NMR to produce 12 carbon structural parameters was a significant advance in enhancing comparison of coals structural features. With lattice fringe extraction techniques coal HRTEM micrographs went from a hazy micrograph to the elucidation of the distribution of the aromatic lattice fringes, their size, orientation, and clustering across the rank range in coal products. Laser desorption ionization mass spectroscopy has yielded further insights into the molecular weight distributions of coal. Electrospray ionization (ESI) FT-ICR MS is expanding our understanding a coals' compositional and structural diversity by directly determining the elemental compositions of the ions of coal extracts (by accurate mass measurement alone) and capturing/visualizing the high resolution MS data with Kendrick mass defect plots vs. nominal Kendrick mass plots, heteroatom class consideration, color isoabundance plots, and van Krevelen diagrams.

Physical properties and coal behavior are also further quantified by HRTEM lattice fringe images, porosity evaluation through small angle X-ray (or neutron) scattering (SAXS/SANS) approaches, and X-ray computed tomography evaluations. Specifically the HRTEM lattice fringes shows the distribution of the stacking and orientation of aromatic fringes aiding quantification of aromatic arrangements on the atomic scale. Through SAXS and SANS, particularly at U.S. National Laboratory user facilities, with contrast matching approaches the behavior of coal with gases and solvents has been elucidated. For example the pore filling of CO<sub>2</sub> in sequestration related studies has been captured as has changes to the pore structure with in-situ devolatilization or gasification. X-ray computed tomography has allowed the non-destructive evaluation of the physical structure of coal with resolutions in the 35µm range with the promise of

significantly higher resolution. This has permitted 3D evaluations of: the cleat structure, quantification of coal swelling/contraction with addition/removal of gases and solvents, determination and anisotropy of strains, kinetics of gas uptake, coking transitions, and impacts of microwave exposure on the cleat network.

Analytical advances have resulted in the ability to quantify coal data and further constrain molecular representations. Restricting models to the average NMR parameters, while capturing a portion of the structural diversity has resulted in new computer aided tools for structure creation and evaluation. Several tools have evolved such as SIGNATURE (Stochastic generation), computer aided molecular design, with advances in the evaluation of the resulting structure (POR-pore size distribution), NMR evaluations, pair distribution modeling, etc. Building on these approaches the state-of-the-art couples HRTEM analysis (diversity of fringe lengths and orientations) to directly construct constrained molecular representations (Fringe3D) which can be manipulated in 3D structures further constrained by: multiple NMR parameters, FT-ICR data (diversity of heteroatom classes for example), SAXS and SANS data for pore size distributions (limited to a limited extent by the scale of the representation). Automated approaches have expanded the scale of representation with greater accuracy and improved ease with improvements in communication of structural information via 3D and 2D lattice structures. Thus, there has been increased utility and applicability for molecular modeling and analytical advanced to the rationalization of coal science.

### Kinetic Aspects of Coal Classification

Marek Sciazko, Institute for Chemical Processing of Coal, POLAND

Pyrolysis experiments on different types of coal were carried out on the laboratory scale using a LECO TGA-501 thermogravimetric analyzer. The studies were performed in a nitrogen atmosphere at heating rates of 5, 20, 40 and 99 K/min until a final temperature of 900°C was achieved. Kinetic parameters defined by the pre-exponential factor and activation energy were determined using experimental data collected for 8 types of coal. The coal samples were selected from a Polish coal basin representing the entire spectrum of metamorphism, ranging from subbituminous to semianthracite. Our analysis showed that two basic factors, coal grade and heating rate, have a strong effect on calculated values for the frequency factor,  $k_0$ , and the activation energy,  $E$ . To investigate the effect of the heating rate, the activation energy for pyrolyzed coal was represented by a generalized expression consisting of linear equations with variable volatile matter content and heating rate.

If the geochemical coalification of original organic matter is considered to be a slow form of pyrolysis, then the defined kinetic parameters of coal reflect its ability to transform when heated. In particular, the determined kinetic parameters of coal can generally be understood as characteristic of coal's reactivity. Therefore, a classification system was proposed that reflects the coal's ability to degrade thermally as a function of its kinetic parameters.

### Gaseous Product Formation during CO<sub>2</sub> Heat Treatment of Char Produced from an Inertinite-rich Bituminous Coal Doped with Potassium Salt Catalysts

Kelebogile Leeuw, C.A Strydom, J.R Bunt, North-West University; D. van Niekerk, J.C. van Dyk, Sasol Technology Pty (Ltd), SOUTH AFRICA

The catalytic effect of K<sub>2</sub>CO<sub>3</sub> and KCl on the reactivity and gaseous products formed from chars derived from a South African inertinite-rich bituminous coal using TG/MS were investigated. Catalysts (0.5, 1, 3, 5 wt %) were loaded to an inertinite-rich bituminous coal, to a demineralized sample of the same coal and to the demineralized coal sample with an added model synthetic mineral mixture. All samples were then subjected to a heat treatment step up to 900 °C in a nitrogen atmosphere to produce the respective char samples. These char samples were then subjected to heat treatments in a CO<sub>2</sub> atmosphere up to 1200°C. The composition of the product gases formed during the treatment of the chars in the CO<sub>2</sub> atmosphere were identified (but not quantified), and the gasification temperatures and rates determined. The results obtained show that gasification temperatures are lowered (i.e. gasification rate is enhanced) with increasing catalyst loadings, and the initial and termination time of evolution of gaseous species is lowered. The catalytic activity of K<sub>2</sub>CO<sub>3</sub> was found to be superior to that of KCl. The 5 wt% doped coal samples were subjected to heat treatments in a tube furnace under CO<sub>2</sub> atmosphere and the product samples analyzed by XRF and XRD in order to determine the extent of interaction and inactivation of K<sub>2</sub>CO<sub>3</sub> and KCl during these reaction conditions. The amount of potassium species retained after the employed experimental conditions was also determined.

### Fractal Characteristics of Coal Powders in Different Grinding Technologies under a Planetary Mill

Zhiyuan Yang, Liang Gong, Anning Zhou, Xi'an University of Science & Technology, CHINA

Four kinds of Chinese coal are pulverized using a planetary mill in different grinding conditions. The granularity of coal powders is analyzed by Laser Sizer and the profiles of coal fine particles are investigated under SEM. On the basis of fractal theories, fractal dimensions of the granularity distribution (Dg) of coal powders are calculated by Wheatcraft method. The results indicate that the Dg can be calculated from data gathering from Laser Sizer Analysis and an indicator of uniformity of coal grains.

## SESSION 31

### Clean Coal Demonstration and Commercial Projects: Technical - 3 (CCUS)

#### The Global Status of CCS: 2012

Holger Bietz, Global CCS Institute, AUSTRALIA

In early October 2012 the Global CCS Institute releases the annual edition of the Global Status of CCS, the international benchmark report on CCS projects and their progress towards commercial deployment. The report presents data compiled from the Institute's annual survey sent to project proponents, as well as from interviews with projects, and a range of other information sources. This presentation delivers a brief on the report's content and its underlying survey findings into the global status of CCS as related to the progress of CCS projects of various scales and aspects including developments in capture and storage; legal, regulatory and policy aspects; the business case for CCS projects; barriers and public engagement; costs and financing; and global CCS funding status. Over the last two years the Institute has concentrated on large-scale integrated CCS projects (LSIPs) to ensure high data quality. LSIPs involve the capture, transport and storage of CO<sub>2</sub> at a scale of not less than 800 000 tonnes of CO<sub>2</sub> annually for a coal-based power plant, and not less than 400 000 tonnes of CO<sub>2</sub> annually for other emission-intensive industrial facilities including natural gas-based power generation. The global portfolio of the current 75 LSIPs (of which 15 are either operating or under construction – or as the Institute characterizes it, at the Execute Stage) is analyzed by asset lifecycle, region/country, industry, technology, volume of CO<sub>2</sub> targeted to be captured and stored, and other criteria. The Institute is starting to extend the survey to include an initial selection of mid-sized projects which are especially interesting with regards to technology and methodology trends and developments. A dedicated capture technology discussion update is provided on key developments in this area since the release of the *Global Status of CCS: 2011* report. Currently we envisage only incremental improvements on existing commercial technology, although there have been some improvements in the host facility technology. It is also anticipated that there will be further progress in oxyfuel combustion in 2012. The capture technology discussion further highlights the pressure that LSIPs are under to go forward. Also discussed are the benefits of sub-commercial scale (pilot and larger) demonstration projects that test promising technologies having potential for significant (cost) improvements. The discussion on storage elaborates on key findings and lessons learnt from the Institute's supported projects and other LSIPs and provides an update on the status of country-scale storage screenings. CO<sub>2</sub> utilization activities, observations and options for CCS stemming from CO<sub>2</sub> injection for EOR are examined, including EOR affects the CCS business case and impacts of CCS developments on the EOR market. Key policy, legal and regulatory developments since 2011 are also presented, including the transposition of the EU directive and highlighting areas where implementation has lagged in-place policy signals. Building on the 2011 Status Report we further examine the business case for CCS projects that are proceeding, including project structure, financing, risk balance among project contracts. In addition, we examine the key barriers that have prevented some projects proceeding. Also discussed is private sector financing and what may be needed for the private sector to be more involved in CCS. The results of the annual project survey on public engagement, highlighting key developments and project level issues are discussed. In addition, developments with regards to CCS project costs in a real world setting and aim to improve the understanding of project level costs and interactions within a policy parameter setting. The status of global government funding support for CCS is also discussed and analyzed including the instruments applied for allocation. Finally, CCS in the UNFCCC is discussed, including a perspective on the potential future mechanisms that are currently being considered. This discussion also analyzes the pace of the international negotiation process for climate change and CCS against national processes that are occurring, and a snapshot of existing legislation in developing countries that could support CCS.

#### Lessons Learned from EPRI'S CCS Demonstration Program

Jeff Phillips, Andrew Maxson, Electric Power Research Institute, USA

In 2008, the Electric Power Research Institute (EPRI) put together a collaborative program designed to help support larger-scale, first-of-a-kind carbon capture and storage (CCS) demonstration projects. The goal was to provide industrial members and the public insights into real-world CCS projects focusing on: understanding regulatory issues (especially concerning geological sequestration of CO<sub>2</sub>); providing independent capture performance testing; performing economic scale-up analyses; monitoring storage activities; and giving industrial members access to project experts and the demonstration sites themselves for detailed discussions on operations, reliability, and integration.

EPRI was able to put together collaborative programs to support two CCS projects:

- **American Electric Power Services Corporation (AEP) Demonstration Project:** Designed to capture and store CO<sub>2</sub> at ~100,000 tons (90,000 tonnes)/year (20-MW<sub>e</sub> equivalency) using Alstom's chilled ammonia post-

combustion capture (PCC) process at AEP's Mountaineer Plant with geologic sequestration in two on-site wells.

- **Southern Company Services (SCS) Demonstration Project:** Designed to capture and store CO<sub>2</sub> at ~550 tons (500 tonnes)/day (25-MW<sub>e</sub> equivalency) using Mitsubishi Heavy Industries, Ltd. KM-CDR™ advanced amine PCC process at Alabama Power's Plant Barry with geologic sequestration in the nearby Citronelle site.

A brief overview of these projects will be given with a status update on each. EPRI also actively pursued participating in CCS demonstration projects that proposed using other advanced coal technologies including both integrated gasification combined cycle (IGCC) and oxy-combustion, but was ultimately unsuccessful.

This presentation and paper are designed to present lessons learned from these projects – both the ones that went forward and those that did not – related to financing, business, and risk management. At a high-level, these include key topics such as:

- Challenges associated with fundraising for CCS projects
- Needs and wants of various project stakeholders
- Issues associated with confidentiality and how to protect intellectual property while still learning about the process
- Key contractual and commercial terms that are important to all parties
- Project business risks and means to try to mitigate them
- Design of the knowledge transfer process and overview of the key items industry needs/wants to get out of such projects.

The paper and presentation will conclude with how this effort impacted EPRI's view of where CCS is at and where (and how) it needs to go both in general and in terms of next-generation demonstrations.

#### **Proposed New EPA GHG Emissions Standards for Coal-fired Power Plants - Determining the Applicability of Carbon Capture and Storage under Best Available Control Technologies (BACT) for Any New or Modified Prevention of Significant Deterioration (PSD)**

Steven M. Carpenter, Advanced Resources International, USA

The Environmental Protection Agency is anticipated to issue the first limits on greenhouse gas emissions from new power plants. This regulatory act may end the construction of conventional coal-fired facilities in the United States. The proposed rule will require any new power plant to emit no more than 1,000 pounds of carbon dioxide per megawatt hour of electricity produced. The average U.S. natural gas plant, which emits 800 to 850 pounds of CO<sub>2</sub> per megawatt hour, meets that standard; coal plants emit an average of 1,768 pounds of carbon dioxide per megawatt hour.

A mechanism to evaluate the potential applicability of CCS for coal fired power production in the US. The ever changing, ever increasing, ever tightening regulatory climate that requires consideration of Best Available Control Technologies (BACT) for any new or modified Prevention of Significant Deterioration (PSD) and Title V requirements is a key mechanism to accomplish both the "letter and spirit of the law".

In principle, Carbon Capture & Storage (CCS) would provide reduction of greenhouse gases and therefore should be considered. However, since CCS is neither a proven commercial technology nor is it mandated (as of yet), it seems that requiring consideration now is confusing at best.

EPA guidance states that permit applicants and permitting authorities should consider all "available" GHG control options that have the potential for practical application to the source under consideration. The guidance further suggests that once permitting authorities gain experience with GHG BACT determinations, useful information on GHG permitting decisions will be presented.

The expression of regulatory decisions and permitting based on "future tense" terms makes planning, operational, and strategic decisions very difficult for the electric generation market. This presentation will endeavor to discuss and navigate specific details in the PSD requirements for power generation as they apply to carbon capture and storage, and more specifically, how coal fired plants can comply with both the spirit and intent of the rule.

#### **China's Coal Sector Outlooks, A New Phase Development**

Huaibin Lu, 3E Information Development & Consultants, USA

As a major barometer of the economy, coal demand in China is somewhat weakening over the recent months following the slowing down economic growth. However, the country's heavy dependence on coal will unlikely be materially reduced in any near future with the advancement in the course of industrialization – speeding up in heavy industries in the West regions, and urbanization – accelerating electricity demand in the East Coast. 2011 was a landmark year in the Chinese coal sector. The share of coal consumption in China went over 50 percent of the global total. China exceeded Japan as the largest coal importer in the world, and its foreign coal dependence reached 5 percent. After years' strong increases higher than corresponding economic and energy demand growth, coal contribution to the country's overall primary energy output climbed back to 80 percent. The Chinese coal sector is developing into a new stage. In

addition to the sustained coal production and demand growth, several new features emerged are shaping up this new phase development. Significant amounts of new coal reserves have been found in western and northern frontiers, giving more incentives to mining capacity building and coal usage. Coal producing bases are further shifted northwestbound, farther away from consuming centers in China, creating great challenges to the already-burdensome coal transportation logistics. The coal industry has become much consolidated with a government-led campaign to shut down and merge small mines, reinforcing state-run enterprises' dominant positions. Government's policy shift is bringing coal for chemical investment in the full swing, adding extra requirements for coal supply and pressures on the environment and CO<sub>2</sub> emissions. Irrational domestic energy pricing mechanism and cost concerns are encouraging a trend of integration both along the coal industrial chain and across related industries, in particularly between coal mining and downstream sectors including power generation, iron and steel mills, coal chemicals and coal-bed methane extraction. These features and trends will likely continue being developed and strengthened during the State 12<sup>th</sup> Five-year Development Plan period (2011-2015).

In addition to the economic development, how the Chinese coal sector will be evolving and what roles coal will be playing will be much driven by a few factors in the future including clean coal technologies, the development of renewable energy and natural gas, and international pressures of global warming.

#### **SESSION 32**

#### **Coal-Derived Products: General – 4**

#### **Improvement of Coal De-ashing Process by Sorting Coal by Particle Size**

Koji Sakai, Shigeru Kinoshita, Takuya Yoshida, Noriyuki Okuyama, Maki Hamaguchi, Naoki Kikuchi, KOBE STEEL, Ltd., JAPAN

Hyper-Coal (HPC) is produced by extracting a coal in 2-ring aromatic solvent and separating insoluble component (residue-Coal: RC) from soluble component by gravity settling separation. It is important for HPC process to select the coal that has high solubility in solvent and its RC has first settling velocity.

In this study, we focused on different particle size group in coal because we think it has different solubility in solvent and settling velocity of its RC. First, we separated a coal several particle size groups by screen. Next we examined about solubility of each particle size coal. It was shown that the each group of particle size has different behavior to dissolve in solvent. It was thought the difference property for pulverization about the component that was easy to dissolve in solvent. Finally we measured the settling velocity of RC from each group of particle size. The RC from different particle size coal group also showed different behavior to settling velocity. It seemed that settling velocity depended on RC aggregation in actual condition. So, it suggests that knowing RC aggregation mechanism is important for solid-liquid separation.

#### **Progress of Shenhua Proprietary FT Technology Development**

Mingsheng Luo, Yulin Shi, Yijun Lv, Yunjian Hu, Hai Chang, National Institute of Clean-&-Low-Carbon Energy, CHINA

In light of the requirements of ICL (in-direct coal liquefaction) industrial development, Shenhua launched the development of FT (Fischer-Tropsch) iron catalyst for SBCR (slurry bubble column reactor) in 2006, as a sequential step of 180,000 t/y (tons/year) FT demonstration project which was kicked off on 29<sup>th</sup> of August, 2005. The catalyst study was initiated from conventional iron, copper and potassium recipe with the other proprietary active additives for synergistic effect. An extensive fundamental research work has been done over the iron catalyst in order to improve the overall FT synthesis performances. A 5-kilogram/batch scale CPU (catalyst preparation unit) was commissioned and effectively utilized as a scale-up technology development platform, where the validation and the further expanding of the laboratory results were implemented. The finalized proprietary SFT418 catalyst preparation unit was successfully scaled up to a 300t/y production line. Meanwhile, a pilot plant with a capacity of 100t/y FT liquids for catalyst evaluation unit (CEU), which was characterized by a novel filtration technology of external auto recycle and filtration of slurry has been established, to carry out a long term test over the Shenhua SFT418 catalyst. With a superior attrition resistance of 5.0-7.0% under ASTM5757-95 method, the catalyst showed competitive performance at the conditions of 523-528 K, 2.3MPa, H<sub>2</sub>/CO=1.5, during the slurry bed FT synthesis in both CSTR and CEU. The total carbon monoxide conversion with a recirculation ratio (2.0 for CSTR and 2.0-3.0 for CEU) reached above 91%, while CO<sub>2</sub> selectivity was less than 25% and CH<sub>4</sub> selectivity was less than 4.0%. In 2009, the SFT418 iron-based catalyst was utilized to the 180,000t/y demonstration plant. The first shakedown test for over 1100hr generated good productivity and selectivity: 3.1% LPG, 36.4% naphtha, 49.8% diesel, 6.7% upgraded oil & wax besides 4% mixed alcohols.

### Study on De-oiling Process and Kinetics of Spent Catalyst

Hui Ma, Yunjian Hu, Huannian Jin, Yulin Shi, Zhi Guo, National Institute of Clean- & Low-Carbon Energy, CHINA

Shenhua direct coal liquefaction (DCL) plant with a capacity of 1M tons per year has been commissioned in 2008 and runs smoothly up to now. The hydrotreating unit of this plant is one of the key parts of whole technology, and the catalyst, marked as HTS-358, was used in the hydrotreating unit. Generally the catalyst needs to be partially replaced by the fresh or regenerated continuously during the operation to maintain the stable activity. Since the spent HTS-358 catalyst is discharged online, the oil content on the catalyst surface is more than 25%, so the oil on the catalyst surface should be removed (de-oiling process) prior to spent HTS-358 catalyst regeneration.

Studying on de-oiling process parameters of spent HTS-358 catalyst is a critical step for HTS-358 regeneration. Due to the feed of hydrotreating unit is the heavier distillate from direct coal liquefaction (DCL) oil, in which aromatic content takes over 70% above and lots of carbon residue in it. So de-oiling process is a crucial step to ensure minimum carbon deposit on catalyst surface. And after de-oiling process, oil content on spent catalyst surface should be less than 5%, meeting the regeneration requirements.

Suitable de-oiling process parameters, including de-oiling time, de-oiling temperature, ratio of gas to catalyst, need to be studied. This study found that Temperature is 250-280°C, the Ratio of gas to catalyst is 300 h<sup>-1</sup>, and De-oiling time is 3h.

### Analysis of Pyrolysis Oils of Coal By High Performance Analytical Methods

Philipp Rathsack, Marius Kroll, Matthias Otto, TU Bergakademie Freiberg, GERMANY

Currently there is an increasing interest in the utilization of coal as a feedstock for the production of fuels and chemicals. This is due to the foreseeable depletion of fossil fuels like crude oil and natural gas. At least there will be a steady rise of the price of these resources. This makes alternative ways for the production of similar products more competitive. Although there has already been an era of coal as general feedstock for the chemical industry, innovative technologies have to be developed to be able to use the resources in an efficient manner and adjusted to modern requirements. Among thermochemical conversion methods, pyrolysis receives special attention, as it provides a promising way for the production of commodity chemicals. During research, chemical characterization of product streams is indispensable to monitor the objectives set.

At the German Centre for Energy Resources Freiberg (DER) innovative concepts and technologies for the post-oil era are developed. Researchers and practitioners collaborate to develop technical innovations to make the energy sources coal and biomass sustainable and future-oriented. At the Institute of Analytical Chemistry, products from conversion processes are analyzed using sophisticated instrumental analytical methods, e.g. comprehensive gas-chromatography (GCxGC) or fourier-transform ion-cyclotron-resonance mass-spectrometry (FT-ICR-MS).

In this contribution the analysis of products from a laboratory scale pyrolysis reactor is demonstrated. As feedstock different coals were used. The liquid product from the pyrolysis of coal, the pyrolysis oil, consists of a very broad range of organic compounds. These range from low to high molecular weight and from unpolar to polar nature. Different analytical methods have to be combined to be able to characterize the pyrolysis oils comprehensively.

The analysis of hundreds to more than thousand compounds being amenable to GC is shown. Substance classes found range from alkanes, alkenes, aromatics and PAH to oxygen functionalized compounds like phenols, guaiaoles and benzenediols, depending on the feedstock and the reaction conditions. Among the numerous separated compounds only a part can be identified, since for all of them this is impossible due to the lack of reference compounds. For this, a classification procedure was developed, based on mass spectral information and supervised learning.

Less volatile and high molecular components were analyzed by means of FT-ICR-MS. Different ionization techniques were used to address the utmost variable molecular structures. Highly accurate mass measurements of the observed compounds allowed the assignment of sum formulas, which in turn can be transformed into van-Krevelen plots and Kendrick mass-defect plots allowing further interpretation and comparison of characteristics of different pyrolysis oils regarding the high molecular compounds.

### SESSION 33

#### Gasification: Coal and Biomass – 1

### Gasification Kinetics of Char From Coal and Biomass Mixtures in CO<sub>2</sub>

Nicholas C. Means, DOE/NETL/URS; Nathan T. Weiland, DOE/NETL/West Virginia University; Chris Guenther, DOE/NETL, USA

The United States Department of Energy's National Energy Technology Laboratory (NETL) is working to develop technologies that reduce the cost of electricity, while increasing power plant availability and efficiency, and maintaining the highest environmental standards. Coal, an abundant natural resource, can be utilized by

thermochemical processes to produce electricity, hydrogen, liquid fuels or other chemicals. Co-gasification of coal and non-food oriented biomass can prolong national fossil energy resources while reducing net greenhouse gas emissions. Coal and biomass co-feeding may influence gasification reaction kinetics due to synergistic coal-biomass interactions. In order to better understand co-gasification phenomena, both pyrolysis and gasification reactions are being investigated at various coal/biomass feed ratios and reactor conditions. The focus of this study is to evaluate reaction kinetics of char from coal and biomass mixtures in CO<sub>2</sub> and to provide co-gasification kinetic data under transport gasifier conditions for inclusion into NETL's Carbonaceous Chemistry for Computational Modeling (C3M) platform.

An experimental study on the reaction kinetics from CO<sub>2</sub> co-gasification of Powder River Basin (PRB) coal and Southern Yellow Pine wood biomass (WB) was done in an isothermal drop reactor at pressures between 1-4 atm and temperatures ranging from 850-975°C. Co-gasification experiments were performed in an effort to gain an understanding of the effect of coal-biomass co-feed on reaction kinetics in a CO<sub>2</sub> environment. Coal char, biomass char and char from an 80/20 wt% mixture of coal and biomass were fed to the reactor at various temperatures and partial pressures of CO<sub>2</sub>. Primary gaseous products (CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>S) were monitored and analyzed online using quadrupole mass spectrometry. Due to the reaction of carbonaceous char with CO<sub>2</sub>, the major gaseous product was CO and this data was used to evaluate reaction kinetics of these feeds. The results of this kinetic analysis and the influence of the addition of biomass to coal during gasification are discussed. In addition, the effect of operating pressure on the characteristics of the pyrolysis chars and their subsequent gasification are also explored.

### Integration of Coal and Biomass Gasification Process with Fuel Cell System for Small Scale Industrial CHP Applications

Alberto Pettinau, Francesca Ferrara, Carlo Amorino, Mario Porcu, Sotacarbo S.p.A.; Simonetta Palmas, University of Cagliari, ITALY

Clean syngas from coal or biomass gasification could be used for a series of applications such as power generation and production of hydrogen, substitute natural gas, liquid fuels and chemicals.

Currently, Sotacarbo is engaged in a series of experimental tests in its pilot platform, which includes a fixed-bed air-blown gasifier equipped with complete syngas treatment line for hydrogen production and power generation based on an internal combustion engine. But it is under evaluation the possibility to equip the plant with a high efficiency fuel cell system directly fed by clean syngas.

This study analyses the possibility to apply the Sotacarbo coal and biomass gasification technology for high efficient power generation in a small-scale combined heat and power (CHP) industrial system by a potential integration of the gasification process itself with a molten carbonate fuel cell (MCFC) system.

The mass and thermal balances of the gasification and syngas treatment processes (the pilot plant is equipped with a catalytic COS hydrogenation system followed by a zinc oxides-based hot gas desulphurization process; this system allows a final H<sub>2</sub>S concentration lower than 1 ppm by volume, compatible with the fuel cell specifications) have been evaluated on the basis of the experimental data collected during the gasification and hot gas desulphurization tests. In particular, according to the results obtained from about 1350 hours of experimental tests in the Sotacarbo plant, coal gasification process is characterized by a relatively high cold gas efficiency, whereas raw syngas composition and properties strongly depend on the feedstock and the specific operating conditions. On the other hand, the performance of the MCFC fuel cell stack has been assessed by developing a mathematical model based on thermodynamic-electrochemical analysis.

### The Activity of the Lignite Hydro-Gasification with Potassium Catalyst for Production of Methane

Xingjun Wang, Bingqing Hong, Guangsuo Yu, Hai Feng Liu, Fuchen Wang, East China University of Science and Technology, CHINA

The activity, selectivity and gas release of the lignite hydro-gasification was studied in a pressurized fixed bed bench reactor. Under the condition of 4.0MPa, 800°C, the effects of temperature, pressure and potassium catalyst loadings on reactivity of hydro-gasification of lignite were investigated. The amounts of methane gases produced were significant for catalytic hydro-gasification, compared to those released in the non-catalytic hydro-gasification. In the case of non-catalytic gasification, the contents of CH<sub>4</sub> were in the range of 80–95%. However, in the case of catalytic gasification, the contents of CH<sub>4</sub> were slightly increased in the range of 92–96%. The temperature of the lignite hydro-gasification with potassium catalyst dropped more than 150°C to achieve the same carbon conversion, compared to the temperature of the lignite hydro-gasification without catalyst. The experimental results showed that the potassium catalyst has superior catalysis on hydro-gasification of the lignite, and the carbon conversion of hydro-gasification could be up to 95%. The surface morphology and pore structure of coal samples with potassium catalyst loadings had been analyzed using scanning electron microscope (SEM) and gas adsorption/ desorption analysis and the results showed that the specific surface areas and total pore volume decrease initially, and then increase with catalyst loadings increasing.

**SESSION 34**  
**Combustion: Ash and Combustion – 3**

**Single-Step Process for Simultaneous Removal of CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> from Coal Combustion Flue Gas**

Niranjani Deshpande, Nihar Phalak, L. S. Fan, The Ohio State University, USA

Prior research has shown the effectiveness of carbon, derived from inexpensive sources like coal char, in controlling post-combustion NO<sub>x</sub> emissions. The reduction of NO using char is a widely researched phenomenon. Some of the existing combustion modification methods such as re-burning employ this principle to reduce NO emissions. Based on this concept, the CARBONOX Process was developed at The Ohio State University (OSU) from lab-scale to pilot-scale demonstration.

Pure carbon materials require very high temperatures for the C-NO reaction. However, the presence of mineral matter in char and the presence of O<sub>2</sub> in flue gas significantly reduce the required temperature of NO capture. Studies conducted at OSU have revealed that up to 98% reduction in NO levels using bituminous and lignite chars is achievable at moderate to high temperatures (500-800 °C). OSU's recent research has focused mainly on the development of the Carbonation-Calcination Reaction (CCR) Process for post-combustion removal of CO<sub>2</sub> and SO<sub>2</sub> using a calcium-based sorbent. Like CARBONOX, the CCR Process has been demonstrated successfully at the sub-pilot scale. >90% CO<sub>2</sub> capture and complete SO<sub>2</sub> removal has been achieved in a 120 kWth unit at OSU.

This work combines the two processes to result in a unique high-temperature (>500 °C) process for simultaneous removal of CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub>. The carbon-NO reaction is known to be catalyzed by presence of alkali or alkaline earth metals, which further favors the development of such a process. In this study, tests were conducted to demonstrate the simultaneous capture of NO and CO<sub>2</sub>, using a mixture of coal char and calcium sorbent. The effect of variables such as temperature, calcium to char loading ratio, oxygen concentration, and char source, was quantified using a fixed-fluidized bed reactor. The results of these tests will be presented in the form of net NO and CO<sub>2</sub> capture, as well as selectivity of char toward NO. The merits and potential challenges of this novel process will also be discussed.

**CCSEM Investigation of Respirable Quartz in Air Samples Collected During Power Plant Maintenance Activities**

Gerald P. Huffman, Naresh Shah, Frank E. Huggins, Nick Cprek, University of Kentucky; Gary Casuccio, Everett Ramer, RJ Lee Group, Inc.; Jeffrey B. Hicks, Exponent, Inc., USA

In an earlier investigation, computer-controlled scanning electron microscopy (CCSEM) and X-ray diffraction (XRD) were used to investigate respirable quartz in several bulk coal fly-ash samples. It was shown that the XRD results for quartz in bulk fly-ash were much larger than the amounts of respirable quartz determined by CCSEM because the XRD signal was derived primarily from quartz particles too large to be classified as respirable. In the current paper, CCSEM and XRD were used to investigate coal fly-ash collected using cyclone-filtered personal and area samplers at two different power plants during maintenance activities. The amounts of respirable quartz determined by the two methods were found to be in good agreement, confirming the need for cyclone-filtered samples. The amounts of respirable quartz determined by CCSEM ranged from 1.5 to 3.5 vol.% for the plant burning a Southwest sub-bituminous coal and from 0.6 to 1.9 vol.% for the plant burning a Mid-West bituminous coal. Very small amounts (average of approximately 0.2 vol.% for both plants) of Si-rich glass or amorphous silica were also detected by CCSEM. These results are important because of the health implications associated with inhaling quartz particles. They demonstrate that the amounts of respirable quartz to which power plant workers are exposed can be accurately measured by two very different measurements on samples collected in cyclone-filtered samplers designed to emulate the inhalation process of human airways.

Research supported by the Electric Power Research Institute (EPRI).

**Detailed Investigation of Pyrolysis Modeling for Pulverized Coal Mild Combustion**

Michele Vascellari, Christian Hasse, Martin Pollack, ZIK Virtuhcon – Technische Universität Freiberg, GERMANY

Pulverized coal combustion is a complex process, which involves several chemical-physical phenomena, such as multiphase flows, inter-phase mass exchanges, homogeneous and heterogeneous chemical reactions, radiation, etc.. Its mathematical modeling requires therefore a significant effort to describe every phenomena through submodels, which are to be implemented in a "comprehensive" model developed in the frame of a fluid dynamic computational code. The term "comprehensive" is used to signify that submodels for all pertinent physico-chemical mechanisms have been assembled into an integrated model with a solution approach that can adequately simulate the overall combustion process of interest. However, every sub-model is

generally developed and validated considering sub-scale testing developed in small laboratory scale experimental set-up, in order to clearly examine all phenomena in separate way. Uncertainties are clearly related to each submodel considered, and it becomes really difficult to distinguish the effects considering comprehensive approach. In particular, during rapid heating of coal particles, devolatilization and ignition play a fundamental role for characterizing flame behavior, such as stability, pollutant formation, flame extinction, etc.. Therefore, its understanding and modeling are essential for designing coal thermo-conversion processes. Two main features of devolatilization modeling are investigated in this work. At first, the influence of the pyrolysis rates is investigated considering the most common used models in technical literature. In particular, both empirical and advanced network devolatilization models are considered for the investigation. Then, the influence of volatile matter composition is investigated with the aim of better understanding its interaction with surrounding gas atmosphere.

The detailed investigation of coal pyrolysis modeling is performed considering a MILD combustion test case, for which detailed experimental data are available for velocity, temperature and chemical species.

**Image Analysis Techniques for Particle Air Flames – A Review**

Sreenivasan Ranganathan, Brian Elias, Ali Rangwala, Worcester Polytechnic Institute, USA

Image analysis is a key method for investigating the characteristics of a flame, including the flame surface area and ultimately, the burning velocity. The process of image analysis involves both optical data collection by experiment and more importantly post processing of the collected images. Experimentally, three primary methods exist for optical data collection: direct imaging, shadowgraph, and Schlieren techniques. In the case of direct imaging, only the optical data visible to the naked-eye is captured by the laboratory camera – primarily luminance and color, with possibilities for polarization depending on the lens configuration. In addition to this directly observable data, the flow-field around the flame contains small differences in the refractive index compared to the background atmosphere. These differences represent a density gradient, and can be visualized by either a shadowgraph or Schlieren technique, with the latter providing a focused image more useful for quantitative analysis. Additionally, a color Schlieren technique may be employed to graphically depict the various density regions by a shift in color. In order to analyze the optical data obtained by the methods described above, a variety of post-processing methods exist. In a region approach, each pixel is assigned to a particular object or region. In a boundary approach, one attempts only to locate the boundaries that exist between the regions. Finally, in an edge approach one seeks to identify edge pixels and link them together to form the required boundaries. Based on these approaches, algorithms such as thresholding, edge-detection, region growth (Chan-Vese-binarization), and hybrid methods have been developed and used extensively in different fields of science and engineering. The objective of this work is to quantitatively compare and review the different experimental as well as post-processing (image analysis) techniques on hybrid flames. A specific case study of turbulent premixed coal particle-methane-air flame is used for the comparison (equivalence ratio of the methane-air flame = 0.9, coal particle concentration range: 0 – 80 g/m<sup>3</sup>, particle size of coal ~70 μm, turbulent intensity  $u'$  range = 0.1 - 0.7 m/s). Effectiveness without de-noising and pre-processing is also discussed.

**SESSION 35**  
**Carbon Management: CO<sub>2</sub> Capture - 5**

**Current and Future Technologies for Power Generation with Post-Combustion Carbon Capture**

Robert W. Stevens, Jr., DOE/NETL; Dale Keairns, Richard Newby, Vasant Shah, Marc Turner, Mark Woods, Booz Allen Hamilton, Inc., USA

The U.S. Department of Energy's National Energy Technology Laboratory (NETL) is funding research aimed at improving the performance and reducing the cost of conventional pulverized coal (PC) power plants adapted to use post-combustion carbon capture technologies. The objective of this study is to support DOE's Carbon Capture and Advanced Combustion R&D Programs by completing an "R&D Pathway" study for PC power plants that employ post-combustion carbon capture. Post-combustion carbon capture pathway steps have been conceived and assessed that represent a possible scenario for the evolution of the PC power plant technology with post-combustion carbon capture from today's current state-of-the-art systems to future advanced systems. Carbon capture technologies considered in the study include solvent, membrane, and solid sorbent-based systems. The results represent the future potential benefits from successful post-combustion carbon capture technology development. The results also provide a basis to guide technology development and to measure and prioritize the contribution of research and development.



## A Novel Gas Pressurized Stripping Based Process for CO<sub>2</sub> Capture from Post-Combustion Flue Gases

Shiaoguo (Scott) Chen, Zijiang Pan, Zhiwei Li, Kevin O'Brien, Carbon Capture Scientific, LLC; Timothy Fout, DOE/NETL, USA

Carbon Capture Scientific teaming up with CONSOL Energy, Nexant and Western Kentucky University is developing a breakthrough Gas Pressurized Stripping (GPS) process-based technology for CO<sub>2</sub> capture from post-combustion flue gases. One of the key advantages of GPS is that it reduces the energy requirements for CO<sub>2</sub> compression relative to conventional absorption/stripping process. GPS based process has the potential to partially or even entirely eliminate CO<sub>2</sub> compression, which will reduce the total parasitic power consumption by 60% as compared to the baseline amine case. The impact of this 60% reduction in parasitic power would be a reduction of 21 mills/kWh in the incremental cost of electricity (COE). This result coupled with future improvements related to direct costs, create a scenario in which DOE's aggressive cost target (no more than 35% increase in COE from non-capture case) would be within reach.

This effort combines computer simulation, experimental testing, and techno-economic analysis to demonstrate the feasibility of the GPS process at the bench-scale. Experimental testing of each individual unit operation involved in the GPS process is being conducted. To help understanding the GPS process, extensive computer simulations are also being performed using Pro-Treat simulation software. Our preliminary results showed that GPS process based technology has the potential to significantly reduce energy consumption of the post-combustion CO<sub>2</sub> capture. Using commercially available solvents the novel GPS process is able to reduce energy consumption of CO<sub>2</sub> capture and compression to about 0.20 kWh/kgCO<sub>2</sub>. With further improvement in solvents as well as future process equipment, the GPS process has the potential to achieve energy consumption much less than this value.

## Techno-Economic Analysis of a CO<sub>2</sub> Capture-Ready Supercritical Pulverized Coal Unit

Eric Grol, DOE/NETL; Paul Myles, Steve Herron, WorleyParsons Inc./DOE/NETL, USA

This analysis examines the cost and performance of newly constructed CO<sub>2</sub> capture-ready supercritical pulverized coal units that achieve a 30-year average emission rate of 1,000 Lb CO<sub>2</sub>/MWh. New units can meet this limit either by capturing CO<sub>2</sub> starting at the outset of the unit's full operation, or by achieving this level over a 30-year average (with CO<sub>2</sub> capture starting in the beginning of the 11<sup>th</sup> year). The latter compliance option allows for the construction of CO<sub>2</sub> capture-ready (CCR) power plants.

Initial CCR plant construction will take into account the future CO<sub>2</sub> capture that will occur, and will incorporate certain elements into the design that will minimize the retrofit burden later on (such as allowing for additional space in pipe racks and cable trays, access to utilities like water and instrument air, and pouring foundations where future capital equipment will be installed).

However, it is the means by which carbon capture readiness is achieved and the timing of the transition into CO<sub>2</sub> capture that could have a major effect on the capital cost (\$/kW) and cost of electricity (\$/MWh). A techno-economic evaluation of different retrofit strategies and timing scenarios will be presented and discussed.

## The Decision-Tree: How Cleaner-Coal Technology Links to Climate Change

Alex Wormser, Wormser Energy Solutions, Inc., USA

The role of cleaner-coal technology on climate change is analyzed with the help of a decision tree. Cleaner-coal technology, as the term is used here, repowers existing coal plants by converting them into IGCCs with 90% carbon capture, at a cost of electricity that is competitive with power generated by conventional coal and gas plants without it. Such technology is being developed by the author's company, and is described in another session at this conference.

The analysis is prompted by the observation that the pace with which the world is reducing its greenhouse gas emissions is incompatible with what the climatologists conclude is needed to avoid the global warming tipping point. The analysis first examines how a greater emphasis on bridge fuels might compare with rate at which emissions are reduced using the conventional basket of technologies currently in use.

From there, it compares the merits of natural gas as a bridge fuel against those of coal, and the use of the cleaner-coal technology against the use of conventional carbon capture systems. The conclusion is that cleaner coal technology has an unexpectedly large role to play in accelerating the fight against climate change, even in the absence of carbon taxes such as cap-and-trade, if it can be developed in a timely fashion.

## SESSION 36 Coal Science: General – 3

### Halogens in Coal: Review of Geologic Variation and Influence on Mercury Capture

Allan Kolker, U.S. Geological Survey; Jeffrey C. Quick, Utah Geological Survey; Connie L. Senior, ADA Environmental Solutions, USA

The halogen content of coal is one of the most important factors in determining the potential for mercury capture in combustion systems with conventional air pollution control devices (APCD's). Halogen content varies with coal rank, with bituminous coals having higher mean Cl contents than low rank coals. This difference corresponds to differences in depth of burial in coal-forming sedimentary basins. Chlorine and bromine are thought to occur as anions associated with coal moisture and are weakly bound to coal by organic-ionic complexes [1]. Variation in halogen content with depth is explained by the increase in salinity of formation waters with depth, combined with exchange between coal and these waters. Halogen enrichment may also result locally by interaction of coal with hydrothermal fluids or proximity to geologic structures that have acted as pathways for influx of saline fluids [2].

Halogens in coal influence mercury emissions by oxidation of elemental Hg at flue gas temperatures to form Hg-halogen complexes that can be captured by APCD's. On a mass equivalent basis, heavier halogens (Br, I) are more effective Hg oxidants than lighter halogens (Cl, F), although in wet FGD systems, I is less likely than Br to promote Hg capture because its solubility is much lower. Most commercial coals have mass fractions of Br that are a few percent of that for Cl, regardless of rank [3]. In deep basin saline waters, Br enrichment can result from exclusion of Br during halite (NaCl) precipitation [4]. Halite-bearing "salt coals" have unusually high Cl concentrations and may have atypically high Br/Cl ratios [5, 6]. High Cl coals are known to cause boiler corrosion problems but may be useful in blending with low-rank coal to promote Hg capture.

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### Lanthanides in Coal Combustion Fly Ash

James C. Hower, University of Kentucky Center for Applied Energy Research, USA; Shifeng Dai, China University of Mining and Technology, CHINA; Irena Kostova, Sofia University, BULGARIA; Luis F.O. Silva, Institute of Environmental Research and Human Development – IPADHC, BRAZIL

The growing need for a variety of lanthanide (rare earth elements or REE) elements in modern electronic and related components has driven the need to broaden production from both previously productive locations and to expand production to new sources, possibly including coal-derived fly ash. The concentration of lanthanides in coal-combustion fly ash depends on a number of factors, one of the most important being the concentration of the elements in the feed coal. Unlike some elements, such as Zn and As, the REE concentration is largely not a function of element volatility.

In this study, we review the concentrations of REE in a power plants burning low-rank Bulgarian coals, high volatile A bituminous eastern Kentucky coals, and Chinese anthracites. In addition, a power plant burning 2-3% tires in a cyclone boiler and a plant burning 30% pet coke were also investigated. In general, the Yttrium + REE concentrations do not systematically vary between ESP rows. However, the light REE/heavy REE (LREE/HREE) ratio generally decreases with a decrease in flue gas temperature. The element partitioning responsible for the LREE/HREE decrease is not fully understood.

### The Genesis and Evolution of Neogene Achlada Lignite Deposits (NW Greece)

Ioannis K. Oikonomopoulos, Thomas Gentzis, Core Laboratories LP, USA; Maria Perraki, National Technical University of Athens, GREECE; Nikolaos Tougiannidis, University of Cologne, GERMANY

The Greek peninsula is an area where vivid neotectonic activity takes place and many lignite deposits are located. During the period from the Neogene to the Quaternary were formed the most economically important lignite deposits in Greece, such as Florina, Ptolemais, Megalopolis and Drama.

The aim of the present study is the specification of the palaeoenvironmental types that evolved during the formation and evolution of the Achlada lignite deposits (Florina basin) and the role of the intercalated inorganic seams that appear in the same lignite-bearing sequence. For this purpose field observations, coal-petrographical, mineralogical and palaeobotanical data were combined and interpreted. The Achlada

lignite deposits are located at the east borderlands of the Florina basin. The latter is part of the broader tectonic trench of Monastiri-Florina-Ptolemais-Kozani-Servia, which is NW-SE directed. The basement of the basin consists of Palaeozoic and Mesozoic formations. Upwards, are Neogene sediments in which the Achlada lignite deposits are included. The stratigraphic sequence finalizes with the Quaternary-recent sediments. The total thickness of the examined lignite sequence is ~26m whereas the samples were taken successively indicating different type of layers with an average thickness ~12cm each. The layers consist of organic and inorganic cyclical alternations with intercalated typical xylite horizons. The macroscopic description of lignite horizons resulted in the classification of the organic matter into three main lithotypes: the xylite, the matrix and the mixed tissue/matrix one. According to the macerals analysis the prevailing maceral group is huminite (60,7-98,2%). Liptinite contents range up to 38,3%, whereas inertinite content is very low (<2,9%). These contents of macerals imply that peat formation took place under wet and anoxic conditions favorable to fine cell tissue preservation and gellification of the organic matter. The palaeobotanical data showed that the lignite seams derived from terrestrial higher plants mainly arboreal and herbaceous Gymnosperms and Angiosperms and imply that peat-forming took place so in a mixed forest palaeoenvironment as a reedmoor one. Moreover, during the evolution of the palaeomire these two palaeoenvironments were alternating one another, whereas the reedmoor was periodically toggled to open water one. The mineralogical composition of both lignite and inorganic intercalated seams of the lignite-bearing sequence was investigated by means of X-ray diffraction (XRD), fourier transform infra-Red (FT-IR) spectroscopy and thermo-gravimetric (TG/DTG) and differential thermal analysis (DTA). The mineral matter of lignite horizons consists mainly of aluminosilicate minerals that were introduced periodically into the palaeomire by surface waters during flooding episodes. The carbonate minerals are almost absent except from siderite, whereas authigenic minerals such as pyrite and gypsum are also present in the majority of the lignite horizons. Furthermore, the clay minerals prevail in all inorganic intercalated seams with illite being the dominant phase, kaolinite and chlorite to be the next. No smectite was found. The other mineral phases identified are mainly quartz and feldspars. The presence of siderite is also remarkable.

The interpretation of the field observations, coal-petrographical, mineralogical and palaeobotanical data showed that the studied lignite-bearing sequence was formed in a forest swamp environment on the floodplain area of a meandering river system that was flowing the Achlada area.

#### **Distribution of Major Oxides and Trace Elements Concentration of Mancılık (Gönen – Balıkesir) Coal Deposit**

Mehmet Maral, Fikret Suner, Didem (Maral) Temel, Istanbul Technical University, TURKEY; James C. Hower, University of Kentucky Center for Applied Energy Research; Jennifer M.K. O'Keefe, Morehead State University; Cortland F. Eble, Kentucky Geological Survey, USA

Coal is clearly important for Turkey, with over half of electric generation provided from fossil fuels (coal and natural gas). Therefore, large amounts of various trace elements are isolated every year with the coal ash. Coal's trace element concentration is getting more important in terms of environmental, economic, by-product, and technological behavior of coals and their effects on public health.

The investigation is focused on trace elements in Mancılık (Gönen) coal deposit, Biga Peninsula, NW Turkey. The basement of the region, which consists of the Paleozoic - Mesozoic metamorphic rocks (mainly of gneisses, amphibolites, marbles, and metaophiolites) and crystallized limestone, is in the subsurface near the Mancılık coal field. The Tertiary volcanics are andesitic, dacitic, and rhyodacitic. The Miocene coals were deposited and alternated with volcanic-sedimentary rocks, which consists of sandstone, conglomerate, claystone, bituminous shale, agglomerate, and tuff.

The coal occurrence was sampled and analyzed. The analyses were correlated and interpreted with the previous studies. Chemical investigations were performed on the coal ashes via XRF and ICP-EAS methods at University of Kentucky Center for Applied Energy Research's laboratories.

The trace element analyses show that As, Ga, and U are significant enriched in the samples. The contents of Mo, Pb, V, Rb and Sb are also higher than world coals. The abundance of the investigated trace elements can lead to cause some environmental problems and related disease, factors which should be considered in the usage potential of the coals.

### **SESSION 37 Clean Coal Demonstration and Commercial Projects: Technical - 4 (Polygeneration)**

#### **Global Perspective on Coal Gasification for Polygeneration**

Alison Kerester, Gasification Technologies Council (GTC), USA

Presentation and discussion on current economic and technical drivers worldwide for the utilization of coal gasification to deliver polygeneration products, including

chemicals, transportation liquids, SNG, hydrogen, methanol, fertilizers, and other materials.

The presentation will identify specific projects in commercial operation, and those currently in development, and will include information on coal type, technologies in the process configuration, product slate, and any special features or project attributes.

Additionally, emerging coal gasification technologies nearing readiness for commercial applications for production of polygeneration offtake, will be presented and discussed.

A summary of the global marketplace for the utilization of coal gasification in polygeneration scenarios will be provided, and a perspective on future growth opportunities worldwide.

#### **The Benefits of Co-producing Electric Power, Chemicals, and Fuels from IGCC Polygeneration Plants**

Charles E. Miller, Gary Stiegel, Thomas Sarkus, John Rockey, Jason Lewis, DOE/NETL; William Ellis, KeyLogic, USA

Integrated Gasification Combined Cycle (IGCC) polygeneration (polygen) plants have the flexibility to simultaneously generate electricity and produce high-value commodity products such as chemicals and fuels. Polygen plant operators seek to maximize revenue by optimizing the relative amount of each output product.

This paper will provide a basic introduction to the coal-based polygen process, alternative configurations to produce a variety of products, and the market drivers for optimization of plant output. Publicly-available information on market demand and market prices of polygen products will be presented.

The paper will also include an overview of U.S. Department of Energy Office of Fossil Energy's assistance to develop and deploy gasification projects, including two commercial demonstrations of IGCC polygeneration with fertilizer production: the Texas Clean Energy Project and the Hydrogen Energy California Project. Both of these projects plan to divert part of the hydrogen-rich synthesis gas (syngas) to produce ammonia for on-site manufacture of urea and/or urea ammonium nitrate fertilizer. These projects intend to use CO<sub>2</sub> captured from the syngas for Enhanced Oil Recovery. Both projects are in the development phase and are pursuing private-sector investment.

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

Karl Mattes, Summit Power Group, USA

The Texas Clean Energy Project (TCEP) is a carbon capture, utilization and storage (CCUS) commercial demonstration facility featuring integrated gasification combined cycle (IGCC) poly-generation. The project description and technical aspects of how carbon is captured in the project design were presented at the 2010 Pittsburgh Coal Conference. This 2012 presentation will update the project's progress and the current expected status since the 2011 Pittsburgh Coal Conference, including: site, linear facilities, supply, product off-takes, plant layout and overall schedule.

#### **Hydrogen Energy California Solutions for a Low Carbon World while Utilizing**

##### **America's Most Abundant Energy Resource**

Tim Bauer, Hydrogen Energy California, USA

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

Supporting the project are the US Department of Energy (Fossil Energy), Mitsubishi Heavy Industries and Fluor. The US Department of Energy is providing funding to the project through an award made under Round 3 of the Fossil Energy Clean Coal Power Initiative (CCPI-3). Mitsubishi Heavy Industries is providing oxygen-blown gasification technology, the gas turbine/steam turbine/generator and will facilitate a portion of the project funding. Fluor is performing engineering for the FEED phase in conjunction with the selected licensors for the various process units.

HECA will utilize Integrated Gasification Combined Cycle technology to produce synthetic gas from coal and petroleum coke that can then be separated into hydrogen for energy and fertilizer production and CO<sub>2</sub> for capture, utilization and sequestration. Over 90 percent of potential CO<sub>2</sub> emissions from the synthesis gas that is produced during steady state operations will be captured and used for EOR (approximately 3 million standard tons per year). This CO<sub>2</sub> will be compressed and transported via buried pipeline to the adjacent Elk Hills Field, where it will be injected underground. The CO<sub>2</sub> enhanced oil recovery (EOR) process involves the injection and reinjection of CO<sub>2</sub> into the oil fields to recover otherwise unrecoverable oil. During the process, the injected CO<sub>2</sub> becomes sequestered in a secure geologic formation. This process is referred to as CO<sub>2</sub> EOR and Sequestration. Elk Hills Field is considered an excellent long-term sequestration site due to the geology of the reservoir. The CO<sub>2</sub> EOR and Sequestration process will employ existing, well-tested technology that minimizes potential risks and is protective of human health and the environment. As a result, the

project will provide low-carbon power, clean fertilizer and produce additional oil, while generating revenue for the state and creating hundreds of jobs. CCUS offers a solution to CO<sub>2</sub> emissions associated with energy production from our abundant domestic energy sources. Safe implementation of CCUS on a large scale could significantly aid in climate change mitigation while at the same time improve US energy security, and production of other products in a low carbon footprint manner. With one of the best sites for EOR Elk Hills and HECA are well poised to be leaders in the commercial demonstration of large-scale power generation with CCUS.

**SESSION 38**  
**Coal-Derived Products: General – 5**

**Elimination of All CO<sub>2</sub> Emissions During the Production of Liquid Fuels from Coal and Natural Gas by Combining Fischer-Tropsch Synthesis with Catalytic Dehydrogenation**

Gerald P. Huffman, Naresh Shah, Xuepei Shi, Frank E. Huggins, Wenqin Shen,  
University of Kentucky, USA

Synthesis gas (syngas) produced by coal gasification typically has hydrogen to carbon monoxide ratios in the range of 0.6 to 1.0. In order to produce liquid fuels from this syngas by Fischer-Tropsch synthesis (FTS), the H<sub>2</sub>/CO ratio must be raised to 2.0 or higher. Traditionally, this has been accomplished by the water-gas shift (WGS) reaction, which emits one CO<sub>2</sub> molecule for each H<sub>2</sub> molecule it produces. Our calculations show that most or all of the H<sub>2</sub> required could be produced with no CO<sub>2</sub> emissions by catalytic dehydrogenation (CDH) of the gaseous C1-C4 products of FTS, which produces pure H<sub>2</sub> and multi-walled carbon nanotubes (MWCNT). If additional H<sub>2</sub> is needed to achieve the desired H<sub>2</sub>/CO ratio, it could easily be produced by feeding some natural gas to the CDH reactor. Since natural gas production by hydraulic fracturing of shale formations is increasing rapidly in the United States, this could be an easy and economical option. Our calculations indicate that a FTS-CDH plant producing 50,000 barrels of liquid fuel per day could avoid the emission of approximately 16,000 tons/day of CO<sub>2</sub> and save 1.6 million gallons/day of water relative to a conventional FTS plant, while producing 3,200 tons/day of a valuable by-product, MWCNT. Preliminary experiments to confirm this concept have been completed using a small-scale laboratory FTS-CDH reactor. These experiments succeeded in dehydrogenating about a third of the C1-C4 FTS products and raised the H<sub>2</sub>/CO ratio of the incident syngas by about 0.6. Our future research will focus on building a more robust FTS-CDH system with a CDH reactor capable of dehydrogenating ~80-90% of the FTS C1-C4 products, which would produce enough H<sub>2</sub> to increase the H<sub>2</sub>/CO ratio by about 1.5. Since syngas produced from coal is typically in the range of 0.6 to 1.0, this would produce syngas with H<sub>2</sub>/CO ratios of ~2.1 to 2.5 for FTS with no emissions of CO<sub>2</sub>. Research supported by the U.S. DOE, Office of Fossil Energy, National Energy Technology Laboratory (NETL).

**Development of Dense Membranes for Hydrogen Production and Purification from Coal with CO<sub>2</sub> Capture**

U. (Balu) Balachandran, T. H. Lee, C. Y. Park, S. E. Dorris, Argonne National  
Laboratory, USA

We are developing dense hydrogen transport membranes (HTMs) for separating hydrogen from coal gasification streams. Membrane separation units that can selectively permeate H<sub>2</sub> and retain CO<sub>2</sub> at elevated pressures are promising for pre-combustion CO<sub>2</sub>-capture in integrated gasification combined cycle (IGCC) plants. Hydrogen separation with Argonne's HTMs yields high-purity hydrogen, thereby eliminating the need for post-separation purification steps. Our project aims to identify materials with suitable hydrogen permeability and develop methods for fabricating thin, dense membranes from such materials. Extensive tests have been conducted with HTMs made by mixing ~50 vol.% Pd with Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub>. Using several feed gas mixtures, we measured the hydrogen permeation rate, or flux, for the membranes in the temperature range 400-600°C. With 90% H<sub>2</sub>/balance He at ambient pressure as feed gas, an ~20-µm-thick membrane on a porous substrate gave a measured flux of ~26 cm<sup>3</sup>[STP]/min-cm<sup>2</sup> at 400°C and ~32 cm<sup>3</sup>[STP]/min-cm<sup>2</sup> at 500°C. We also measured the hydrogen flux through a thicker (~150 µm) membrane at 400°C using a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, and He at ~200 psig as feed gas. Because good chemical stability is critical for HTMs, due to the corrosive nature of product streams from coal gasification, we evaluated the effect of various contaminants on the chemical stability of membranes. Our membranes were found to withstand cycling of temperature and hydrogen concentration in the feed gas without exhibiting significant changes in microstructure or performance. Long-term (~4-months) flux measurements showed that the membranes are stable at ≤500°C in wet simulated syngas mixture. The present status of membrane development at Argonne and the challenges involved in bringing this technology to fruition will be presented in this talk.

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**Modes of Fixation of Radioactive Metal Cations by Bituminous Coal Fly Ash**

Roy Nir Lieberman, Ariel University Center of Samaria and Bar-Ilan University; Haim Cohen, The Ariel University Center and The Ben-Gurion University of the Negev; Yitzhak Mastai, Bar-Ilan University, ISRAEL

Pulverized bituminous coal combustion in Israel is the main source of electrical power (more than 50% of the electrical power in 2011). The main solid residue produced during the combustion is flyash (~10% residues) which. It is observed that it can serve as an efficient scrubber for acidic wastes of the Israeli Chemical industry, mainly due to the high lime content at the surface of the fly ash particle. Furthermore, it has been proved that trace elements are trapped efficiently at the surface of the flyash particle and that the scrubbed waste product can serve as a partial substitute to sand and cement for concrete production. Bricks produced using the aggregate as sand substitute, have proved to be strong enough according to the concrete standards and the fixation of the trace element in the concrete was excellent (checked via the improved TCLP1311, the European Directive EN12457-2 and the CAL WET methods). Thus, fly ash might be a potential efficient fixation reagent for radionuclides.

The feasibility of the fly ash as a potential fixation reagent for radionuclides has been studied via simulation experiments in aqueous solutions containing cesium ions, Cs<sup>+</sup>, divalent strontium, Sr<sup>2+</sup> and Ce<sup>3+/4+</sup> as simulation reagents to the radionuclides. The fixation mechanisms will be discussed in detail.

**Deformation-deterioration Phenomenon of Marine Concrete by Chloride Penetration and the Effect of Silica Fume**

Nguyen Viet Quang Hung, Nguyen Viet Cuong, Vietnam Academy of Science and Technology, VIETNAM; Masakatsu Nomura, Osaka University, JAPAN

Studies on concrete and reinforced concrete with silica fume (produced from raw materials such as coke, coal, wood chips and quartz) in tidal zone influenced by hot-dry Western wind from Lao's) are carried out step by step. In this paper three examination steps have presented.

The first step is to research the deformation - deterioration phenomenon by comparing in the case of with load samples (making tension zone and compression zone, i.e. pulling stresses and pressing stresses) and samples without load in two areas such as Hanoi and Cua Lo seaport.

Hanoi is about 100km far from sea, and Cua Lo seaport is near Vinh city – Nghe An province at the zone located in the North Middle region of Vietnam where the samples are influenced by the hot-dry Western wind from Lao's to research Vietnam. The site for testing samples is in tidal zone. The results of the first step are correlated with the effects of climate and pulling stresses under the influences of chloride from sea water in tidal zone affecting in the working process of reinforced concrete samples without silica fume which are measured by ultrasonic equipment.

The second step is to examine chloride penetration by determining the concentration of chloride at each depth of concrete samples soaked in tidal zone for 4 years and to determine the amount of chloride in the normal concrete samples and the concrete samples with silica fume and super-plasticizer. The results of the second step show the chloride concentration in the concrete sample with silica fume and super-plasticizer less than in the normal concrete at the same depth from the face of concrete samples.

The third step is to determine the lifetime of the reinforced concrete with silica fume and super-plasticizer in a tidal zone, this being an important factor. Based on chloride concentration at the depth of face of the steel bar in concrete, the authors have calculated the first stage lifetime (trace of corrosion on the face of steel bar is observed). The results of the third step are as follows: the first stage lifetime of the reinforced concrete with silica fume and super-plasticizer is 23 years; the first stage lifetime of the reinforced concrete with only super-plasticizer without silica fume is 17.2 years.

The second step and the third step show the role of silica fume for the marine concrete influenced by hot-dry Western wind from Lao's to Vietnam.

**SESSION 39**  
**Gasification: Coal and Biomass – 2**

**Bloodwood Creek UCG Pilot 2010-2012**

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

In October, 2008 Carbon Energy Ltd installed their next generation commercial version of the KeySeam CRIP, a parallel UCG CRIP module configuration, at their site at Bloodwood Creek, 50 km west of Dalby, Queensland Australia. They demonstrated

the commercial feasibility of their UCG process at Bloodwood Creek with a 100-day field trial with both air and oxygen/steam injection. The second module, capable of accessing 200,000 tonne of coal during its operational life, has been operational since April, 2010. It is providing UCG syngas (6.0 to 7.5 mj/scm) to a 5 MW electricity plant, with power being sold into the local electricity grid. The next phase of the program will involve installation of a 20 MW facility for electricity sale into the power grid.

#### **Performance Analysis of Entrained-Flow Bed Co-Gasification of Biomass and Coal**

Xueli Chen, Jianliang Xu, Guangsuo Yu, East China University of Science and Technology, CHINA

Biomass is one of the most promising renewable energy sources. Co-gasification of biomass and coal has been proposed as a bridge between energy production based on fossil fuels and energy production based on renewable fuels. Based on ASPEN PLUS, the entrained-flow co-gasification of biomass and coal was simulated, and its economic and environmental benefits were analyzed. The results showed that with the increase of the biomass mass fraction in mixture ( $R$ ), the ash fusion temperatures of the biomass and coal mixtures totally decreased; the content of effective gas in syngas decreases a little; specific oxygen consumption has little change, specific raw material consumption increases significantly, however, specific coal consumption decreases observably. Compared with pure Baodian coal gasification, when  $R$  is 10%, 20% and 30%, the  $H_2/CO$  molar ratio is enhanced by about 4%, 8% and 13% respectively, specific coal consumption is reduced by 5.8%, 11.9% and 18.3% respectively. The entrained-flow co-gasification of biomass and coal is feasible as long as  $R$  is controlled within appropriate range. Moreover, it contributes significantly to the preservation of coal reserves and the reduction of the net  $CO_2$  emission into the atmosphere.

#### **An Experimental Study on Co-Gasification of Coal-Biomass Blended Chars with $CO_2$**

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

In a lab scale tube furnace, mixtures of coal and biomass were co-pyrolyzed under nitrogen atmosphere condition to become chars. Then these chars were co-gasified with  $CO_2$  under isothermal conditions.  $CO$  concentration was measured by a real time gas analyser with NDIR (Non-dispersive infrared)  $CO$  and  $CO_2$  sensor. The furnace temperature was varied between 900-1100°. The Volume Reaction Model (VRM), Shrinking Core Model (SCM) and Random Pore Model (RPM) were used to interpret the experiment data. The activation energy ( $E_a$ ) and frequency factor ( $A$ ) of coal and biomass char- $CO_2$  reaction were determined using the Arrhenius equation. As a result, the reactivity on co-gasification of blended chars was improved than single coal char because of catalysis of alkaline minerals which were included in biomass char.

### **SESSION 40 Combustion: Mainly Mercury**

#### **Particulate Carbon Emissions from ESPs During Injection of Powdered Mercury Sorbents: Updated Estimates Based on the U.S. EPA Report to Congress on Black Carbon**

Herek L. Clack, University of Michigan, USA

A previous analysis explored a broad range of parameters and their potential impacts on unintended emissions of sub-micron powdered activated carbon (PAC), injected into coal combustion flue gas to reduce mercury emissions, from electrostatic precipitators (ESPs). This present analysis updates the previous analysis in several important ways, better aligning it with the recently released U.S. EPA Report to Congress on Black Carbon. The result is a narrower range of estimates for potential increases in emissions of  $PM_{2.5}$  particulate carbon. Such increases are projected in association with current and anticipated new limits on mercury emissions from coal-fired power generation and the use of PAC injection for controlling mercury emissions. The principal uncertainty in the projections is the unknown ESP collection efficiency differential between residual  $PM_{2.5}$  from combustion and  $PM_{2.5}$  PAC.

#### **Economic Mercury Emission MATS Compliance**

Bruce A. Keiser, John Meier, Rebecca L. Stiles, Nalco Company, USA

The EPA published the Mercury and Air Toxics Standards (MATS) on December 16, 2011. Under the federal mandate, electricity generating units (EGUs) burning fossil fuels will need to limit total mercury emission to less than 1 lb/Tbtu with some variation for fuel type. EPA estimates that compliance to the standard will cost about \$9.6 billion by 2015. While EPA projects 5 GW of coal-fired capacity being retired by 2015, an analysis by NERA indicates 19 GW of capacity being retired due to MATS. Costs of meeting MATS include installation of new or improving the efficiency of existing capital equipment such as wet flue gas desulfurization units (WFGDs). The

role of WFGDs as an air quality control device (AQCD) is expanding due to MATS. Now beside sulfur capture, WFGDs will need to be optimized for mercury removal. In order for WFGDs to scrub mercury from flue gas, two conditions must be met. First, the mercury must exist as ionic mercury,  $Hg^{2+}$ , almost exclusively. Methods of shifting mercury speciation in flue gas include the addition of halogen-based boiler additives such as MerControl® 7895. The second required condition to maximize WFGD capture of ionic mercury from flue gas is the control and suppression of mercury re-emission. Mercury re-emission occurs in the WFGD scrubber liquor when absorbed ionic mercury is reduced to elemental mercury and released back into the flue gas exiting the WFGD. The net result is an observed increase in elemental mercury concentration in the flue gas across WFGDs. Mercury re-emission has been documented in laboratory studies and on commercial units. In such cases, mercury re-emission can be responsible for EGUs with WFGDs failing to be compliant with the mercury emission standard put forth in MATS.

The present paper documents cost effective methods to improve mercury capture efficiency of WFGDs facilitating compliance with MATS. Experience on commercial units will be presented demonstrating the critical nature of the two requirements, i.e. flue gas mercury speciation control and mercury re-emission control, and mercury control strategies to accomplish both critical conditions. Practical experience gathered on commercial units will be provided demonstrating how the application of MerControl® 8034 improves the mercury capture efficiency of existing WFGDs and facilitates compliance. Information will also be provided on the impact of these strategies on plant effluent.

#### **Suppression of Self-Ignition Tendency of Low Rank Coals Using Degradative Solvent Extraction at Around 350°C**

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

Although the deposits of low rank coals such as brown coal or lignite are huge and widely distributed in the world, they have been just utilized only near coal mines for power generation. This is because the heating value of the coal is very low due to high moisture and oxygen contents and because the coal can neither be stored nor transported due to its high self-ignition tendency especially when dewatered. It is therefore essential to suppress the self-ignition tendency as well as to dewater and upgrade for effective utilization of the low rank coal.

We have been proposing a new method effective for simultaneous dewatering and upgrading of brown coal. The method treats the coal in a non-polar solvent at around 350°C and separates the coal into upgraded, clean, and low-molecular extract and residue. We call this method degradative solvent extraction of brown coal. In this work the possibility of the application of the method for suppressing the self-ignition tendency was examined from fundamental aspects. It was found that the self-ignition tendency of an extract from a brown coal was much smaller than that of the raw coal. This was mainly because the extract softens and melts when heated over 100°C, and hence it has much smaller pore surface area than the raw coal. This result suggested the possibility of using the extract as an additive for suppressing the self-ignition tendency. The applicability of the proposed method was further examined for several low rank coals.

#### **Investigation of Catalytic Mercury Oxidation Kinetics on Supported Gold**

Kyoungjin Lee, Erik C. Rupp, Dong-Hee Lim, Jennifer Wilcox, Stanford University, USA

Gold catalysts ( $Au/\gamma-Al_2O_3$ ,  $Au/\alpha-Al_2O_3$ ,  $Au/TiO_2$ , and  $Au/SiO_2$ ) for mercury oxidation are tested in a packed-bed reactor in a flue gas stream generated by methane combustion. In a typical experiment, 100 mg of catalyst is exposed to the flue gas stream containing 16%  $H_2O$  and 390  $\mu g/m^3$   $Hg^0$ . The mercury concentration is controlled by a PS Analytical Cavkit, which uses the vapor pressure of a heated Hg reservoir to provide a constant source. The gas downstream of the packed bed is analyzed for Hg using a PS Analytical system consisting of a dilution/cracker probe (which allows for speciation of Hg between  $Hg^0$  and  $Hg^{2+}$ ) and a Sir Galahad instrument, which uses atomic fluorescence detection. In this manner, we are able to investigate the effect of the various supports, Au loading (ranging from 0.2 to 2 wt%) and that of flue gas additives (e.g., HCl,  $Cl_2$ ,  $SO_2$ , and  $NO_x$ ) on the extent of mercury oxidation. Since the system operates in real time, temporal changes in Hg concentration, such as sorption on the catalyst surface, which is expected to be limited, and loss of catalytic activity may be tracked. The reacted catalysts are further characterized ex situ using X-ray photoelectron spectroscopy (XPS) to determine the extent of surface halogenation or sulfur adsorption.

In addition to the bench-scale experiments, density functional theory (DFT) studies have been carried out to investigate various reaction pathways of mercury oxidation across defective gold surfaces. The Climbing Image-Nudged Elastic Band (CI-NEB) method is employed to calculate activation energies of  $HgCl$  and  $HgCl_2$  formation pathways using the Vienna *ab-initio* simulation package (VASP). It has been found that Hg oxidation via HCl is more likely to occur than via  $Cl_2$  in terms of activation energies required for the formation of  $HgCl$  and  $HgCl_2$ . The clarified mechanism may help to design a proper Hg catalyst based on the composition and grade of the coal used at a power plant. This approach, which uses theoretical calculations in conjunction with experimental results, may be applied more extensively to investigate

the catalytic mechanism of different precious metals in a wide range of flue gas compositions.

**SESSION 41**  
**Carbon Management: CO<sub>2</sub> Storage - 1 (Coal)**

**Assessment of Factors Influencing Effective CO<sub>2</sub> Storage Capacity and Enhanced Gas Recovery in the Marcellus Shale**

Michael L. Goddec, Advanced Resources International, USA

A significant concentration of large CO<sub>2</sub> emission sources exists in the Eastern United States (mainly from coal-fired power plants), but finding suitable geologic CO<sub>2</sub> storage sites has proven elusive. Although still at a conceptual stage, CO<sub>2</sub> storage in gas shales is attracting interest in Appalachian states with extensive shale deposits, but limited CO<sub>2</sub> storage capacity in conventional porous reservoirs. This paper reports on research to date, sponsored by the U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL) designed to assess factors influencing effective CO<sub>2</sub> storage capacity and injectivity in the Marcellus shale in the Eastern United States.

Organic-rich gas shale appears to behave similarly to coal and desorb methane while preferentially adsorbing CO<sub>2</sub>. In addition, the pore volume containing “free” (non-adsorbed) methane is expected to be available for CO<sub>2</sub> storage, especially where previous hydraulic fracturing has enhanced injectivity. In theory, CO<sub>2</sub> injection into organic-rich gas shale could provide dual benefits of incremental recovery of adsorbed methane and secure CO<sub>2</sub> storage.

This paper summarizes the results of a geological characterization effort that estimates total gas in-place and potential CO<sub>2</sub> storage capacity within the Marcellus Shale for a study area extending from southern NY to southern West Virginia through Pennsylvania and southeast Ohio. It goes on to summarize the results to-date of reservoir simulation work to develop a better understanding of shale characteristics influencing storage capacity and injectivity. A reservoir model for the Marcellus shale was developed, and various scenarios were generated for well vertical and horizontal wells, the amount of well stimulation and various well spacings. Simulated production results are compared to available data in the study area to demonstrate that the reservoir models are representative of existing field conditions. Next, CO<sub>2</sub> is injected to estimate potential CO<sub>2</sub> injection rates into the Marcellus shale, total volume of CO<sub>2</sub> to be potentially stored, initial dimensions of the CO<sub>2</sub> plume and the disposition of CO<sub>2</sub> in the reservoir over time. The modeling work will provide insights regarding the parameters with the greatest influence on methane recovery and CO<sub>2</sub> storage capacity. Significant sources of uncertainty include limited CO<sub>2</sub> and methane isotherm data and the representation of reservoir matrix and fracture properties in the reservoir simulations.

**Development of ECBMR Simulator for Coal-Bearing Formation and Its Application**

Sohei Shimada, Yukiya Sakou, The University of Tokyo, JAPAN

CO<sub>2</sub> geological storage (CGS) has been recognized as an indispensable and cost-efficient abatement measure against the Global Warming by the CO<sub>2</sub> emission from large-scale energy-related sources. Within the CGS, the disposal of CO<sub>2</sub> into deep saline aquifer (DSA) and injection of CO<sub>2</sub> into deep unmineable coal seam (UCS) for enhanced coalbed methane recovery (ECBMR) are two promising technologies, which have been widely studied. DSA storage initiated from its tremendous global storage capacity and relatively even distribution all over the world, while UCS storage caught the stakeholders’ eyes because of its financial return by producing excessive methane gas which is originally adsorbed in the coal matrix and then replaced by CO<sub>2</sub> immediately after the pressurized injection of CO<sub>2</sub>, as well as its secure storage mechanism and comparatively well-investigated geological properties.

An numerical simulator of non-isothermal multiphase multi-component fluid dynamics in the geological reservoir model for coal-bearing formation (CBF), ECOMERS(CBF)-UT (Enhanced Coalbed Methane Recovery Simulator for Coal-Bearing Formation, the University of Tokyo), were developed.

The simulator was used for the calculation of CO<sub>2</sub> storage in the under sea coal-bearing formation in Ariake Area, Kyushu, Japan. This area has two main coal seams with the distance of 100m. CO<sub>2</sub> was injected into the lower coal seam. The upper coal seam showed the retarding effect of CO<sub>2</sub> flow upward due to adsorption. The free CO<sub>2</sub> in sandstone and shale is dissolved into saline water and the dissolution flows downward in about 100 years after injection. It suggests that the CO<sub>2</sub> is stored safely in Ariake Area. However, one problem revealed is the liberation of CH<sub>4</sub> from upper coal seam due to displacement.

**Comparison of High-Pressure CO<sub>2</sub> Sorption Isotherms on Eastern and Western US Coals**

Vyacheslav Romanov, Bret Howard, DOE/NETL; James Fazio, ORISE/DOE/NETL;  
Tae-Bong Hur, University of Pittsburgh, USA

Accurate estimation of carbon dioxide (CO<sub>2</sub>) sorption capacity of coal is important for planning the CO<sub>2</sub> sequestration efforts. In this work, we investigated sorption and swelling behavior of several Eastern and Western US coal samples from the Central Appalachian Basin and from San Juan Basin. The CO<sub>2</sub> sorption isotherms have been completed at 55°C for as received and dried samples. The role of mineral components in coal, the coal swelling, the effects of temperature and moisture, and the error propagation have been analyzed. Changes in void volume due to dewatering and other factors such as temporary caging of carbon dioxide molecules in coal matrix were identified among the main factors affecting accuracy of the carbon dioxide sorption isotherms. The (helium) void volume in the sample cells was measured before and after the sorption isotherm experiments and was used to build the volume-corrected data plots.

**An Examination of MVA Techniques Applicable for CCUS in Thin, Stacked Coals of the Central Appalachian Basin**

Ellen Gilliland, Nino Ripepi, Michael Karmis, Virginia Tech; Matthew Conrad,  
Cardno-MM&A, USA

The goals of monitoring, verification, and accounting (MVA) for carbon capture, utilization, and storage (CCUS) studies include improved understanding of injection and storage processes, evaluation of interactions between CO<sub>2</sub>, reservoir fluids, and formation solids, and assessment and minimization of environmental impacts (DOE and NETL, 2009). With these critical objectives in mind, it is important to design a strong, tailored MVA program that is site-specific and addresses all phases of the project lifecycle. Site factors to consider include the risk profile, geology and geologic structures, and access. The project lifecycle consists of pre-operation (characterization, baseline tests, etc.), operation/injection (plume assessment, imaging, etc.), closure and site restoration, and post-closure (long-term monitoring). MVA methods can be categorized by the setting in which they are used—atmosphere, near-surface, or subsurface—although some methods, such as isotopic tracers, apply to multiple settings. Common atmospheric MVA methods include CO<sub>2</sub> detectors and eddy covariance measurements, which both quantify atmospheric levels of CO<sub>2</sub> and can, therefore, help to detect a leak or confirm storage. Near-surface methods include groundwater monitoring, which can also indicate leakage or proper containment, and surface deformation meters, such as tiltmeters, which can help define the CO<sub>2</sub> plume by delineating the inflated portion of the reservoir and/or new fractures induced by the pressure of the plume. Subsurface methods include borehole logging techniques and geophysical imaging techniques, such as seismic or electrical conductivity/resistivity surveys. Both logging and imaging techniques are often conducted in a time-lapse manner, pre- and post-injection, in attempt to record a change in properties due to the presence of the CO<sub>2</sub> plume.

A small-scale CCUS study in southwest Virginia presents a novel application for several established, effective MVA methods. The study, located in an active coalbed methane (CBM) field in Buchanan County, will involve injecting 20,000 tonnes of CO<sub>2</sub> into a series of thin, unmineable coal seams. Three CBM production wells will be converted for use as injection wells. The goals of the study are to test the injection and storage potential of the coal seams and to assess the potential for enhanced coalbed methane (ECBM) recovery at offset wells. The reservoir consists of approximately 15 coal seams, averaging 1.0 foot in thickness and distributed over 1000 feet of section. This reservoir geometry creates an unusual target for CO<sub>2</sub> injection and also a challenging one for many monitoring and imaging techniques.

A smaller CO<sub>2</sub> injection test was conducted 7.5 miles away in Russell County, VA, in 2009. The MVA used for the Russell County test produced several important findings that have implications for the Buchanan County test. The MVA plan for the Buchanan County test will use the same suite of technologies used at the Russell County test as well as some additional methods. MVA for the Buchanan County test will include gas content measurements at offset wells, groundwater monitoring, tracer analysis, well logging, microseismic monitoring, surface deformation measurement, and time-lapse seismic imaging (crosswell or vertical seismic profile). Multiple monitoring wells will be drilled in order to facilitate the MVA efforts. Because the reservoir is composed of several seams, ranging in depth from 900-2100 feet, multiple tracers may be used to better understand the injection and storage potential of specific zones. Surface deformation meters, microseismic monitoring, and time-lapse seismic imaging are state-of-the art tools that have potential to define the subsurface CO<sub>2</sub> plume beyond the borehole scale. The reservoir of thin, dispersed coals is a unique application for these methods, and their use will provide a feasibility test that will help improve MVA design for CCUS in similar settings. Assessing the results of time-lapse seismic surveys will be especially complicated due to the several reservoir processes and factors that may produce detectable changes in seismic properties. These include the potential for CO<sub>2</sub> to exist in gas and/or liquid phase within different seams, the presence and amount of water in the formation, the swelling of the coal matrix in the presence of CO<sub>2</sub>, and seasonal or other natural variation in the acoustic properties of the formation. Distinguishing the individual contributions of these processes to the observed change will be a challenge but would provide important insights into reservoir processes. The results of MVA for this study can be used to improve design for potential future studies of CCUS in thin coals.

**SESSION 42**  
**Coal Science: General – 4**

**CO<sub>2</sub> Adsorption During Weathering of Coal Piles: Effect of Coal Rank**

Uri Green, The Ariel University Center and The Hebrew University of Jerusalem;  
Zeev Aizenshtat, The Hebrew University of Jerusalem; Haim Cohen, The Ariel  
University Center and The Ben-Gurion University of the Negev; Franz Geldmeister,  
The Ariel University Center and The TU Bergakademie Freiberg, ISRAEL

Steam coals are used in utilities worldwide for electrical power production. During monitoring of gases evolved via the weathering processes of large coal piles under open air storage and laboratory simulations, it has been observed that large amounts of carbon dioxide are adsorbed by the coal. Thus, one should take into account that appreciable amounts of CO<sub>2</sub> formed by the low temperature oxidation (LTO) of the coal are trapped inside the pore structure of the coal as well as when studying LTO processes and performing kinetic evaluations of CO<sub>2</sub> production, the amounts of CO<sub>2</sub> released and adsorbed should be calculated. As the coals used for power production are often stored in large piles (>100 000 tons) for long periods, these piles are prone to undergo weathering which might result in self-heating of the coal piles and, in extreme cases, can spontaneously combust. Furthermore, the adsorption is also rank dependent and deviates from coal to coal. The effect of coal rank has been characterized with a South African bituminous coal and with Indonesian sub-bituminous coal which are currently in use in Israeli utilities as well as two German lignites which are consumed in German utilities. The results indicate that only the higher rank coals (bituminous and sub-bituminous) exhibit significant adsorption of CO<sub>2</sub>.

**Gaseous Emissions and Sublimates from the Truman Shepherd Coal Fire, Floyd County, Kentucky**

James C. Hower, Kevin R. Henke, Gregory Copley, Samuel Morton, Trent Garrison,  
University of Kentucky Center for Applied Energy Research; Jennifer M.K. O'Keefe,  
Morehead State University; Donald R. Blake, University of California at Irvine, USA;  
Nicola J. Wagner, University of Witwatersrand, SOUTH AFRICA; Carlos H.  
Sampaio, Universidade Federal do Rio Grande do Sul; André Jasper, Luis F.O. Silva,  
Centro Universitário UNIVATES, BRAZIL

The Truman Shepherd fire is burning in abandoned mine works in the high volatile A bituminous Pennsylvanian-age Upper Elkhorn No. 3 coalbed in Floyd County, Kentucky. The expression of the fire is subtle, being noted more by the smell of the emitted gases and, at times, emitted smoke, but never visible flames.

At the time of our initial February 2009 investigation, the emissions were from abandoned mine entries. In 2009, the U.S Office of Surface Mining attempted to extinguish the fire by pumping a mixture of 0.5-1.0% foam with water, halted when the foam was found in the well water of nearby houses. Excavation was then attempted, but the fire was deep to reach given the project budget and the oversight was turned over to Kentucky's Department of Abandoned Mine Lands. The fire continues to burn, prompting this investigation of the reconfigured site.

Site visits were made in July and November 2011 and January 2012 in order to measure gas emissions, collect volatile organic gases, and collect mineral and tar deposits at the vents. Significant variation exists in the emissions, both between vents during each visit and at the same vent at different times of the year, illustrating the dynamic nature of the coal fire.

The fire has continued to expand, growing from five vents in July 2011 to 10 vents in January 2012. In a later visit (April 2012), an additional five vents were found to the east of the 10 vents. The advance of the fire is in the direction of a small town.

**ReaxFF Molecular Dynamics Pyrolysis Simulations of a Large-Scale Model of Illinois no. 6 Coal Including the Role of Organic Sulfur**

Fidel Castro-Marciano, Adri C.T. van Duin, Jonathan P. Mathews, The Pennsylvania  
State University, USA

Reactive molecular dynamics simulations are a useful computational approach for investigating chemical reactions and structural transformations in complex processes. Pyrolysis of coal is one such area where additional insight would be beneficial for utilization improvements and pollution control. Here, ReaxFF was utilized to perform pyrolysis simulations on a large-scale molecular model for Illinois no. 6 coal to examine coal pyrolysis chemistry. A previously constructed large-scale molecular model of Illinois no. 6 coal composed of 51,001 atoms within 728 molecules was used in ReaxFF pyrolysis simulations at 2000 K for 250 ps. The ReaxFF simulation was performed until 50% of the cross-links had been cleaved primarily through thermolysis. During pyrolysis the molecular weight distributions shifted to lower molar mass values as a result of thermal decomposition of coal molecules to form smaller fragments. Analysis of sulfur forms distribution showed that aliphatic-bonded sulfurs decomposed more rapidly while thiophenic-bonded sulfurs were more thermally stable in agreement with expected chemistry. The thermal degradation of sulfur-containing

cross-links was more substantial than that of alkyl linkages, in accordance with their higher reactivity (aliphatic > aromatic > thiophenic). To further analyze the role of organic sulfur forms on coal pyrolysis chemistry, a non-sulfur containing Illinois coal model was created by substituting sulfurs for carbons, that were hydrogen adjusted, and the Reaxff simulation was repeated. Analysis of trajectories showed that the rate of light gases and tar generation was higher for the Illinois coal model (sulfur containing) compared to the non-sulfur containing coal structure, indicating that sulfur atoms enhanced reaction kinetics during coal pyrolysis as expected. This work further demonstrates that ReaxFF integration with representative coal molecular models can be a useful tool for probing chemical processes associated with coal pyrolysis.

**Radical Formation in Coals Undergoing Weathering: Effect of Coal Rank**

Uri Green, The Ariel University Center and The Hebrew University of Jerusalem;  
Sharon Ruthstein, The Bar Ilan University; Zeev Aizenshtat, The Hebrew University  
of Jerusalem; Haim Cohen, The Ariel University Center and The Ben-Gurion  
University of the Negev, ISRAEL

Once coal is excavated it comes into contact with atmosphere oxygen and begins to undergo low temperature oxidation. Over the years there have been several studies related to the oxidation process occurring at these low temperatures (30-120C). The mechanism by which the molecular oxygen interacts with the coal macromolecule is suggested to occur in several steps. These steps primarily involve diffusion to the surface where physical adsorption followed by chemical adsorption takes place. The chemical adsorption forms several types of oxides that can subsequently react to form several types of products, primarily CO<sub>2</sub>.

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

Several different rank (lignite-subbituminous-bituminous) coals were isothermally heated at 95C in an air atmosphere for a period of up to 6 months and samples were collected at two week intervals. The radical concentration of each sample was measured by Electron Paramagnetic Resonance (EPR) Spectroscopy. It is apparent that there are distinct differences between the lower rank (lignite) and the higher rank coals (subbituminous, bituminous). The low rank coals exhibited only carbon centered radicals with an adjacent oxygen atom and the high rank coals exhibited only carbon centered radicals. Interestingly, the lower rank coals exhibited no change in radical concentration due to the long term oxidation treatment while the higher rank coals showed a distinct increase in the radical concentration. These findings shed new light onto the complex heterogeneous low temperature oxidation reactions occurring at the coal surface.

**Elution Control of Toxic Ions from Ashes**

Takahiro Kato, Katsuyasu Sugawara, Akita University; Yukio Enda, Akita Industrial  
Technology Center, JAPAN

A unique control method was developed for toxic ions elution from coal fly-ash and sewage sludge-ash in acid solution. Coated fly ash pellets were prepared by covering with bottom ash produced from the same coal-fired boiler and subsequent sintering at 1300°C. The elution test was carried out in the acid solution of pH 3, 4 and 5.5 for the fly ash pellets with and without the bottom ash coating. The coating of fly ash pellet suppresses the elution of lead ion, independent of acidity of solution, while the fly ash pellet without coating shows an increase of lead elution with lowering of pH.

Coated sewage sludge-ash pellets were also prepared by covering with the bottom ash from the coal-fired bottom-ash. Since the melting temperature of inner sewage sludge-ash was lower than that of outer coal bottom-ash, coated sewage sludge-ash was heated rapidly in order to melt only the surface of a pellet. The heating condition was determined based on the observed thermal conductivities of sewage sludge-ash and coal bottom-ash. Elution tests in hydrochloric and nitric acid solutions showed that the coating of sewage-ash completely suppressed the elution of arsenic ion in both solutions, whereas the uncoated pellets showed considerable elution.

**SESSION 43**  
**Clean Coal Demonstration and Commercial Projects: Technical - 5**  
**(Industrial CCUS)**

**The US Economic and Energy Outlooks and the Implications for Domestic Coal**  
Augustine Faucher, PNC Financial Services Group, USA

The United States economy continues its recovery from the Great Recession, although the pace of economic and job growth remains disappointing. The U.S. economy will continue to expand at a moderate pace over the next few years, with a gradually

declining unemployment rate. As the economy continues to expand, demand for energy will continue to increase. The U.S. energy landscape is evolving, with increasing domestic production of oil and especially natural gas. However, with increasing concerns about global climate change and other environmental issues, and natural gas prices extremely low on an historical basis, domestic coal production will face increasing market and political pressures. This will cause economic disruptions for major U.S. coal-producing regions.

**Port Arthur CCS: Demonstration of Carbon Capture and Sequestration of Steam Methane Reforming Process Gas Used for Large-Scale Hydrogen Production**

Anthony Zinn, DOE/NETL; Ken Welch, Bob Hutchison, Kurt Metzler, Kent Kisenbauer, Keith Adams, Air Products and Chemicals, Inc., USA

Air Products and Chemicals, Inc. (APCI) is designing and constructing a state-of-the-art system to concentrate the carbon dioxide (CO<sub>2</sub>) from two steam methane reformer (SMR) waste streams for delivery of the CO<sub>2</sub> via pipeline for sequestration by injection into the Hastings oil field (near Galveston, TX) as part of an enhanced oil recovery (EOR) project. APCI will retro-fit their two SMRs, located in Port Arthur, TX, using Vacuum Swing Adsorption technology to separate the CO<sub>2</sub> from the stream, followed by a drying process and compression. The CO<sub>2</sub> capture facility will convert the initial stream containing greater than 10% CO<sub>2</sub> to greater than 98% purity for delivery to the pipeline. The technology will remove more than 90% of the CO<sub>2</sub> from the process gas stream used in a world-class scale hydrogen production facility. Approximately 1 million metric tons per year will be delivered for sequestration and EOR, which will result in additional domestic oil production.

This paper will provide both background and a status update for the Port Arthur, TX demonstration project. The topics to be covered include a background/ summary of the current Port Arthur site and process; objectives and scope of the demonstration program; project work/ site modifications included in the demonstration program; current status of project work; and a forward schedule for the demonstration period.

**Illinois Industrial Carbon Capture and Storage Project**

Scott McDonald, Archer Daniels Midland Company, USA

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

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

Illinois Industrial Carbon Capture and Storage Project (IL-ICCS), (Status- under Construction). This project is led by ADM and will expand the sites CO<sub>2</sub> injection and storage capability to that of a commercial-scale operation. The project is scheduled for startup in the third quarter of 2013 and will inject up to 1.0 million metric tons per year over an operational period of approximately 2.5 years. ADM will integrate the IBDP compression and dehydration facilities with the new facilities constructed under the IL-ICCS project upon completion of IBDP injection operations in fall 2014. A significant benefit of these two complimentary projects is the unique opportunity to better understand the interaction between the CO<sub>2</sub> plumes and pressure fronts emanating from two injection wells in the same sandstone formation.

IL-ICCS project has the following objectives:

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

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

The IL-ICCS project has leverage the knowledge and experience gained during the IBDP project. Site selection, reservoir modeling, MVA development, risk assessment, community outreach, engineering design, and facility construction are many of the areas in which the project team benefitted from the experience and lessons learned during the IBDP project. Because of this experience, the IL-ICCS project has an accelerated design and construction schedule and plans for operation within 24-30 months.

**Lake Charles Industrial Scale Carbon Capture, Transport and Sequestration**

Thomas J. Leib, Leucadia Energy, USA

The Lake Charles CCS Project is a large-scale industrial carbon capture and sequestration (CCS) project which will demonstrate advanced technologies that capture and sequester carbon dioxide (CO<sub>2</sub>) emissions from industrial sources into underground formations. Specifically the Lake Charles CCS Project will accelerate commercialization of large-scale CO<sub>2</sub> storage from industrial sources by leveraging synergy between a proposed petroleum coke to methanol plant (Lake Charles chemical project) and the largest integrated anthropogenic CO<sub>2</sub> capture, transport, and monitored sequestration program in the U.S. Gulf Coast Region. The Lake Charles CCS Project will promote the expansion of Enhanced Oil Recovery (EOR) in the Gulf region and supply greater energy security by expanding domestic energy supplies. The capture, compression, pipeline, and injection infrastructure will continue to sequester CO<sub>2</sub> capture many years after the completion of the term of the DOE agreement.

**SESSION 44**

**Coal-Derived Products: General – 6**

**Using Coal Ash as the Layer onto the Steel Tank Protecting its Walls and Bottom when Steel Bars being Dipped in Hot-Melt Zn in it**

Nguyen Viet Quang Hung, Nguyen Viet Cuong, Vietnam Academy of Science and Technology, VIETNAM; Masakatsu Nomura, Osaka University, JAPAN

Protecting the walls and bottom of normal steel (C% high content) tanks for plating steel bars in hot-melt Zn metal is an important work, which has a great value in view of technology and economy. However, it requires very high technical points. The authors have proposed, studied and used two protecting layers. The main components of the outer layer are coal ash, zinc and poly-silicate. The outer layer is called CAZSIPOL layer. An inner layer is the lining one. Repairing the old special steel 08KP (according to GOST 1050/88 with 0.1% C) tanks and protecting the new 08KP tanks by the layers in the production conditions in Vietnam is very economical. The layers have been developed in Vietnam, especially in some key projects of Vietnam such as the 500KV high-voltage lines. Now the layers have been applied continuously for common steel constructions.

To improve lifetime of the 500KVpoles, the steel bars of electricity poles have to be dipped into hot-melt Zn tank about 13m length for plating of the 12.7m steel bars. In the case of ST3 (according to GOST 380-71 with 0.14-0.22% C - equivalent SPHT2 steel according to JIS G3132) normal steel tanks being 30-40mm thick without protecting layers, after about 20 days for its use a remaining thick of the tank is only 3-4mm. In the case of 08KP special steel tank lifetime of the tanks may be longer. In practice because of trouble sometimes about thermal property supply, the tank is too hot. So that the authors have studied to use the layers for 08KP and ST3 steel tanks to avoid the some accidents in actual processing.

When building 500KV line at North – South, Vietnam lacks 08KP special steel and has a lot of ST3 normal steel plates used for rail floors being 40-50mm thick. Lifetime of the first tank made of the rail floor steel with the two layers is 7 months and its total production weight is 547 tons.

A special effect of coal-ash in the outer layer is a reduction of hard Zn amount. Normally when dipping steel bars into the hot-melt Zn tank, hot hard Zn is formed and workers must scoop the hard Zn, however, on the face of tank walls there is a hard Zn layer being about 2 cm thick. By using the layers the hard Zn thickness becomes only 1-2mm, this meaning that the amount of hard Zn has decreased dramatically about 10 times.

**The Effect of Aqueous Solutions Interactions with Bituminous Coal Fly Ash on the Surface of the Particles Treatments with Aqueous Solutions (Acidic and Neutral)**

Roy Nir Lieberman, Ariel University Center of Samaria and Bar-Ilan University; Haim Cohen, The Ariel University Center and The Ben-Gurion University of the Negev; Yitzhak Mastai, Bar-Ilan University, ISRAEL

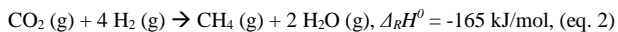
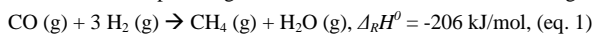
Treatments with aqueous solutions are causing changes in the structure of the coal fly ash. The Coal fly ash in Israel is produced by combustion of class F bituminous coals. The bulk of coal fly ashes produced in Israel stems from South African and Columbian bituminous coals therefore the coal fly ashes were the subject of the present study. It has been reported that the coal fly ash can be used as a potential scrubber and fixation reagent for acidic wastes. Moreover, the scrubbed product was found as a very efficient partial substitute to sand and cement in concrete, while the bricks have proved to be strong enough according to the concrete standards.

Three possible modes of interaction were observed: cation exchange, chemical bonding and electrostatic adsorption of very fine precipitate at the fly ash surface. To understand the fixation mechanism better we have treated the coal fly ashes with acidic (0.1M HCl) and neutral (DDW) solutions, subsequently changing the properties of the surface of the fly ash particles. Surface analysis by SEM and EDAX of the treated and untreated fly ashes have demonstrated that the treated fly ashes have changed appreciably its' interactions with transition metal ions (e.g Cd<sup>2+</sup>, Cu<sup>2+</sup>).

#### Application of a Three Phase Reactor for the Production of SNG

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

Methanation is a heterogeneously catalyzed reaction of CO and/or CO<sub>2</sub> with H<sub>2</sub> (eq. 1 and 2) which can be used to produce Synthetic Natural Gas (SNG). For this purpose, coal or biomass can be gasified producing a synthesis gas consisting mainly of CO, H<sub>2</sub> and CO<sub>2</sub>, which can be converted to methane. Furthermore, in countries with fluctuating surplus electricity from wind and sun power this surplus energy can be used to produce hydrogen via electrolysis. The hydrogen can then be reacted with CO<sub>2</sub> from various sources (biogas plant, coal power plant, chemical industry, coal gasification) to produce SNG. This process chain is referred to as "Power to Gas". The rapid increase of wind power plants makes such a process chain advisable, especially in Europe. The use of SNG has some advantages as compared to the solid fuels coal or biomass. First, SNG can easily be transported via pipelines. In most western countries the natural gas infrastructure is well developed. Second, its combustion is highly efficient and causes low emissions of harmful gases like SO<sub>2</sub>. Finally, SNG is a versatile fuel which can be used to produce heat and power but it can also be applied as a highly efficient and low polluting fuel for cars in internal combustion engines.



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

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

A new methanation process aims to combine some of the advantages of fixed- and of fluidized-bed reactors such as an effective removal of the reaction heat and simultaneously a low thermal and mechanical load on the catalyst. The idea is to use a three phase reactor (more precise: a slurry reactor) by filling the reactor volume with an inert heat transfer liquid and to suspend the catalyst in this liquid. The reacting gases would flow as bubbles through the liquid. As a result of the high heat capacity of the liquid phase, a three phase reactor system is able to intermediately store the heat of the methanation reaction with only a small rise in temperature. Thereby, the heat can easily be removed via external heat exchangers allowing an easy temperature control.

Possible disadvantages include mass transfer limitations in the liquid phase as well as decomposition and evaporation of the heat transfer liquid. Current research activities focus on identifying suitable heat transfer liquids and optimizing the liquid-side mass transfer. Additionally, the catalyst lifetime in a three phase system has to be compared with the lifetime in a two phase system.

The heat transfer liquid is used directly inside the reactor and therefore it needs to have high thermal and chemical stability. Moreover, a low vapor pressure is highly desirable. Ionic liquids are promising fluids for this purpose because of their very low vapor pressure, but their thermal stability has to be improved. Alternatively siloxane-based oils could be used.

In the presentation, results of the current research will be reported. This includes measured data for a three phase reactor (data for bubble size, gas holdup and CO-conversion in the slurry reactor) as well as calculations comparing the potentials of the different reactor types (comparison of reactor size and catalyst utilization).

#### Case Studies for Various IGCC Parameters Using Blended Coal/Biomass with Supercritical Steam Bottom Cycles

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

Great efforts have been continuously spent on improving the efficiency of the Integrated Gasification Combined Cycle (IGCC) and further reducing the greenhouse gas (GHG) emissions of the same. This study focuses on investigating two approaches to achieve these goals. First, replace the traditional subcritical Rankine steam cycle of the overall plant with a supercritical steam cycle. Second, add different amounts of biomass as feedstock to reduce carbon footprint as well as the SO<sub>x</sub> and NO<sub>x</sub> emissions. In addition, several other parameters were tested and a series of case studies were performed, seven in total. The goal of the case studies was to examine the thermal and economical impact of different design implementations for an IGCC plant. The parametric dichotomies investigated were: radiant cooling vs. syngas quenching, dry-fed vs. slurry-fed gasification (particularly in relation to sour-shift and sweet-shift carbon capture systems), oxygen-blown vs. air-blown gasifiers, low-rank coals vs. high-rank coals, and, in the case when it is not possible to achieve the desired steam turbine inlet temperature using the gas turbine's exhaust alone, whether it is better to import a secondary burnable fuel to raise the temperature, or use the GT syngas as the source of heat.

Employing biomass as a feedstock to generate fuels or power has the advantage of being carbon neutral or even carbon negative if carbon is captured and sequestered (CCS.) However, due to a limited supply of feedstock, biomass plants are usually small, which results in higher capital and production costs. Considering these challenges, it is more economically attractive and less technically challenging to co-gasify biomass wastes with coal. Using the commercial software, Thermoflow®, the case studies were performed on a simulated 250 MW coal IGCC plant located near New Orleans and co-fed with biomass from 10% to 50% by weight.

From an LHV thermal efficiency point of view, the results show that syngas coolers are better than quench systems (by 5.5 percentage points), dry-fed systems are better than slurry-fed systems (by 2.2-2.5 points), air-blown gasification is better than oxygen-blown (by 2.5 percentage points), natural gas is a better fuel for a duct burner than syngas (by 1.7 percentage points), sour-shift CCS is better than sweet-shift CCS (by 3 percentage points), and, finally, higher-ranked coals are better than lower-ranked coals (by 2.8 points without biomass, or 1.5 points with biomass.)

From an economic point of view, associated with capital and energy costs, however, the results show that quench systems are better than syngas coolers (by \$500/kW and 0.6 cents/kW-hr), dry-fed systems are still better than slurry-fed systems (by \$200/kW and 0.5 cents/kW-hr), sour-shift CCS is still better than sweet-shift CCS (by \$600/kW and 1.5 cents/kW-hr), air-blown gasification is still better than oxygen-blown gasification (by \$300/kW and 0.5 cents/kW-hr), natural gas is still better than syngas as a duct burner fuel (by \$400/kW and 0.5 cents/kW-hr), higher-ranked coals are better than lower-ranked coals without biomass (by \$600/kW and 0.1 cents/kW-hr), and higher-ranked coals are \$400/kW less expensive in capital cost but 0.21 cents/kW-hr more expensive in energy cost).

#### AVESTAR™ Center: Dynamic Simulation-Based Collaboration Toward Achieving Operational Excellence for IGCC Plants with Carbon Capture

Stephen E. Zitney, Eric A. Liese, Priyadarshi Mahapatra, AVESTAR

Center/DOE/NETL; Richard Turton, Debangsu Bhattacharyya, AVESTAR Center/West Virginia University; Graham T. Provost, Fossil Consulting Services, Inc., USA

To address challenges in attaining operational excellence for clean energy plants, the National Energy Technology Laboratory has launched a world-class facility for *Advanced Virtual Energy Simulation Training And Research (AVESTARTM)*. The AVESTAR Center brings together state-of-the-art, real-time, high-fidelity dynamic simulators with operator training systems and 3D virtual immersive training systems into an integrated energy plant and control room environment. This paper will highlight the AVESTAR Center simulators, facilities, and comprehensive training, education, and research programs focused on the operation and control of an integrated gasification combined cycle power plant (IGCC) with carbon dioxide capture.

#### Economic Analysis of Fossil Fuel Power Plants Meeting Future GHG Regulations

Nicholas Siefert, DOE/NETL; Shawn Litster, Carnegie Mellon University, USA

We present an economic analysis of both conventional fossil fuel power plants (PCC, NGCC, IGCC) and advanced fossil fuel power plants (PCC-CCS, NGCC-CCS, IGCC-CCS, Adv. IGCC-CCS, IGFC-CCS, Adv. IGFC-CCS). The 'Adv. IGCC-CCS' case is a standard IGCC-CCS power plant design, but with hydrogen separation via palladium membranes and oxygen separation via ceramic membranes. The 'IGFC-CCS' case is an entrained flow gasifier and an atmospheric pressure solid oxide fuel cell (SOFC). The 'Adv. IGFC-CCS' case is a catalytic gasifier coupled with a pressurized SOFC



(0.5 MPa.) For the carbon capture and sequestration (CCS) cases, we analyze sequestration both in saline aquifers and for enhanced oil recovery. We calculate the levelized cost of electricity and the rate of return on investment for these power plant configurations as a function of the price of emissions of CO<sub>2</sub> emissions and a function of the price of natural gas, holding all other variables constant. Relevant variables, such as capital costs, O&M costs, availability, lifetime, were estimated using previous estimates by Gerdes *et al.* [1], Grol *et al.* [2] and Rubin *et al.* [3]. In addition, we analyze the economics of two cases, which we call the PCC-50%CCS and IGCC-50%CCS cases, which were designed to meet the potential future EPA greenhouse gas standard of 1 lb of CO<sub>2</sub>/kWh of electricity generated. In this case, we calculate at what price of natural gas, holding all other variables constant, are the PCC-50%CCS and IGCC-50%CCS power plant designs economically viable.

[1] Gerdes, K., Grol, E., Keairns, D., and Newby, R., 2009, "Integrated Gasification Fuel Cell Performance and Cost Assessment: DOE/NETL-2009/1361."

[2] Grol, E., and Wimer, J., 2009, "Systems Analysis of an Integrated Gasification Fuel Cell Combined Cycle: DOE/NETL- 40/080609."

[3] Rubin, E. S., Chen, C., and Rao, A. B., 2007, "Cost and performance of fossil fuel power plants with CO<sub>2</sub> capture and storage," *Energy Policy*, 35(9), pp. 4444-4454.

#### **Control System Design for Maintaining CO<sub>2</sub> Capture in IGCC Power Plants While Load-Following**

Debangsu Bhattacharyya, Richard Turton, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

Load-following requirements for future integrated gasification combined cycle (IGCC) power plants with precombustion CO<sub>2</sub> capture are expected to be far more challenging as electricity produced by renewable energy is connected to the grid and strict environmental limits become mandatory requirements. In this work, loadfollowing studies are performed using a comprehensive dynamic model of an IGCC plant with pre-combustion CO<sub>2</sub> capture developed in Aspen Engineering Suite (AES). Considering multiple single-loop controllers for power demand load following, the preferred IGCC control strategy from the perspective of a power producer is gas turbine (GT) lead with gasifier follow. In this strategy, the GT controls the load by manipulating its firing rate while the slurry feed flow to the gasifier is manipulated to control the syngas pressure at the GT inlet. The syngas pressure control is an integrating process with significant time delay mainly because of the large piping and equipment volumes between the gasifier and the GT inlet. A modified proportional-integral-derivative (PID) control is considered for IGCC syngas pressure control. The desired CO<sub>2</sub> capture rate must be maintained while the IGCC plant follows the load. For maintaining the desired CO<sub>2</sub> capture rate, the control performance of PID control is compared with linear model predictive control (LMPC). The results show that the LMPC outperforms PID control for maintaining CO<sub>2</sub> capture rates in an IGCC power plant while load following.

#### **Investigation of the Gasification Performance of Lignite Feedstock and the Injection Design of a E-Gas Like Gasifier**

Yan-Tsan Luan, Yau-Pin Chyou, Institute of Nuclear Research, Atomic Energy Council, TAIWAN; Ting Wang, University of New Orleans, USA

In the last three years, Institute of Nuclear Energy Research (INER) has been developing the E-GAS gasification numerical model and analyzing the gasification performance by conducting several parametric studies. A preliminary numerical model considering coal particles tracking, volatiles thermal cracking, and nine chemical reactions with assigned reaction rate constants has been established. In last year's results, the single lateral injector design in the 2nd stage of E-GAS gasifier is found as a non-ideal condition for the gasification process. Therefore, one of the objectives in this study is to reform of 2nd stage injection and investigate its effect on gasification performance. Besides, due to the raising interest of the usage of low-rank coal as the feedstock for the power plants, the second goal in this paper is to conduct a feasibility assessment of the gasification of North Dakota (N.D.) Lignite.

The result shows that a two-injectors design in the 2nd stage injection of E-GAS gasifier can eliminate the non-ideal recirculation zone and contribute to the gasification performance. Furthermore, a tangent-jets design make average temperature reach equilibrium more quickly, and the height of the E-GAS gasifier could therefore be shortened. Moreover, by examining the energy needed for the 2nd stage injection, a tangent-jets design saves more energy as compared to the opposing-jets design. In other words, the gasification performance will increase due to the saved input energy. The result of the assessment of N.D. Lignite shows that under the same O<sub>2</sub>/Coal and Coal/Slurry ratios condition, no matter to fix the feedstock flow rate or the total input heating value, the gasification performance of N.D. Lignite is always lower than when Illinois #6 Coal is employed. However, the cheaper price of N.D. Lignite makes itself more competitive, and therefore if the electricity generating industries can accept a lower gasification performance, the usage of N.D. Lignite is still a choice to be considered.

#### **Small Scale Coal-Biomass to Liquids Production Using Highly Selective Fischer-Tropsch Synthesis**

Santosh Gangwal, Southern Research Institute; Arun Bose, DOE/NETL, USA

This project seeks to advance coal to liquids (CTL) and coal-biomass to liquids (CBTL) processes by demonstrating cost-effective, novel Fischer-Tropsch (FT) catalysts that selectively convert syngas derived from the gasification of coal and coal-biomass mixtures predominantly to drop-in gasoline and diesel, thereby eliminating expensive upgrading operations. The project also seeks to evaluate the impacts of adding moderate amounts of biomass to coal on liquid products, CBTL economics, and compare CBTL carbon footprint with petroleum based fuels production processes. This technology development effort is supported by the U.S. Department of Energy. Other project partners include Southern Company, Nexant, and Chevron Energy Technology Company.

The project will implement a full coal and coal-biomass to liquids bench-scale FT synthesis reactor system to produce liquid transportation fuels. The project will use an existing air-blown transport gasifier (also known as TRIG<sup>TM</sup>) operated by Southern Company at its National Carbon Capture Center as the source of both coal and coal-biomass derived syngas. Southern Research will design and fabricate a bench scale skid mounted FT reactor system to produce liquid FT products. Southern Research will carry out a suite of analyses to characterize all liquids from the CTL and CBTL test runs and compare the property differences/similarities and product quality produced by coal vs. coal-biomass blends. A preliminary technical and economic analysis will be carried out to evaluate the relative economics of CTL and CBTL processes and cost reduction due to selective transportation fuel production, and to determine the potential of moderate biomass addition to coal for reducing the carbon footprint of the CBTL process compared to petroleum-based fuel production processes.

#### **Pyrolysis Behaviour of Brown Coal in a Pressurized Drop Tube Reactor**

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

Pyrolysis is a key process for the thermochemical conversion of solid fuels (e.g. coal, biomass) in energetic and non-energetic applications. Decisive is its relevance as a sub-step of other thermo-chemical conversion processes like gasification and combustion as well as an individual step for the production of char/coke or tar/oil and for fuel conditioning. Due to the complex mechanisms taking place during the decomposition of these heterogeneous, macromolecular fuels, pyrolysis is affected by a multitude of parameters depending on feedstock properties, process conditions and designs. Especially the pyrolysis behavior under pressure is a less investigated topic, but it plays an important role if pyrolysis is considered as a pre-step in coal gasification processes, which are generally operated under elevated pressure. Relevant parameters, having an impact on gasification, are affected by the behavior of the feedstock during pyrolytic decomposition – e. g. char yield and reactivity as well as yield of gases/vapors and their composition.

Consistent data for product yields and properties as well as kinetic parameters are a basic requirement for the implementation of the pyrolysis process into models representing fuel conversion. They are further necessary for the evaluation of technical processes via compilation of detailed material and heat balances. Thus, the pyrolysis behavior of German brown coal in a pressurized drop tube reactor was investigated with regard to the influence of temperature (600 to 800 °C), pressure (1 to 30 bar) and particle residence time. The experiments were carried out in a drop tube reactor with an inner diameter of 20 mm and a heated length of 1.100 mm. The yields of the products (char, gas, tar/oil, reaction water) as well as their elemental composition and heating value were determined. Pyrolysis gas composition was measured using online gas chromatography. The obtained total gas yield as well as the yields of the main gas components including H<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub> related to particle residence time are used for calculation of kinetic parameters (activation energy, frequency factor) based on a single-step model and the Arrhenius equation. Furthermore, a comparison with thermogravimetric investigations of German brown coal and the results of an atmospheric fixed bed pyrolysis reactor are presented.

The obtained results improve the understanding of reactions and mechanisms taking place during brown coal pyrolysis especially under high pressure. The results can also be used as basis for further modeling of pyrolysis or gasification processes using process simulation software or CFD. Thus, the achieved information contributes to a future utilization of brown coal in gasification or pyrolysis plants to produce chemical products.

## Recent Development in Carbonaceous Chemistry for Computational Modeling (C3M)

Kiran Chaudhari, Richard Turton, Nathan Weiland, West Virginia University; Chris Guenther, Mehrdad Shahnam, Dirk VanEssendelft, DOE/NETL; Tingwen Li, Phil Nicoletti, URS; Aytekin Gel, ALPEMI Consulting, LLC, USA

The features and capabilities of Carbonaceous Chemistry for Computational Modeling (C3M) were introduced during 2011 International Pittsburgh Coal Conference. Since then, the development of C3M has progressed significantly. The new features of C3M will be discussed in this presentation. Specifically, the new modifications in C3M's kinetic expressions and its CFD compatibility will be discussed.

Currently, coal/ biomass/ petcoke gasification process simulation is linked to computational fluid dynamic (CFD) software programs such as Multiphase Flow with Interphase Exchanges (MFIx) developed at NETL, ANSYS-Fluent by ANSYS Inc. and Barracuda by CPFD Software with chemical kinetics and laboratory data. These kinetic expressions describe the fundamental steps taking place in the gasification of coal/petcoke/ biomass, namely, devolatilization, tar-gas chemistry, soot formation, and the subsequent heterogeneous and homogeneous gasification and combustion reactions. For this purpose, the kinetic data generated through a number of detailed models such as METC Gasifier Advanced Simulation (MGAS), PC Coal Lab (PCCL), Chemical Percolation Model for Coal Devolatilization (CPD), Solomon's Functional-Group, Depolymerization, Vaporization, Cross-linking (FGDVC) model, or experimental data currently being generated at NETL can be used as input.

C3M provides the option to select the fuel type that includes a wide variety of coals, biomass and petcoke. The kinetic packages used to generate the kinetic expressions for various reactions along with fuels are:

Devolatilization: MGAS (coal), PCCL (coal/biomass/petcoke), CPD (coal), FGDVC (coal), experimental data (coal/biomass).

Tar cracking: MGAS (coal), PCCL (coal/petcoke), FGDVC (coal), experimental data (coal/biomass).

Char gasification: MGAS (coal), PCCL (coal/petcoke/biomass), experimental data (coal/biomass).

Char oxidation: MGAS (coal), PCCL (coal/petcoke/biomass).

Soot formation: PCCL (coal/petcoke/biomass), CPD (coal).

Soot oxidation and gasification: PCCL (coal/petcoke/biomass).

The C3M graphical user interface (GUI) has been modified to allow users to run the various kinetic models and evaluate graphically the effect different fuels and/or gasifier operating conditions have on gasification kinetics along with the yield of product species. After displaying the data, the C3M GUI allows the user to select kinetic information from a particular kinetic model and then correctly formats the data and seamlessly integrates it into the CFD input files thus allowing the user to run the CFD code without extensive development effort for implementing the governing reactions.

Uncertainty Quantification (UQ) analysis for coal gasification process is a unique feature provided by C3M. With the UQ analysis capability, a user can better understand the effect of variations in operating conditions and fuel properties in the product yields and reaction rates. This is achieved through a Monte Carlo type simulation consisting of many sampling runs on the kinetic packages available in C3M by randomly drawing values for input parameters and statistically analyzing the output. The fact that computational cost per sample is very cheap, direct Monte Carlo simulation is possible as opposed to a surrogate model based sampling approach, which is commonly used when the computational cost per sample is high. This UQ work is on-going and will be extended to the CFD packages in the future.

### The Study on Kinetics of LRC Mild Pyrolysis

Lijuan Gao, Xianglong Zhao, Zhe Cui, Li Weng, Ke Liu, National Institute of Clean-and-Low-Carbon Energy, CHINA

Low rank coals (LRCs) are characterized by their high moisture content and high reactivity, which greatly restricted their utilizations unless they were upgraded. The "Coal Refining" technology developing by National Institute of Clean-and-low-carbon Energy of China (NICE) is one of the technologies that upgrade LRCs to value-added products with improved transport safety and economics. In the technology, LRC was pyrolyzed at mild conditions to decrease its volatile and then passivated to stable high-BTU upgraded coal. Pyro-oil was another high value product produced during the mild pyrolysis of LRC. Though the kinetics of coal pyrolysis have been investigated by many people, most of them are conducted in high temperature regarding pyrolysis as the first step of combustion and gasification. The research on coal pyrolysis at mild conditions is still limited in literatures. In order to understand the mild pyrolysis of LRC, the kinetics of mild pyrolysis is studied in this paper.

Experimental studies on mild pyrolysis of typical Chinese lignite were done in a TGA-FTIR system at atmospheric pressure and temperatures ranging from 480–593°. The primary gas species (CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O) from coal mild pyrolysis are analyzed quantitatively. Not like high temperature pyrolysis, a portion of the volatiles in coal will never cracked and released at mild conditions because the bonds of these volatiles are strong enough at this temperature level. The mild pyrolysis reaction rate depends not only on the temperature, but also the "effective volatile" in coal, which means the theoretical cracked volatile in coal after a long time at certain temperature. The

relationship between the effective volatile and temperature was studied. The pyro-oil yield increased with temperature, but the increasing rate became slowly at high temperature, probably because more pyro-oil was secondly-cracked to gas species at higher temperature. The gas compositions were different at different temperatures so that different species should have distinct kinetics. Therefore separate kinetics of CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and pyro-oil were built from the experimental data.

## SESSION 47

### Carbon Management: CO<sub>2</sub> Storage - 2 (Coal)

#### New Interpretations of Micropore Diffusion of CO<sub>2</sub> and CH<sub>4</sub> in Bituminous Coals

Gregory Staib, Richard Sakurovs, Stephen Weir, CSIRO; Evan Gray, Griffith University, AUSTRALIA

Enhanced Coal-Bed Methane (ECBM) recovery is a proposed method of enhancing methane (CH<sub>4</sub>) extraction from deep coal seams by injecting carbon dioxide (CO<sub>2</sub>). Recovered CH<sub>4</sub> can provide a relatively low polluting fuel to offset costs associated with the sequestration of CO<sub>2</sub>. Adsorption is the primary physical mechanism by which the CH<sub>4</sub> is held and by which captured CO<sub>2</sub> will be stored. Published adsorption experiments encouragingly report the replacement of CH<sub>4</sub> by CO<sub>2</sub> in coal but this process has been notoriously difficult to model. Complicating effects such as site accessibility, swelling, confining stress and mineral matter of coal along with new observations and experimental approaches have called into question whether these traditional adsorption experiments can be used to accurately predict the CH<sub>4</sub>-CO<sub>2</sub> gas exchange expected in the coal seams [1]. We have focused on studying the diffusion mechanism of CO<sub>2</sub> and CH<sub>4</sub> in coal and have designed and constructed a volumetric system with improved temperature and pressure stability in which the whole sample cell and attachments have a temperature stability and uniformity of less than 0.03°C variation. Kinetic data have been obtained at 45°C for CO<sub>2</sub> and CH<sub>4</sub> on one Australian bituminous coal (particle size 0.6-1 mm). The kinetic data shows general agreement that the CO<sub>2</sub> diffusivities are larger than CH<sub>4</sub> diffusivities and that they increase with temperature. However, the effect of pressure on measured diffusivity constants appears model dependent. Different models of diffusion can give calculated values of diffusion constants that can either increase or decrease with increasing pressure using the same data [2]. Whilst it is expected that variation would exist between different coals we argue that (i) different measurement procedures or experimental technique and (ii) different models will give different interpretations of the diffusivity of CO<sub>2</sub> and CH<sub>4</sub> on coals. We demonstrate here that through the application of different gas loadings and use of an unmodified bidisperse model [3] on one bituminous coal using CO<sub>2</sub> that its calculated diffusion shows a pressure dependence, and depends on the concentration of the gas entering the coal's micropores. This means that the magnitude of the pressure step needs to be considered as well as the absolute pressure before considering trends in diffusion rates in coal: this discovery may help clear up some of the uncertainty in the apparent pressure dependence of diffusion other researchers have found. Such a relationship with concentration for CH<sub>4</sub> was not found and this has been attributed to it having a much lower sorbate activity than CO<sub>2</sub>. It has been suggested that the use of the bidisperse model is not justified since coal has nonlinear isotherms [2, 4, 5]; we find however, that the bidisperse model can be used if the obtained diffusivity be considered as an *effective diffusivity* that depends on the magnitude of the gas loading. Additionally, a relationship has been found that if the limiting diffusivity of CO<sub>2</sub> is known (i.e. as the increased gas loading – pressure step size – approaches zero) the apparent micropore diffusivity can be approximately predicted from step size data alone.

#### The Application of Constitutive Laws to Model the Dynamic Evolution of Permeability in Coal Seams for the Case of CO<sub>2</sub> Geologic Sequestration and Enhanced Coal Bed Methane Recovery

Foteini Vasilikou, Nino Ripepi, Zach Agioutantis, Michael Karmis, Virginia Center for Coal and Energy Research, Virginia Tech, USA

Injection and storage of carbon dioxide (CO<sub>2</sub>) in deep unmineable coalbeds decreases anthropogenic greenhouse gas emissions and presents a financially viable solution by enhancing recovery of coalbed methane (ECBM). Coalbeds are commonly characterized by a dual porosity system, which is comprised of a network of natural fractures (cleats) and matrix blocks of coal exhibiting highly heterogeneous porosity. The gas transport through the cleat system is governed by Darcy's Law. This study reviews and critically evaluates available models for describing coalbed permeability that can be applied to calculate gas flow in such systems. In addition, the potential of using geomechanical models to better account for the physical processes that occur during coalbed methane production and CO<sub>2</sub> injection and storage is also investigated. The results of this review can be used for evaluating modeling approaches when employing reservoir simulators to simulate injection and storage in ECBM cases.

### **CoalSeq III Consortium: Advancing the Science of CO<sub>2</sub> Sequestration in Coal Seam and Gas Shale Reservoirs**

George Koperna, Anne Oudinot, Advanced Resources International; Satya Harpalani, Southern Illinois University; Khaled Gasem, Oklahoma State University; Ian Palmer, Higgs-Palmer Technologies, USA

Coal-Seq III, a 3-year consortium sponsored by the US Department of Energy (US DOE) and performed by Advanced Resources International (ARI) in partnership with Southern Illinois University (SIU), Oklahoma State University (OSU), and Higgs-Palmer Technologies has the primary objective to advance scientifically-based simulation capabilities for CO<sub>2</sub> storage in coalbed methane and gas shale reservoirs in the presence of multi-component gases and other fluids. Current simulators lack essential information on the effects of high pressure CO<sub>2</sub> on the integrity and swelling/shrinkage of the coal matrix and its permeability as well as proper algorithms for the adsorptive capability of wet coals.

To accomplish this goal, coal samples from various US basins are being used in the laboratory to study the potential existence of change in mechanical properties of coal (weakening/failure) under high-pressure CO<sub>2</sub>. Laboratory experiments also include the investigation of coal shrinkage (during production) and swelling (during injection) under field replicated conditions. In addition; new improved adsorption models are being developed to realistically simulate sequestration in wet coal and gas shale reservoirs. Based on the laboratory and theoretical results, three new geochemical and geomechanical modules will be developed. Finally, the feasibility of storing CO<sub>2</sub> in shale reservoirs will be studied using actual datasets, leveraging the basic science work developed by this effort.

To do so, the Coal-Seq III Consortium work will calibrate the accuracy of these modules with data from large-scale field studies, such as the CO<sub>2</sub> injection demonstration within the San Juan basin's Fruitland coal, and incorporate these modules into an advanced, coupled simulation model. The end result will be improved tools that are informed by Coal-Seq laboratory efforts tuned to field data. This paper will describe the efforts to date in meeting these research objectives.

Specifically, this project is developing robust mathematical models to accurately predict how coal permeability and injectivity change with CO<sub>2</sub> injection, and that correctly accounts for multi-component (CH<sub>4</sub>-CO<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O) matrix shrinkage/swelling, coal-weakening, competitive adsorption, bi-direction diffusion, and system PVT behavior. To achieve these project goals, the tactical objectives are:

- Perform CO<sub>2</sub> core-flood experiments in the laboratory with coal samples to observe and measure any changes in coal mechanical properties ("weakening") in the presence of high pressure CO<sub>2</sub>.
- Investigate coal shrinkage during production and coal swelling during CO<sub>2</sub> injection through laboratory core flood experiments. These tests would be conducted at in-situ pressures and stresses
- Develop improved algorithms and adsorption models to facilitate realistic simulation of CO<sub>2</sub> sequestration in wet coal seams and shale gas reservoirs.
- Set forth new quantitative formulations accounting for the above three physical and chemical processes. Incorporates these formulations within simulations codes and modules to deliver an advanced and benchmarked model that rigorously accounts for coal permeability changes during CO<sub>2</sub> injection and storage.
- Validate the theoretical and experimental results with large-scale field projects and data sets.
- Explore the feasibility of storing CO<sub>2</sub> in gas shale reservoirs, using advanced shale completion techniques (horizontal wells and multi-stage, massive hydraulic fracture stimulations). A detailed modeling effort will be undertaken to explore the feasibility of this concept, using "real-world" datasets.
- Using these newly generated simulation modules, assess the CO<sub>2</sub> storage potential of the San Juan Basin's Fruitland Coal as well as the Marcellus and Utica shales of the Appalachian Basin.
- Disseminate the project findings to industry, Regional Carbon Sequestration Partnership Working Groups, and the scientific/engineering communities via publications and presentations.
- Foster international collaboration on CO<sub>2</sub> sequestration in coal seams and shale reservoirs via the Coal-Seq website and Coal-Seq forums.

### **The Dynamic Permeability of Propped and Non-Propped Artificial Fracture in Granite and Bituminous Coal with Changes in Effective Stress**

Hemant Kumar, Derek Elsworth, Jonathan P. Mathews, Pennsylvania State University; Denis Pone, ConocoPhillips, USA; Jishan Liu, University of Western Australia, AUSTRALIA

Low permeability coalbed reservoirs are often fractured to aid productivity. Typically a proppant-slurry is injected during the fracturing process to induced fractures and place proppants to retain the enhanced permeability. However, the dynamics of effective stresses in the reservoir may result in proppant embedment. This occurs wither when the coal surface is softer than the proppant or in the case of enhanced coalbed methane

recovery CO<sub>2</sub> induced coal softening or coal swelling may cause coal penetration into the propped fracture. The resulting permeability is expected to be dynamic with effective stress and the pore gas pressure. We investigate permeability transformations through a suite of laboratory experiments conducted on selected granite (non-sorbing hard rock), and bituminous coal cores sawn into two halves with a thin diamond coated blade. The permeability of the artificial "fracture/cleat" was measured for a non-sorbing gas (He) and a sorbing gas (CO<sub>2</sub>) at constant confining stress of 10MPa. Permeability was also determined with a uniform monolayer of #70-140 mesh proppant sand within the fracture. The presence of proppant increases the gas permeability in granite and coal by more than an order of magnitude, depending on the gas injected for the conditions evaluated. When a sorbing gas (CO<sub>2</sub>) was injected, there was a reduction in permeability for the non-propped and propped coal experiments. However the gas permeability of the propped fracture was always higher than that for the non-propped fracture. Surprisingly the relative reduction in permeability, due to sorbing gas exposure, for the propped fracture was higher than that for the non-propped fracture. The helium permeability of non-propped and propped artificial fracture in granite decreases with effective stress. This decrease may be 2-3 times if the effective stress increases from 4 MPa to 6 MPa. The permeability of propped fracture was 10-15 times higher than that of non-propped fracture in granite. Similar observations are made for artificial fracture in bituminous coal. The increase in He permeability may be as high as ~10 folds if monolayer proppant is sandwiched in the coal fracture. Similar increase is observed in the case of sorptive gas (CO<sub>2</sub>) permeability. These observations are consistent with a combination of coal swelling and/or an enhanced coal softening in the presence of this sorbing gas allowing proppant penetration into the coal or coal swelling encroaching into the fracture.

### **Environmental Monitoring for CO<sub>2</sub> Gas Sequestered in Underground Coal Associated with the CONSOL Energy Research Project, Marshall County, West Virginia, USA**

Henry W. Rauch, Brad D. Hega, Katherine Felton, Richard A. Bajura, Thomas H. Wilson, West Virginia University; James E. Locke, Richard A. Winschel, CONSOL Energy, Inc.; Arthur W. Wells, J. Rodney Diehl, DOE/NETL, USA

A pilot test is being conducted in Marshall County, West Virginia, to evaluate enhanced coal bed methane (CBM) recovery and simultaneous CO<sub>2</sub> sequestration of up to 20,000 short tons in the unminable Upper Freeport coal bed in the Northern Appalachian Basin, at a depth of 1,200 (under valley stream) to 1,800 ft (under hill). The field test site, a 1 km<sup>2</sup>, 200 acre test square, is situated in a valley and hill side setting along the Pennsylvania Fork of Fish Creek. Two vertical CO<sub>2</sub> gas injection wells at the test square center connect to two forked horizontal access wells within the Upper Freeport coal. To date ~2,600 short tons of CO<sub>2</sub> have been injected starting in September 2009 and continuing intermittently to the present, under a class II underground injection control (UIC) permit from the West Virginia Department of Environmental Protection (WVDEP). Past CO<sub>2</sub> gas injection pressure has ranged up to 933 psig, and will increase (has been permitted for) up to 1,450 psig. This injection will continue until either 20,000 short tons of CO<sub>2</sub> have been injected or the CO<sub>2</sub> gas content of peripheral or overlying wells exceeds 10 % by volume above pre-injection background amount. Since 2004 CBM has been produced from four vertical wells connected to four horizontal wells located peripherally along the sides of the test square and within the unminable Upper Freeport coal bed and within the unmined Pittsburgh coal bed situated 500 ft above the Upper Freeport coal.

Environmental monitoring for determining one year of baseline (background pre-injection) conditions began in October 2008. West Virginia University (WVU) personnel have been monitoring for any signs of near surface pre-injection contamination, and especially of surface seepage of CO<sub>2</sub> or methane gas after the September 2009 start of CO<sub>2</sub> injection. Sampling and testing of all on-site deep wells is done monthly by CONSOL Energy personnel for gas content. Sampling and testing by WVU personnel is done weekly for three ~100 ft deep monitoring wells for shallow ground water chemistry and head space gas chemistry; weekly for eight ~5 ft deep soil gas wells for vadose zone gas chemistry; and biweekly for Fish Creek for water chemistry (with testing at CONSOL Energy's Research lab) and discharge. Also, selected domestic supply wells and one spring, located within one mile of the test site, were sampled and tested biweekly during 2008 – 2011. In addition, US-DOE-NETL personnel are sampling and periodically testing for perfluorocarbon (PFC) tracer gas compounds, weekly to biweekly within CBM producing wells, and monthly within other selected wells, soil, and atmospheric monitoring sites; the first set of PFC tracers were injected within the CO<sub>2</sub> gas injection wells in April, 2011.

To date there have been two contamination episodes not related to CO<sub>2</sub> gas injection. One was brine contamination of ground water (2008 – 2012) and stream water (2008), probably derived from a temporarily leaky tank containing brine pumped from CBM producing wells at the southern end of the test site square, but no domestic water supplies were impacted. The other contamination episode is a continuing case of excessive methane gas in a ~100 ft deep monitoring well (not a domestic supply well) located at the western end of the test site square; this well exhibits high methane content in both ground water and the deep vadose zone (well head space gas), a very high pH, and high alkalinity (DIC). The indirect source of this methane is probably deep coal bed gas.

There is no evidence to date of any microseepage of injected CO<sub>2</sub> gas based on stream and shallow ground water chemistry. However, there is some direct evidence of the beginning of deep CO<sub>2</sub> gas microseepage associated with tested CBM producing wells at the southern end of the test site square. Chemical tracers PTCH and PMCH were injected into the two CO<sub>2</sub> gas injection wells in April 2011, and were detected in CBM producing wells (well MH12 2 to 5 weeks later for PTCH, and well MH11 7.5 to 9.5 months later for PTCH and PMCH). The slow well MH11 Upper Freeport coal bed leakage was expected, but not the quick well MH12 Pittsburgh coal bed leakage. Antecedent correlation analysis shows that tracer microseepage is strongly and directly correlated with prior CO<sub>2</sub> gas injection rates, with peak correlations for lags of ~2 months for well MH12 and 2-3 and 9-11 months for well MH11. An additional circumstantial indirect clue for deep gas microseepage is the unusually high soil CO<sub>2</sub> gas concentration, adjusted for seasonal effects, observed in soil gas monitoring wells located near the center of the test site square, relative to those wells outside the test square site. Also, the ground water monitoring well on the western test square side is showing an increasing CO<sub>2</sub> gas content, adjusted for seasonal effects, within the lower vadose zone over three years of time. None of this evidence suggests that the injection shutdown threshold level of 10 % CO<sub>2</sub> gas by volume, exceeding pre-injection background levels, is yet being approached. Chemical tracers travel more quickly through the ground than does CO<sub>2</sub> gas due to the higher retardation (adsorption-desorption) rate for the CO<sub>2</sub> gas.

**SESSION 48**  
**Coal Science: General – 5**

**Development of Dry a Beneficiation Scheme for Soma-Imbat Lignite by Allair Jig and Akaflow**

F. Boylu, T. Çetinel, K. Çinku, Ö. Kurulu, N. Yalçın, M.S. Çelik, Istanbul Technical University, TURKEY

Soma-Imbat lignite is a typical lignitic coal produced by Turkish Coal Enterprises. It is characterized by relatively moderate ash levels (37-40 %), low sulfur (0.54 %) and medium calorific values of 3062 Kcal/kg. Wet cleaning of this coal produces reasonably good quality clean coal with 15.5 % ash and combustible recoveries of 80.5 %. Problems with wet separation techniques such as the need for water shortage in arid areas and high cost of dewatering of coal fines make it necessary to introduce dry cleaning techniques. For this purpose, a pilot scale Allair Jig was used to determine the dry cleaning characteristics of Soma-Imbat lignite in size of -13 mm. Prior to application of dry beneficiation, some basic test were performed to determine the feed size or size fractions on separations to achieve maximum separation efficiencies. Beneficiation studies were conducted on size fractions of -13+4 mm and -4+1 mm using Allair Jig and on -1 mm using Akaflow aerodynamic separator. Different conditions of feed/discharge stargate, ventilator and flutter valve rates and vibration frequency (for Akaflow) were tested for optimization. The results reveal that dry separation for this particular coal is possible with relatively good coal recoveries. The results obtained with Allair Jig are discussed with the help of data on separation efficiencies.

**Transported Fine Wet Coal, in Contact with Steel, Causes Corrosion**

Frans Waanders, North-West University, SOUTH AFRICA

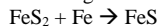
South Africa is one of the largest exporters of sub-bituminous coal in the world with the bulk of the coal mined in the Mpumalanga region of South Africa and the coal is then transported over distances of more than 500 km to the coastal ports in railroad cars. During the journey the water-containing fine coal typically separates out to the top of the load in the railroad cart and significant corrosion can occur at the interface between the steel and the coal. The same action and processes occur during the shipping of the coal to the different overseas destinations. Furthermore coal compaction occurs, resulting from the vibration during transport and leads to sticking and various problems during unloading.

In the present investigation some aspects of the corrosion and compaction processes associated with the transport of the two fine wet coal samples with different sulphur contents are discussed. The influence of compaction pressure, corrosion rates and corrosion products are determined.

Steel coupons were metallographically polished and weighed and then embedded in the coal, which had a typical size fraction of between 250-600µm. Distilled water was added to the coal and the coupon and coal was placed in a hardened steel die and a pressure of 40MPa was applied to the die for a predetermined time. The corroded surfaces of the steel coupons used, were studied by means of Mössbauer Spectroscopy. Inspection of the steel coupons after they have been subjected to the high pressure load and being in contact with the coal, showed pitting to be the dominant corrosion mechanism. The water content of the coal, at a compaction pressure of 40MPa, was found to vary in the samples, depending on the sulphur content of the coal with the sulphur content of the coal an important factor in determining the corrosivity of the coal. The weight loss of the steel coupon that was in contact with the coal containing a

higher amount of sulphur was a factor 7 higher than was found for the sample containing less sulphur. Of further interest was the fact that the high sulphur coal contained considerably less water than the low sulphur containing coal, but still was the more corrosive.

From the Mössbauer spectrum it was apparent that FeS was present and formed as a result of the reaction of pyrite (FeS<sub>2</sub>) in the coal with the steel surface, possibly according to the reaction:



In addition to the FeS that formed, iron oxyhydroxides were also formed and the mechanisms of formation of these species will be elaborated on.

**Effect of Charring Temperature on the Physical Structure Properties of Large Particles of Typical Vitrinite-Rich South African Coals**

Rufaro Kaitano, Hein WJP Neomagus, Joachim HC du Plooy, Raymond C Everson, North-West University, SOUTH AFRICA

In coal to liquid (CTL) conversions the coals used are generally high inertinite rich coals, however high vitrinite rich coals are sometimes encountered, hence the behaviour of both coals need to be investigated as both may become part of feedstock in CTL processes. The physical behaviour of the two different coals especially when exposed to high temperatures is quite different. Unlike the inertinite rich coals, the high vitrinite coals tend to swell on exposure to high temperatures during conversion processes this leads to operational challenges. The experiments carried out help understand pore development during charring of large coal particles at the specified temperatures. A vitrinite rich coal (60%) bituminous medium rank C coal from the Highveld, Witbank area of South Africa geologically part of the Karoo Basin was characterised by three techniques, namely mercury submersion, helium pycnometry and mercury intrusion. The effect of particle size on the pore structure and how charring (isothermally) affected the structures of the coal, all as a function of temperature of the coals charred at 110°C, 300°C, 600°C and 900°C was investigated. Total volatile content of the vitrinite coal was in the region of 33%. For the lower charring temperatures, where the reaction was mainly a physical drying process, the coals exhibited a shrinking behaviour and at higher temperatures devolatilisation led to swelling of the vitrinite coal samples. This is also confirmed from the pictures taken before and after charring, the vitrinite rich coal showed shrinking tendencies for temperatures below 600°C. The coal expanded during devolatilization at temperatures above 600°C.

A comparison and relevance of different techniques used to determine the structural properties of coals and chars were investigated, using a single coal sample of three particle sizes of 10mm, 20mm and 30 mm. Mercury submersion yielded the density of the particle,  $\rho_p = \frac{m_p}{V_p}$ , helium pycnometry yielded the skeletal density  $\rho_s = \frac{m_s}{V_s}$  and mercury intrusion yielded porosity of the particle as well. A comparison between the skeletal volume and helium volume gives a good indication of the particle porosity, however  $\rho_s > \rho_{\text{particle}}$ . This difference was found to decrease with increase in particle size. This gives an indication of variation in porosity across the particle sizes range analysed. The coal results revealed that all the particle sizes had over 75% pores within the meso-pore range which also confirmed the bituminous grouping of the coal. The micro-pore range was less than 10% in all analysed cases and macro-pores ranged between 11.6 and 22.2. The mercury intrusion porosity measurement yielded results which did not show a consistent trend but the density method showed a decrease in porosity with increase in particle size. Typical density figures showed a decrease from 110°C (1270kg/m<sup>3</sup>) to 900°C (779kg/m<sup>3</sup>) and skeletal density decreases as well from 110°C (1469kg/m<sup>3</sup>) to 900°C (1118kg/m<sup>3</sup>). These trends are the opposite of inertinite rich coals where density always increases with increase in charring temperature. However, for vitrinite coals this shows the swelling tendency of the coal with increase in temperature.

**Self-Heat Recuperative Fluidized Bed Drying of Low Rank Coal**

Yuping Liu, Yasuki Kansha, Atsushi Tsutsumi, The University of Tokyo; Muhammad Aziz, Tokyo Institute of Technology, JAPAN

An advanced drying system for low rank coal drying with a very low energy consumption was designed based on self-heat recuperation technology. In self-heat recuperation technology, all the energy involved in drying is always re-circulated/re-utilized. The proposed advanced system could reduce the total energy consumption significantly up to 70% of which was required in conventional heat recovery drying system. The drying medium (non-condensable gas) is separated from the evaporated steam and only compressed pure steam flows inside the heat exchanger tube. Thus, the proposed advanced-drying system has a significant better performance during heat exchange inside the dryer due to better heat exchange following condensation of pure steam rather than air-steam mixture. Superheated steam was also used for the low rank coal drying. Further energy saving which is 1/7-1/12 of that required in a conventional heat-recovery dryer can be achieved.

## SESSION 49

### Clean Coal Demonstration and Commercial Projects: Technical - 6 (Combustion & Post-Combustion CO<sub>2</sub> Capture)

#### CCUS Demonstration Project at WA Parish Station - Results of FEED Study

David J. Stopek, Roger Smith, Sean McHone, Sargent & Lundy LLC; Anthony Armpriester, PetraNova, LLC, USA

NRG Energy, Inc. (NRG) has been selected by U.S. Department of Energy (DOE) to install a Post Combustion slipstream Carbon Capture, Utilization, and Storage (CCUS) demonstration project. The carbon dioxide (CO<sub>2</sub>) captured from the facility's flue gas will be transported to a nearby oilfield, where it will be used for enhanced oil recovery (EOR).

The facility will use an amine-based chemical absorption technology to capture the CO<sub>2</sub>. The process requires heat in the form of steam to regenerate the solvent. In lieu of using steam from the existing power plant cycle, the facility will be designed to use a new cogeneration plant, consisting of a combustion turbine generator (CTG) with a heat recovery steam generator (HRSG) to provide the thermal energy to the capture facility. This design provides opportunities for advanced integration concepts between the cogeneration plant, the capture facility, and the existing plant systems. This approach has the potential to improve the economics while minimizing the impacts of retrofitting Carbon Capture System (CCS) technologies on existing power plants.

The front-end engineering design (FEED) study has been completed with a draft report submitted to the DOE summarizing the projected costs of the CCS. The air permit has been prepared and submitted to the state of Texas. DOE is currently preparing the Draft Environmental Impact Statement (EIS), which is required by the National Environmental Policy Act (NEPA).

This presentation reviews the general design concept of the facility with a focus on balance-of-plant (BOP) integration, and provides an update on the project status. Summary schedule results of the FEED are also presented with this update.

#### FutureGen 2.0 – Project Status Update

Jeff Hoffmann, Nelson Rekos, DOE/NETL; Ken Humphreys, FutureGen Alliance, USA

FutureGen 2.0 is a first-of-its-kind, near-zero emissions coal-fueled power plant. In cooperation with the U.S. Department of Energy (DOE), the FutureGen 2.0 project partners will upgrade a power plant in Meredosia, Ill. with oxy-combustion technology to capture approximately 1.1 million tonnes of carbon dioxide (CO<sub>2</sub>) each year—more than 90 percent of the plant's carbon emissions. Other emissions typically associated with coal-fired power plants will be reduced to near-zero levels. Using safe and proven pipeline technology, the CO<sub>2</sub> will be transported and stored underground at a nearby storage site, which will also include a CCS visitors center and research and training facilities.

Under the FutureGen Project, the Unit 4 steam turbine of the Meredosia Energy Center will be repowered using state-of-the-art oxy-combustion technology coupled with CO<sub>2</sub> purification and compression. Oxy-combustion burns coal with a mixture of oxygen and CO<sub>2</sub> instead of air to produce a concentrated CO<sub>2</sub> stream that is further processed in the CO<sub>2</sub> purification unit. The resulting clean and compressed CO<sub>2</sub> is then transported approximately thirty miles through a pipeline built specifically to safely transport the CO<sub>2</sub> from the Meredosia power plant to the sequestration site for safe, permanent storage.

Activities accomplished to date include the completion of preliminary designs and cost estimates for the repowering of the power plant with oxy-combustion technology, the CO<sub>2</sub> pipeline, and the CO<sub>2</sub> injection and storage infrastructure including visitor and research facilities. Also completed was a deep well into and below the Mt. Simon sandstone, the target formation for permanent storage. Core samples and characterization tests were conducted to assess the formation and overlying caprock seals to verify the suitability of the storage site geology for the FutureGen project.

This paper will discuss the progress to date and will include information related to the engineering of the power plant as well as findings from the characterization of the geology at the permanent storage site.

#### Flameless Pressurized Oxy-Combustion Technology Development Projects Review

Massimo Malavasi, ITEA Spa, ITALY

Flameless pressurized Oxy-combustion of ITEA has been jointly developed with ENEL for coal fired ZEP at Itea's 5 MWth pilot unit. The result of the three year experimental work, ended 2010, it triggered the detailed engineering of a 50 MWth pilot, and also in parallel the preliminary FEED of a 350 MWe coal fired demo unit, given the clear cut positive result of 5 MWth runs. The preliminary FEED of the 350 MWe project is near to the conclusion, and the key assessment of the study are reported. Firstly, the basic assumption for the engineering are reviewed, both vs established technology industrial performances, and vs the potential of the novel technology. Secondly, the fit of commercially available items (e.g. machinery,

packages, etc) with the potential features of the technology are case by case analysed. Finally, emerging opportunities for further technology development are reviewed, to readdress perhaps the scope of the 50 MWth pilot towards these opportunities.

## SESSION 50

### Coal-Derived Products: General – 7

#### Comparison of Corrosion of Cu-Pd and Cu-Pd-M (M=Y or Mg) Hydrogen Separation Membrane Alloys in Simulated Syngas Containing H<sub>2</sub>S

Ben Nielsen, URS/DOE/NETL; Omer Dogan, DOE/NETL; Eileen Nall, ORISE/DOE/NETL, USA

Utilizing gas separation membranes is an economic way to extract hydrogen from coal-derived syngas. Although a variety of hydrogen separation membrane materials exist today, none of them can be suitably employed in contaminant-laden syngas at elevated temperatures due to surface degradation. Cu-Pd alloys have demonstrated some promise for being resistant against surface poisoning and corrosion. In these alloys with ordered bcc (B2) phase, the superior hydrogen permeability increases up to temperatures at which the alloy transforms primarily into fcc structure where a sharp drop in flux occurs. Additionally, previous results have shown that Mg, Al, or Y additions to the Cu-Pd alloy extend the stability of the B2 phase field, potentially improving the hydrogen permeability at higher temperatures. In the present experiments, the resistance to sulfidation was examined by exposing coupons including Cu-Pd binary alloys and several Y and Mg ternary alloys to simulated syngas containing varying amounts of H<sub>2</sub>S at 500°C. The mass change of the samples was determined and the exposed surfaces were characterized by SEM/EDS and XRD. The best corrosion resistance was observed in the Cu<sub>66</sub>Pd<sub>34</sub> alloy, and a slight decrease was observed when Mg was added to improve the stability of the B2 phase at higher temperatures. The Y addition resulted in a pronounced degradation in the corrosion resistance.

#### Bimetallic Gold-Platinum Nanocatalysts in Water-Gas Shift

Yungchieh Lai, Götz Vesper, University of Pittsburgh, USA

The water gas shift (WGS) reaction plays an important role for hydrogen production from fossil and renewable resources. As an exothermic reaction, it is limited by thermodynamic equilibrium at high temperature and by slow kinetics at low temperatures. In order to achieve a high-equilibrium conversion and overcome slow kinetics, multifunctional catalysts for WGS have been widely studied. Au-based catalysts in particular have recently emerged as promising for low-temperature WGS, but the limited stability of Au is a major concern for technical application of these catalysts.

We have recently demonstrated that alloying of metal particles can result in highly active nanocatalysts with exceptional high-temperature stability. In those studies, metals with essentially complete miscibility across the entire range of compositions were utilized. In the present study, we evaluated the extension of this principle onto catalysts with a wide miscibility gap by alloying Au nanoparticles with Pt. Both metals are known to show good WGS activity, but Pt has a much higher melting point and hence better thermal stability than Au.

AuPt bimetallic nanoparticles (NPs) were prepared by reducing polyvinylpyrrolidone (PVP) protected Au and Pt precursors with sodium borohydride in aqueous solution. Despite the wide miscibility gap between the two (bulk) metals, we were able to form well-controlled, homogeneous bimetallic NPs over a broad range of Pt: Au ratios (1:1, 1:3, 1:9). The as-synthesized NPs were then deposited onto ceria and silica as supports to give catalysts with ~1wt% metal. The materials were characterized using a range of techniques, including XRD, TEM, HRTEM, and UV-Vis, and then evaluated with regard to thermal stability during calcination in air. We found that the bimetallic NPs segregated into two separate groups of NPs during heat treatment on both supports. However, while AuPt/SiO<sub>2</sub> phase-separates into the thermodynamically stable Au-rich and Pt-rich phases already at T>500°C, the bimetallic NPs deposited onto ceria completely phase-separated into pure-metal NPs during deposition, and only fused to form the thermodynamically stable phases at T ~900°C. Clearly, metal-support interactions strongly dominate the behavior of this bimetallic system. Fixed-bed reactor experiments further demonstrate that the WGS activity of these catalysts correlates closely with the phase stability of the bimetallic nanoparticles. The WGS activity of the catalyst generally increased with increasing Pt content and the stability reflects the trends observed in the thermal stability studies.

Overall, our results demonstrate that, while our previously suggested principle of catalyst stabilization via alloying with a higher melting-point component may hold even for systems with a miscibility gap, metal-support interactions are critical in the consideration of materials stability and can even dictate catalytic stability.

## MTO Catalyst Development and Application

Weiping Zhu, National Institute Clean-And-Low-Carbon Energy, USA

The first set of coal to olefin device (1.8 mil ton / a methanol and 0.6 mil ton/a methanol to olefin (MTO) device) in the world ran successfully in Shen Hua Baotou Company in 2010. As for Shen Hua Baotou coal to olefin project put into operation successfully and have shown great economic and technological advantages, the domestic has already emerged in the upsurge of MTO. The plan and construction of coal based methanol to olefin project exceed over 30, olefin capacity will exceed 20 mil ton/a at home.

On the core of MTO technology -- catalyst demand will increase. The performance of catalyst has a great influence on coal to olefin operation and economic benefits. As the only coal to olefin industrialized device operators in the home and abroad, Shen Hua Group must master MTO catalyst and its preparation technology. Therefore, Shen Hua Group began to develop MTO catalysts in 2007. In order to ensure the work orderly, safely, Shen Hua firstly started to develop SAPO-34 molecular sieve in Lab and the project was completed in 2009. Then MTO project team synthesized successfully SAPO-34 molecular sieve by using 5L, 100L and 1000L stirring crystallization kettle. MTO project team prepared MTO catalyst by using 1800t / a size of spray forming device in 2011 and the catalyst performance of the trial production meet the index requirements. In 2012, MTO catalysts was produced and MTO catalysts industrial application on March 8<sup>th</sup> in Baotou Company. By the end of May 17<sup>th</sup>, MTO device had run 70 days and used catalyst about 120t. From March 8<sup>th</sup> to May 12<sup>th</sup>, C<sub>2</sub>H<sub>4</sub>:54626t, C<sub>3</sub>H<sub>6</sub>: 51710t! So far, MTO team has applied 38 patents, of which 10 received authorizations.

## Influence of Reduction Temperature on the Performance of Ni-SiO<sub>2</sub> Catalysts for Methanation in Slurry Bed Reactor

Long He, Shu Zhang, Weibo Gong, Deping Xu, Yong-Gang Wang, China University of Mining and Technology (Beijing), CHINA

Effects of reduction temperature on the performance of nickel catalyst for CO methanation in a slurry-bed reactor was studied. The catalysts of nickel-based on silica support were reduced for 4 hours at the temperature of 400°C, 500°C and 600°C, respectively. All the catalysts were characterized using the N<sub>2</sub> physisorption analyser, XRD and H<sub>2</sub>-TPR before experiments and were then used for the CO methanation in the integral slurry-bed reactor at the temperature of 300°C. The results indicate that the catalyst reduced at 400°C showed the lowest catalytic activity because the active component NiO was not reduced completely even reduced for 12 hours. The catalyst reduced at temperature of 500°C showed a very high catalytic activity, and the yield of CH<sub>4</sub> could reach ~92%. The catalyst reduced at 600°C had a higher activity than that reduced at 400°C, but slightly worse than the performance of catalyst reduced at 500°C.

## Effect of Syngas Composition on Productivity of Fischer-Tropsch Synthesis Over Iron Catalyst at Low Temperatures

Heon Jung, Dong-Hyun Chun, Korea Institute of Energy Research, KOREA

For compact CTL or BTL applications, syngas adjustment process may be obviated to make the overall process simple. In that case, Fe can be the Fischer-Tropsch catalyst of choice because it can handle syngas with various ratios of H<sub>2</sub>/CO. It also has to convert the syngas with significant amounts of CO<sub>2</sub> if a cheaper process other than an expensive Rectisol process is adopted to remove sulfur compounds. We have carried out the low temperature FT (LTFT) syntheses over Fe catalysts with various syngas compositions to find out suitability of the LTFT synthesis for the compact CTL/BTL process. When CO<sub>2</sub> was present in the synthesis gas, it exerted a negative effect on the rate of hydrocarbon formation. We attributed the negative effect of CO<sub>2</sub> to CO<sub>2</sub> being adsorbed competitively on the reaction sites with CO. However, the presence of CO<sub>2</sub> suppressed the water-gas shift reaction which eventually prevented over-consumption of CO to supply hydrogen when H<sub>2</sub>/CO ratio was lower than 2. The presence of CO<sub>2</sub> did not change the carbon number distributions of the product. The extent of the reaction rate loss due to the presence of CO<sub>2</sub> was about its percentage in the reactant gas.

We also evaluated the syngas with the H<sub>2</sub>/CO ratio of one, which is a typical composition of the gas from a slurry-fed coal gasifier. We found the higher productivity from the syngas with the H<sub>2</sub>/CO ratio of one than the syngas with the H<sub>2</sub>/CO ratio adjusted to two when reacted over Fe catalysts in LTFT synthesis.

## Dimethyl Ether Synthesis From CO/CO<sub>2</sub>/H<sub>2</sub> Mixtures Over CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

Faen Song, Yisheng Tan, Yizhuo Han, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, CHINA

The synthesis of dimethyl ether from CO/CO<sub>2</sub>/H<sub>2</sub> mixtures was carried out in a high pressure fixed bed reactor system over CuO-ZnO-Al<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The effect of temperature, pressure, space time and time on stream on CO conversion and dimethyl ether selectivity was studied using CO/CO<sub>2</sub>/H<sub>2</sub> mixtures which was composed of

(H<sub>2</sub>)/(CO)/(CO<sub>2</sub>)/(CH<sub>4</sub>) = 52/24/23/1 (V/V). The catalyst samples before and after reaction were characterized by the means of X-ray diffraction (XRD) and nitrogen adsorption. The experimental results indicated that sintering of Cu particles of the catalyst was the main cause of the catalyst deactivation with time on stream.

## SESSION 51 Gasification: Modeling – 3

### Enhanced IGCC Regulatory Control and Coordinated Plant-Wide Control Strategies for Improving Power Ramp Rates

Priyadarshi Mahapatra, Stephen E. Zitney, AVESTAR™ Center/DOE/NETL, USA

As part of ongoing R&D activities at the National Energy Technology Laboratory's (NETL) Advanced Virtual Energy Simulation Training & Research (AVESTAR™) Center, this paper highlights strategies for enhancing low-level regulatory control and system-wide coordinated control strategies implemented in a high-fidelity dynamic simulator for an Integrated Gasification Combined Cycle (IGCC) power plant with carbon capture. The underlying IGCC plant dynamic model contains 20 major process areas, each of which is tightly integrated with the rest of the power plant, making individual functionally-independent processes prone to routine disturbances. Single-loop feedback control although adequate to meet the primary control objective for most processes, does not take into account in advance the effect of these disturbances, making the entire power plant undergo large offshoots and/or oscillations before the feedback action has an opportunity to impact control performance. In this paper, controller enhancements ranging from retuning feedback control loops, multiplicative feed-forward control and other control techniques such as split-range control, feedback trim and dynamic compensation, applicable on various subsections of the integrated IGCC plant, have been highlighted and improvements in control responses have been given. Compared to using classical feedback-based control structure, the enhanced IGCC regulatory control architecture reduces plant settling time and peak offshoots, achieves faster disturbance rejection, and promotes higher power ramp-rates. In addition, improvements in IGCC coordinated plant-wide control strategies for "Gasifier-Lead", "GT-Lead" and "Plantwide" operation modes have been proposed and their responses compared. The paper is concluded with a brief discussion on the potential IGCC controller improvements resulting from using advanced process control, including model predictive control (MPC), as a supervisory control layer.

### Novel Subgrid Model for Calculation of a Char Particle Gasification

Petr A. Nikrityuk, Sebastian Schulze, Matthias Kestel, Dmitry Safronov, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

This work is devoted to the numerical investigation of dense carbon-particle clusters (agglomerates) that are moving in hot O<sub>2</sub>/CO<sub>2</sub> environments. Such kind of agglomerates can be found in different applications such as fluidized-bed reactors, where they feature a different heat transfer and fluid flow compared to single particles.

This work is devoted to the development and validation of a sub-model for partial oxidation of a spherical char particle moving in an air/steam atmosphere. A particle with diameters 0.2 mm and 2 mm is considered. The coal particle is represented by moisture- and ash-free nonporous carbon while the coal rank is implemented using *semi-global* reaction rate expressions taken from the literature. The submodel includes six gaseous chemical species (O<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>, N<sub>2</sub>). Three heterogeneous reactions are employed, along with two homogeneous semi-global reactions, namely carbon monoxide oxidation and the water-gas shift reaction. The distinguishing features of the subgrid model in comparison to the mainstream Baum and Street model are taking into account species concentrations on the particle surface and the influence of homogeneous reactions on integral characteristics such as carbon combustion rates and particle temperature. The sub-model was validated by comparing its results with a comprehensive CFD-based model resolving the issues of bulk flow and boundary layer around the particle. In this model the Navier-Stokes equations coupled with the energy and species conservation equations were used to solve the problem by means of the pseudo-steady state approach. At the surface of the particle, the balance of mass, energy and species concentration was applied including the effect of the Stefan flow and heat loss due to radiation at the surface of the particle. Good agreement was achieved between the sub-model and the CFD-based model. Additionally, the CFD-based model was verified against experimental data published in the literature (Makino et al. Combust. Flame **132**, (2003)).

Finally, we discuss the influence of particle diameter, the Reynolds number, the ambient O<sub>2</sub> mass fraction and the ambient temperature on the char particle behaviour. In particular, two cases with different inflow gas compositions are considered: the first case corresponds to the so-called 'dry air' atmosphere with 0.233 mass fraction (Y) of O<sub>2</sub> and 0.001 mass fraction of H<sub>2</sub>O, while the second case refers to the so-called 'gasification' condition with Y<sub>O<sub>2</sub></sub> = 0.11 and Y<sub>H<sub>2</sub>O</sub> = 0.074. For the fixed composition of the inflow gas, the inflow gas temperature T<sub>in</sub> was varied from 1000 K to 3000 K in order to illustrate kinetic- and diffusion-based regimes. All calculations were accomplished at a total pressure of 1 bar. The results of simulations showed that

not taking into consideration homogeneous reactions leads to the overestimation of carbon consumption rates and the underestimation of the particle temperature.

### Steady-State Simulation of a Sour Water Gas Shift Reactor

Parham Mobed, Jeevan Maddala, Raghunathan Rengaswamy, Texas Tech University; Debangsu Bhattacharyya, Richard Turton, West Virginia University, USA

A sour water gas shift (WGS) process can reduce the penalty of CO<sub>2</sub> capture in an integrated gasification combined cycle (IGCC) plant by sending the gasifier effluent directly to the WGS reactors through a scrubber. Typical sour shift catalysts can convert COS and other organic sulfur compounds into H<sub>2</sub>S. The sour shift reactors should be operated efficiently for maintaining the COS and CO content in the shifted syngas. With this motivation, a distributed, steady-state, isothermal model of a sour shift reactor is developed in MATLAB®. A cobalt molybdate catalyst is considered in this study because of its high activity and sulfur tolerance. Kinetic parameters for water gas shift reaction are estimated using experimental data. A data reconciliation problem is solved to ensure closure of mass balance. This procedure results in reconciled values for measured variables along with the kinetic parameters. This model is further used to study the effects of steam/CO ratio and residence time on CO and COS conversion.

### CFD Modeling of Entrained-Flow Coal Gasifiers with Improved Physical and Chemical Sub-Models

Jinliang Ma, URS/DOE/NETL; Stephen E. Zitney, DOE/NETL, USA

Optimization of an advanced coal-fired integrated gasification combined cycle system requires an accurate numerical prediction of gasifier performance. While the turbulent multiphase reacting flow inside entrained-flow gasifiers has been modeled through computational fluid dynamic (CFD), the accuracy of sub-models requires further improvement. Built upon a previously developed CFD model for entrained-flow gasification, the advanced physical and chemical sub-models presented here include a moisture vaporization model with consideration of high mass transfer rate, a coal devolatilization model with more species to represent coal volatiles and heating rate effect on volatile yield, and careful selection of global gas phase reaction kinetics. The enhanced CFD model is applied to simulate two typical oxygen-blown entrained-flow configurations including a single-stage down-fired gasifier and a two-stage up-fired gasifier. The CFD results are reasonable in terms of predicted carbon conversion, syngas exit temperature, and syngas exit composition. The predicted profiles of velocity, temperature, and species mole fractions inside the entrained-flow gasifier models show trends similar to those observed in a diffusion-type flame. The predicted distributions of mole fractions of major species inside both gasifiers can be explained by the heterogeneous combustion and gasification reactions and the homogeneous gas phase reactions. It was also found that the syngas compositions at the CFD model exits are not in chemical equilibrium, indicating the kinetics for both heterogeneous and gas phase homogeneous reactions are important. Overall, the results achieved here indicate that the gasifier models reported in this paper are reliable and accurate enough to be incorporated into process/CFD co-simulations of IGCC power plants for system-wide design and optimization.

### Optimal Control System Design for IGCC Power Plants with CO<sub>2</sub> Capture

Dustin Jones, Debangsu Bhattacharyya, Richard Turton, West Virginia University; Stephen E. Zitney, DOE/NETL, USA

Designing an optimal control system for an integrated gasification combined cycle (IGCC) power plant with CO<sub>2</sub> capture addresses the challenge of efficiently operating and controlling a coal-fed IGCC plant with the desired extent of CO<sub>2</sub> capture in the face of disturbances without violating operational and environmental constraints. The control system design needs to optimize a desired scalar objective function while satisfying all the operational and environmental constraints in the presence of measured and unmeasured disturbances. Various objective functions can be considered for the control system design such as maximization of profit, maximization of the power produced, or minimization of the auxiliary power. The design of such a control system makes the plant suitable to play an active role in the smart grid era as the plant will have the required agility. In addition, other penalty function(s) such as emission penalties for CO<sub>2</sub> or other criteria pollutants can be considered in the framework as well as losses associated with any hydrogen or carbon monoxide losses.

The proposed control system design is performed in two stages. In the first stage, a top-down analysis is performed to generate a list of controlled, manipulated, and disturbance variables considering a scalar operational objective and other process constraints. In the second stage, a bottom-up approach for simultaneous design of the control structure and the controllers is used. In this paper, the first stage of the two-stage approach is applied to the IGCC's acid gas removal (AGR) process which removes both H<sub>2</sub>S and CO<sub>2</sub> from the shifted synthesis gas. While these results are still preliminary, they demonstrate the application of the proposed approach for a commercial-scale plant and show some interesting results related to controlled variable selection. Such an approach can be followed not only to design control systems for

new power plants, but also to retrofit control systems for existing plants with suitable modifications.

### Mass Transfer Effects in Low Temperature Gasification Simulations

Ronald W. Breault, DOE/NETL; Phillip Nicoletti, URS Corporation, USA

Multiphase reacting computational fluid dynamics (CFD) codes have a number of simplifications incorporated into them. One of these simplifications is the use of a simplistic mass transfer correlation for the faster reactions and omission of mass transfer effects completely on the moderate speed and slow speed reactions such as those in a fluidized bed gasifier. Another problem is that the mass transfer correlation used in the codes is not universal and is being applied far from its developed bubbling fluidized bed regime when applied to circulating fluidized bed (CFB) riser reactors. These problems occur in all the major CFD codes.

A mechanistic based mass transfer coefficient algorithm has been developed based upon earlier work by Breault et al. [1, 2, and 3] to eliminate this problem. This fundamental approach uses the local hydrodynamics to predict a local, time varying mass transfer coefficient. The predicted mass transfer coefficients and the corresponding Sherwood numbers agree well with literature data and are typically about an order of magnitude lower than the correlation noted above. The incorporation of the new mass transfer model gives the expected behavior for the gasification reactions evaluated in the paper. At the expected and typical design values for the solids flow rate in a CFB riser gasifier an ANOVA analysis has shown the predictions from the new code to be significantly different from the original code predictions. Additionally, its behaviors with changes in solids flow rate are consistent with the changes in the hydrodynamics. The new algorithm should be used such that the conversions are not over predicted.

## SESSION 52

### Carbon Management: CO<sub>2</sub> Use and Methane Abatement

#### First U.S. Full-Scale Coal Mine Ventilation Air Methane Abatement System Operational on CONSOL Energy's McElroy Mine

Deborah A. Kosmack, Richard A. Winschel, Christian Warfield, CONSOL Energy Inc.; Santosh Lakhan, Jeff Liebert, Verdeo, USA

CONSOL Energy Inc., in partnership with Verdeo, a Sindicatum Sustainable Resources Company, has installed the first commercial-scale coal mine ventilation air methane (VAM) emission abatement system on the McElroy underground coal mine in the northern panhandle of West Virginia. Mine ventilation air, is a major source of anthropogenic methane emissions, an important greenhouse gas that is 21 times more potent than carbon dioxide (CO<sub>2</sub>) on a 100-year timeframe. Globally, VAM emissions from coal mines amount to approximately 300 million tCO<sub>2</sub>e each year. Oxidation of methane to carbon dioxide and water reduces its global warming potential by about 87%. The VAM abatement equipment installed on the McElroy 5 North 11A Bleeder Fan has been in operation since May 2012. The system is capturing and destroying methane released during the mining process that would otherwise escape to the atmosphere through the mine's ventilation system. At the system design flow rate of 160,000 standard cubic feet per minute (scfm) and an average methane concentration of 1.2%, the abatement system will reduce methane emissions by 920 million cubic feet per year or the equivalent of 322,308 metric tonnes of carbon dioxide (tCO<sub>2</sub>e) per year. In comparison as a scale, a 50 megawatt (MWe) coal-fired power plant operating at 80% capacity factor emits an average of 2050 lbs of carbon dioxide per megawatt-hour (MWh) or 326,500 metric tonnes of CO<sub>2</sub> per year. The installation and performance of the equipment will be discussed in this presentation.

#### Electric Power Generation From Waste Methane at a Coal Bed Methane Processing Plant

Deborah A. Kosmack, Richard A. Winschel, CONSOL Energy Inc.; Kevin Ellison, CNX Gas, USA

CONSOL Energy Inc., with partial funding from the Pennsylvania Department of Environmental Protection under a Pennsylvania Energy Development Authority (PEDA) Grant, has installed and is operating a waste methane-fueled ultra-low-emission 200 kW microturbine generator on a coal bed methane processing plant in Fallowfield Township, Washington County, Pennsylvania, to eliminate the associated methane emissions by capturing them and converting them into usable electricity. Coal bed methane and many other sources of natural gas often require purification in a natural gas processing plant in order to clean up the gas to meet pipeline specifications. These processing plants typically have a reject stream that contains some wasted methane; in some cases this emitted wasted methane can be of substantial concentration and quantity. This emitted wasted methane is a lost potential resource. Moreover, natural gas operations are one of several major sources of anthropogenic methane emissions, and methane is the second most important non-water greenhouse

gas, with a global warming potential 21 times or more as great as that of carbon dioxide (CO<sub>2</sub>) on a mass basis. Thus, the emitted wasted methane simultaneously represents a lost potential resource and the emission of a powerful greenhouse gas. Installation of the 200 kW microturbine on the waste gas is projected to produce 1,664 MWh of gross electricity in a year. The generator operating at 95% capacity factor and a heat rate of 10,300 Btu/kWh will consume 18,521,000 cubic feet of methane, which has a net global warming potential equivalent to 7,135 short ton (or 6,486 metric tonne) of carbon dioxide each year. The microturbine system at CONSOL Energy Fallowfield Gas Processing Plant has been operational since March 2012. The operating performance of the system has been monitored since then and a techno-economic evaluation was conducted with the performance data. The results of the environmental and techno-economic evaluations will be presented in this paper.

#### Utilization Technologies for CO<sub>2</sub> Derived from North Dakota Lignite

Jason D. Laumb, Robert M. Cowan, Alexander Azenkeng, Loreal V. Heebink, Laura J. Raymond, Melanie D. Jensen, Peter A. Letvin, University of North Dakota Energy & Environmental Research Center, USA

The Energy & Environmental Research Center at the University of North Dakota performed a study to identify the most promising technologies to utilize carbon dioxide (CO<sub>2</sub>) from North Dakota lignite-fired utilities. For the purpose of the study, the best technology was defined as one that requires the use of externally sourced CO<sub>2</sub>, can be implemented using existing technology, can produce a valuable and marketable product, and shows promise for application in a northern latitude environment having cold winters with short days. Enhanced fossil energy recovery methods are recognized as important but were not the focus of the study.

CO<sub>2</sub> utilization technologies include direct use (e.g., enhanced oil recovery, carbonation, refrigeration), mineralization (e.g., metal carbonates, construction materials), use as a feedstock chemical with (e.g., fuels, plastics) or without chemical reduction, and as a feedstock for photosynthesis-based processes (e.g., greenhouse agriculture, algae production).

The technologies that show the most promise for use of externally sourced CO<sub>2</sub> are those where sunlight is used as the primary energy resource. Of these, greenhouse agriculture was determined to be the existing technology having the highest probability of providing economic benefit to North Dakota power producers while at the same time utilizing externally sourced CO<sub>2</sub>. This conclusion was reached primarily because CO<sub>2</sub>-to-chemical-product processes are unlikely to require the use of externally sourced CO<sub>2</sub>, mineralization technologies are still relatively new, and many issues limit the potential for algae production in the northern Great Plains.

Greenhouses use externally sourced CO<sub>2</sub> and could use waste heat from a power plant. Although the industry is unlikely to consume large amounts of generated CO<sub>2</sub>, it does appear to have favorable economic potential. High yields and high market prices for vegetables are positive economic considerations. A market survey determined that there is sufficient interest from large grocery store chains/food service companies in buying locally sourced vegetables. A detailed economic analysis of the opportunity is warranted to determine if the capital and operating expenses for such an enterprise are acceptable.

#### CO<sub>2</sub> Conversion and O<sub>2</sub> Generation Using ODF-Based SOEC

Bruce S. Kang, Huang Guo, West Virginia University, USA

Oxygen-Deficient Ferrite (ODF) particles are mixed with YSZ powders via Mechano-Chemical Bonding (MCB) process. The Solid Oxide Electrolyzer Cell (SOEC) with ODF/YSZ electrodes and YSZ electrolyte is utilized to decompose carbon dioxide (CO<sub>2</sub>) into solid carbon (C) or carbon monoxide (CO) and generate oxygen (O<sub>2</sub>) in a continuous process. The cells are tested in a NexTech Probostate™ apparatus combined with EIS/potentiostat and gas chromatography (GC). In our preliminary tests, we detected high percentages of CO and O<sub>2</sub>, at the cathode and anode sides flue gases respectively, when CO<sub>2</sub> was fed to the cathode side and a small potential bias applied across the electrode. Depending on the applied potential, the system is capable of decomposing CO<sub>2</sub> into CO, even C. Through the in-situ EIS and exhaust gas analyses, and post-test study such as SEM, XRD, XPS of the ODF, the capability and efficiency of CO<sub>2</sub> decomposition are currently being evaluated.

#### Using the Low-Rank Coal as Photocatalysts for Conversion of CO<sub>2</sub> to Methanol

Yating Zhang, Anning Zhou, Rui Yang, Xi'an University of Science and Technology; Jieshan Qiu, Dalian University of Technology, CHINA

Photo-catalytic reduction is an increasingly important approach for transformation and utilization of carbon dioxide in recent year. In our research, a kind of low-rank coal (Shenfu coal, from Shaanxi province, China) first act as photo-catalyst in CO<sub>2</sub> conversion. Its photo-catalytic properties were evaluated by photo-catalytic reduction of CO<sub>2</sub> in 0.1 mol/L Na<sub>2</sub>SO<sub>3</sub> and 0.1 mol/L 250ml NaOH aqueous solutions. The results showed that methanol yield was 137.65μmol/L on 1 g/L Shenfu coal after 14 hours' irradiation time while methanol yield was only 38.72μmol/L on TiO<sub>2</sub> at the same reaction condition.

#### Preliminary Study on CO<sub>2</sub> Utilization Supply Chain

Xinglei Zhao, Li Weng, Ke Liu, Guotao Li, National Institute of Clean-and-Low-Carbon Energy (NICE), CHINA

CO<sub>2</sub> utilization supply chain mainly including CO<sub>2</sub> dehydration, purification, compression and transport process is first developed between high concentrated CO<sub>2</sub> sources and target CO<sub>2</sub> utilization sites. The simple gas-liquid separation is preferred among several CO<sub>2</sub> purification methods including membrane separation, distillation and so on because of lower operating cost with the current technology. A new high concentrated CO<sub>2</sub> purification process was suggested, as the process with lower CO<sub>2</sub> discharge pressure reduces the operation cost and increase CO<sub>2</sub> recovery ratio. Different cooling mediums such as Propylene (C<sub>3</sub>H<sub>6</sub>) and Ammonia (NH<sub>3</sub>) are discussed and NH<sub>3</sub> is recommended as a result of its higher vaporization heat. In order to further reduce the operating costs, higher inlet CO<sub>2</sub> pressure from CO<sub>2</sub> sources is preferred because CO<sub>2</sub> compression ratio decreases very apparently at the higher inlet CO<sub>2</sub> pressure with small penalty of CO<sub>2</sub> recovery. The results in this study are very useful to push the development and application of large scale CO<sub>2</sub>-EOR projects in the world.

#### SESSION 53

#### Carbon Management: CO<sub>2</sub> Storage – 3

#### U.S. DOE's Carbon Storage R&D Program: DOE Sponsored Field Projects Utilizing Carbon Dioxide for Storage during Enhanced Oil and Coalbed Methane Recovery

John Litynski, DOE/NETL; Derek Vikara, Ram Srivastava, Keylog Inc., USA

The Carbon Storage Program being implemented by the U.S. Department of Energy's Office of Fossil Energy and managed by the National Energy Technology Laboratory (NETL) is helping to develop technologies to capture, separate, and store carbon dioxide (CO<sub>2</sub>) to reduce greenhouse gas emissions without adversely influencing energy use or hindering economic growth. NETL envisions having a portfolio of technologies that are safe, commercial-scale, and cost-effective that will be commercially deployable.

A promising CO<sub>2</sub> management option with enormous near-term deployment potential involves geologic storage of CO<sub>2</sub> into depleted oil reservoirs and unmineable coal seams. These types of geologic formations have been extensively evaluated in the past; therefore, a great deal of geologic and other data are already available. The injection of CO<sub>2</sub> into these formations can lead to enhanced oil recovery (EOR) or enhanced coalbed methane recovery (ECBM), in which revenue from produced hydrocarbons can help offset the cost of the capture and storage project. It may also be possible to use existing wells and other infrastructure to reduce overall project costs. This carbon utilization technology offers significant potential for reducing CO<sub>2</sub> emissions and mitigating global climate change, while minimizing the associated carbon capture and storage costs.

NETL has supported the development of solutions to technical challenges associated with CO<sub>2</sub> injection and storage, and associated EOR/ECBM processes, including optimizing both oil production and CO<sub>2</sub> storage in EOR operations, and understanding injectivity loss in ECBM operations to potential coal swelling. To address these issues, DOE has conducted field-based storage projects through the Regional Carbon Sequestration Partnership (RSCP) Initiative. The RSCPs Validation Phase focused on conducting small-scale (> 500,000 metric tons CO<sub>2</sub>) geologic field injection and storage tests on the most promising geologic storage formations in rock types representative of various depositional environments present in North America and throughout the world. A total of seven tests in oil and gas reservoirs, and five in unmineable coal seams were completed to (1) collect physical data to confirm CO<sub>2</sub> storage potential and injectivity; (2) demonstrate effective monitoring practices; (3) develop guidelines for well completion, operations, and abandonment; and (4) determine strategies to optimize the CO<sub>2</sub> storage potential within these geologic formations. A total of more than 1.4 million metric tons of CO<sub>2</sub> were safely injected during the seven oil and gas storage projects, increasing oil production and concurrently demonstrating the ability of the reservoirs to accept and safely store injected CO<sub>2</sub>. More than 18,000 metric tons of CO<sub>2</sub> were injected and stored in coal seams during the five ECBM tests. Test results showed adequate CO<sub>2</sub> containment and an associated increase in methane production. This paper presents results, lessons-learned, and highlights from these field tests.

The potential capacity for CO<sub>2</sub> storage in North America is significant, and although not all depleted oil and gas reservoirs and unmineable coal seams have been thoroughly investigated, NETL's RSCPs have documented the location of 143 to 155 billion metric tons of storage potential in oil and gas reservoirs and an additional 60 to 117 billion metric tons of CO<sub>2</sub> storage potential in unmineable coal seams distributed over 29 states and 4 Canadian provinces. These formations alone have the potential to store current annual CO<sub>2</sub> stationary emissions from the U.S. for decades, and potentially produce an economic incentive through hydrocarbon production.



This presentation will summarize the results of the twelve enhanced recovery projects completed to by the DOE's RCSPs in depleted oil and coal field. It will also focus on the efforts completed to characterize the potential storage resources available in these formations.

### **NETL CO<sub>2</sub> Injection and Storage Cost Model**

Tim Grant, Dave Morgan, DOE/NETL; Jason Valenstein, Andrea Poe, Marta Milan, Booz Allen Hamilton, Inc.; Richard Lawrence, Advanced Resources International, Inc., USA

The U.S. Department of Energy's National Energy Technology Laboratory (NETL) has developed a model to estimate the costs of storing captured CO<sub>2</sub>. This model includes the range of costs from initial regional geologic evaluation through site characterization, permitting, injection/MVA operations, post-injection site care to final site closure and transfer to long-term stewardship. Differences in storage costs across different geologic formations are driven by two basic factors: (1) injectivity which determines the number of injection wells drilled to accommodate a given rate of CO<sub>2</sub> injection, and (2) the volume of CO<sub>2</sub> to be sequestered which determines, per in-situ reservoir parameters, the areal extent of the plume and hence the Area of Review (AoR) of a Class VI well permit. The AoR defines the areal extent of MVA activities which dominates costs during injection and post-injection operations. The basic framework for this model provides costs for compliance with various sections of EPA's Class VI regulation and Subpart RR of the GHG Reporting Program. Cost analysis at two levels is provided by this model: (1) site specific where the modeler can enter their own reservoir data, and (2) regional costs derived from the model's geologic database and presented in the form of cost supply curve output data. Another potential CO<sub>2</sub> storage reservoir incorporated in this model are oil and gas reservoirs utilized in Enhanced Oil Recovery (EOR) operations. EOR reservoirs are important for their utilization of captured CO<sub>2</sub> for additional recovery of original oil in place (OOIP). A test matrix was developed to evaluate this cost model across several simple scenario variations to test for cost sensitivities. For saline reservoirs, scenario variations include: change in time span for site characterization, permitting and post-injection site care; change in application of seismic data acquisition and density of monitoring wells, as well as a change in the number of old wells that require remediation (corrective action). Important cost considerations and modeling scenarios for EOR are the cost of compliance with Subpart RR, conversion to Class VI permits, or concurrent saline storage operations. Both saline and EOR operations will be modeled for change in Financial Responsibility and saline operations will be modeled for change in capital structure. Transportation is the link between capture and sequestration. The test matrix will utilize NETL's Capture-Transport-Storage (CTS) model to analyze the use of dedicated and network pipelines in various intra and inter-regional CCS scenarios.

### **Monitoring and Verification for Carbon Capture Utilization and Storage (CCUS)**

Dwight Peters, Schlumberger Carbon Services, USA

Despite the halt in legislation that would place a price on carbon emissions, and the resultant slowdown of related CCS projects, opportunities and activity remain. The ability to utilize carbon dioxide (CO<sub>2</sub>) for enhanced oil recovery (EOR) has enabled CO<sub>2</sub> storage to be a source of revenue rather than just a cost. The term CCUS has been coined recently to indicate that CO<sub>2</sub> can have value and need not be thought of only as a cost.

CO<sub>2</sub>-EOR technology has been around for more than four decades and to date there have been few recorded environmental impacts. During the last decade of saline CO<sub>2</sub> storage demonstrations, CO<sub>2</sub> enhanced oil recovery took a back seat and was depicted as a niche application in the greater pursuit of reducing carbon emissions. Saline storage, where the greatest potential sequestration capacity exists, was the focus of most research, as it was believed this capacity would need to be validated and brought on line quickly. Due to the lack of an imminent carbon pricing mechanism, pure saline storage projects have declined while CO<sub>2</sub>-EOR related projects have grown. It is to be noted that while CO<sub>2</sub> storage has not been the primary intent of CO<sub>2</sub>-EOR projects, it is a fact that some CO<sub>2</sub> does get stored during the process.

The challenge for the CO<sub>2</sub>-EOR projects, in the context of a CCS demonstration, comes with the need for measurement, monitoring and verification (MMV). These activities to date have not been a significant requirement and have only been used at the discretion of the oilfield operator. In pursuit of claiming some type of financial credit for storing CO<sub>2</sub> during the EOR process, there is bound to be a regulatory monitoring requirement the operators will then have to satisfy. The level of this requirement has been debated and often has been viewed in negative light as simply a "compliance-cost".

MMV systems can be a value adder for CO<sub>2</sub>-EOR, as opposed to a simple compliance vehicle, and viewed in positive light if they are:

- Properly designed into the EOR system based on the local geology and field characteristics.
- Priced appropriately such that the value they bring in increased oil or less utilized CO<sub>2</sub> is greater than their cost.

- Their focus is on ensuring the proper placement of the CO<sub>2</sub> for maximum oil extraction and the minimization of losses either up wellbores, into thief zones or to other unwanted places where oil recovery will not be enhanced.

While MMV systems can be complex, they can be designed in a way to add value beyond simple compliance. Only in this manner will MMV gain the acceptance necessary for it to be deployed correctly and robustly.

### **Opportunities for Utilizing Anthropogenic CO<sub>2</sub> for Enhanced Oil Recovery (EOR)**

Michael L. Godec, Advanced Resources International, USA

The purpose of this presentation is to address three common myths associated with the potential for carbon dioxide (CO<sub>2</sub>) storage in associations with enhanced oil recovery (EOR). The first is that CO<sub>2</sub>-EOR represents only a small fraction of the potential for storage. The paper demonstrates that CO<sub>2</sub>-EOR offers large CO<sub>2</sub> storage capacity potential, and can accommodate a major portion of the CO<sub>2</sub> captured from industrial facilities for the next 30 years. The second is that CO<sub>2</sub> is not stored during EOR. The presentation will show that in fact CO<sub>2</sub> is stored when deployed in association with CO<sub>2</sub>-EOR, and that the amount stored depends on the priority placed on maximizing/optimizing storage. The third myth is that incentives to promote CO<sub>2</sub>-EOR merely benefit oil companies. The presentation will demonstrate that carbon capture and storage (CCS) benefits from CO<sub>2</sub>-EOR, in that the revenues (or cost reduction) from sale of CO<sub>2</sub> to EOR helps CCS economics. It also shows that CO<sub>2</sub>-EOR benefits from CCS; and that large-scale implementation of CO<sub>2</sub>-EOR is dependent on CO<sub>2</sub> supplies from industrial sources, and the financial rewards for CO<sub>2</sub>-EOR with CCS can be broadly distributed, overcomes significant deployment barriers, while producing oil with a lower CO<sub>2</sub> emissions "footprint."

### **CO<sub>2</sub> Sequestration at AEP's Mountaineer Plant – Storage, Post Injection Monitoring and Verification**

Indrajit Bhattacharya, Daniel M. Duellman, Gary O. Spitznogle, American Electric Power, USA

AEP has been on the forefront of Carbon Capture and Sequestration technology development and demonstration. Most of our efforts on CCS focused on work at the Mountaineer plant located in New Haven, West Virginia. First geologic field activity commenced in 2003, followed by construction and operation of a pilot scale (20MW) capture plant (PVF project) with two injection wells, three deep monitoring wells, and nearly 40,000 tonnes of deep saline CO<sub>2</sub> sequestration. The successful operation of this facility from late 2009 to May 2011 was also the basis for a Front End Engineering Design (FEED) study for a commercial scale (235 MW) carbon capture and sequestration project. The FEED study included the drilling and detailed study of an off-site geologic characterization well and phase-1 of the FEED study concluded in September 2011. Due to lack of legislative policy and no mechanism for cost recovery, AEP decided to postpone work on the 235MW project. At present AEP is in the post-injection monitoring phase for the PVF project in accordance with the UIC permit granted by West Virginia Department of Environmental Protection. This paper presents a summary of the injection activity, will focus on post injection monitoring of the injected CO<sub>2</sub> and finally touch on the final site closure plan.

### **Initial Lessons Learned From the SECARB Anthropogenic Test: The First U.S. Integrated CO<sub>2</sub> Capture, Transportation and Storage Test**

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

The Southeast Regional Carbon Sequestration Partnership (SECARB) Anthropogenic Test is a demonstration of the deployment of CO<sub>2</sub> capture, transport, geologic storage and monitoring technologies. The capture component of the test takes place at the James M. Barry Electric Generating Plant in Bucks, Alabama. The capture facility, equivalent to 25 MW, will utilize post-combustion amine capture technology licensed by Mitsubishi Heavy Industries America. CO<sub>2</sub> captured at the plant will be transported by pipeline for underground storage in a saline geologic formation within the Citronelle Dome. This project will be one of the first and the largest fully-integrated commercial prototype coal-fired carbon capture and storage projects in the USA.

The demonstration is currently in the testing and startup phase. The capture unit reached full operational capacity in June 2011. An 11 mile long, 4-inch diameter pipeline was installed to the location where CO<sub>2</sub> injection will take place. A characterization well, drilled in January 2011 provided geologic data that confirmed that the test site represents an attractive location for safe, long-term storage of CO<sub>2</sub>. Two Class V Experimental Injection Well underground injection control (UIC) permits were issued in November 2011 and the project's injection wells have been installed. A robust MVA plan has been developed to monitor and track the CO<sub>2</sub> plume and the associated pressure field.

Starting in the second quarter of 2012, up to 500 tonnes of CO<sub>2</sub> per day will be captured, transported and injected. The injection target is the lower Cretaceous Paluxy Formation, which occurs at 9,400 feet. Transportation and injection operations will

continue for one to two years. Subsurface monitoring will be deployed through 2017 to track plume movement and monitor for leakage.

This paper will discuss the results and lessons learned to date, including permitting efforts, injection startup operations, monitoring and detailed reservoir modeling of the storage site as well as project team integration efforts.

**SESSION 54**  
**Coal Science: General – 6**

**Chinese Coal-in-Title Journal Articles in Chinese and English**

Jonathan P. Mathews, Chunshan Song, Wenting Yue, The Pennsylvania State University; Robert Finkelman, University of Texas at Dallas, USA

China is now the leading nation for coal-in-the-title journal articles, overtaking the US. There has been a rapid rise in coal research within China as it “fuels” much of the electricity generation expansion but also a coal-to-liquids and coal-to-chemical industry. Research was performed to identify journals covering coal science research in the Chinese language(s) and to identify the leading organizations (academic and companies) publishing coal research between 2000 and June of 2012. Unfortunately, locating Chinese language publications, related to coal science, was challenging due to very limited navigation in English and lack of automation for citation collection common for English language journals. Chinese language publications however tend to also include English titles and often abstracts too. Furthermore some of the journals were also available in English-language translations indicating a greater desire for an international presence in coal science. Leading journals for quantity of relevant publications were the Journal of Fuel Chemistry and Technology, Journal of China Coal Society and its associated Journal of Coal Science and Engineering, with other examples such as: Coal Conversion, Boiler Technology, Journal of Engineering Thermophysics etc. Thus it appears that there are limited coal science publications in the Chinese language with the greater volume being in English publications.

for English language publications articles containing “coal” in the title were identified using the ISI Web of Knowledge selecting only the Web of Science (Science Citation Index Expanded) database to identify the leading publishing organizations in China (2000 to 2012 June). Those with > 100 papers during this period were The Chinese Academy of Sciences, China University of Mining Technology, Huazhong University of Science and Technology, and Tsinghua University. Wordle word cloud plots were produced for these and the other leading institutions to identify regional interests and specialties. There was great interest in coal combustion for many of these institutions, often being the leading subject. In other universities there were obvious specializations in coal gasification, coal liquefaction, oxy-combustion, pollution control etc. Of the journal articles some 29% in total were published in the leading international journals Energy and Fuels (238 papers), Fuel (204), Fuel Processing Technology (121), and the International Journal of Coal Geology (115). This is slightly less than the 33% from US academic sources published in these journals. The remaining 1653 articles from China are incredibly well dispersed among 404 other journals with only eight of those journals having more than 30 articles. The other US articles were similarly well dispersed (469 journals). Clearly Chinese coal science has a significant number of coal publications in the leading coal science journals. The greatest frequency of international collaboration (up to 25% of the papers) was between China and the U.S., Australia, Japan, and the UK.

**Study on the Volatilization of O-Containing Functional Groups During the Mild Pyrolysis Using Shengli Brown Coal**

Yong-Gang Wang, Jian-Lin Zhou, Min Xu, De-Ping Xu, Shu Zhang, China University of Mining and Technology (Beijing), CHINA

The purpose of this paper is to investigate the change of the O-containing functional groups in Shengli (SL) brown coal upon to the pyrolysis at low temperatures and pressures. The amounts of different O-containing functional groups of SL brown coal and its resultant chars were mainly quantified by titration methods. SL brown coal was pyrolyzed under the conditions of 200~350° and 1~5 MPa with holding time of 30~ 60 min. The results show that the oxygen mainly exists as carboxyl and hydroxyl functional groups in the coal, accounting for approximate 69 wt% of the total oxygen. At 300 or 350°, the majority of carboxyl and methoxy which were mainly associated to aliphatic and side chains has disappeared, whilst more than 50% of phenolic hydroxyl group still remained in the coal at 350°. The holding time from 30 to 60 min could cause ~10 wt% loss in phenolic hydroxyl group at 350°. However, the effect of pressure within the range on the oxygen removal was ignorable, probably due to the low temperatures used.

**Influence of Interaction between Coal and Caking Additive on Thermoplasticity of Coal Blends**

Noriyuki Okuyama, Takahiro Shishido, Koji Sakai, Maki Hamaguchi, Naoki Kikuchi, KOBE STEEL, Ltd.; Haruo Kumagai, Hokkaido University, JAPAN

A coal extract, produced by thermal extraction and solvent de-ashing in the coal derived methylnaphthalene solvent, has an excellent thermoplasticity even though the parent coal appears no thermoplasticity. We named it “HPC, High Performance Caking additive”, and have been developing to utilize as a thermoplasticity accelerator to make strong coke for blast furnace.

This study concerns with the effect of HPC addition to improve thermoplasticity of coal. The thermoplasticity of coal mixed with HPC was monitored by in-situ high temperature 1H-NMR relaxation measurement. The solid echo pulse sequence was employed to generate 1H-NMR transverse relaxation signals. The echo signals obtained during heat treatment were deconvoluted into a set of one Gaussian and two Exponential decay components which represent the immobile, intermediate and mobile component, respectively. The changes in the intensity of mobile component, I(Hm), corresponded to the softening and resolidification phenomena of coal blend1).

Gieseler plastometry indicated that the fluidity increasing degree of HPC addition to a slightly caking coal was higher than that of a strongly caking coal. It suggested that the interaction of HPC and coals were varied with coal characteristics. The behaviors of mobile component during heat treatment were investigated using coal blends and each component coal mixed with HPC or not. The observed intensity of the mobile component, I(Hm), generated from a coal blend, was compared with the arithmetic composed value of each component. It was confirmed that the observed value was almost agreeable with the composed value when HPC was not added to the coal blend. On the other hand, the observed value mixed with HPC was different from the composed value especially at the lower temperature range. It seemed that the mobile components were not generated independently from HPC and coals by the influence of interactions, and inequalities of the maximum values of I(Hm) between the observed values and the composed values were recognized. The observed maximum I(Hm) was higher than the composed maximum I(Hm) when HPC was added to a slightly caking coal. That tendency was agreeable with the behavior of Gieseler plastometry.

**Recent Trend in Fines Coal Beneficiation – Indian Perspective**

T. N. Das, A. Datta, M. N. Dastur & Company (P) Ltd.; S.Mukherjee, Bengal Engineering and Science University, INDIA

Indian coals, in general are inferior in quality and having difficult washing characteristics. Due to ‘Drift Origin’, the coals contain inherent mineral matter or contaminations. Prior to 1950, there were no beneficiation plants in India for washing the coal as selective mining was in practice at that time. The Research Institute of India had been campaigning for establishment of large coal preparation plants for upgradation of inferior coking coals for using in steel plants. The first Indian coal washery was set up at West Bokaro in 1951, followed by three more washeries which came up by 1955 in eastern region of India. The Beneficiation circuit of the washing plants installed earlier did not include coal fines upgradation. After Nationalization of coal mines in 1972, large number of public sector washeries came up in eastern region. The depletion of good quality reserves and deterioration of quality due to open cast mines called for coal fines (0.5mm fraction) upgradation containing high ash. Hence, the coal fines need to be upgraded to the acceptable quality. Upgradation of coal fines is the real problem of coal preparation in India. The coal fines are normally enriched with vitrinite, a component to increase the coking propensity and hence their presence in total composite clean coal is essential.

In coal beneficiation plant, usually the feed to dense-medium cyclones is deslimed at 0.5 mm and the minus 0.5 mm size fraction is processed with froth-flotation, water only cyclone or spiral. With the introduction of large diameter cyclones, the aperture sizes of desliming screens have progressively increased to about 3 mm in the belief that the larger cyclones are not able to effectively beneficiate coal that has a particle size below the ‘breakaway’ size. The efficiency of separation in the large dense medium cyclones is improved by presenting a coarser feed to the units.

In the above backdrop, this paper reviews the basics of different processing routes for minus 3 mm coal washing in India. The present practices and the latest trend of processing technology that could be adopted to meet the desired quality are also discussed.

**Release Behavior of Boron During Heat Treatments of Coals**

Katsuyasu Sugawara, Yuuki Mochizuki, Takahiro Kato, Akita University; Yukio Enda, Akita Industrial Technology Center, JAPAN

In a series of studies on coal cleaning, the forms and distribution of boron in coal, and the release behavior of boron from coal during pyrolysis and gasification were investigated by using 7 types of coal with different coal ranks. The sequential leaching of the sample coals by using H<sub>2</sub>O, CH<sub>3</sub>COOH, and HCl solutions showed that the content of H<sub>2</sub>O soluble boron has an inverse correlation with coal rank. The analysis of the density separated coals showed that boron is unevenly distributed in the low density fraction of coal. The release behavior of boron was found to vary according to the type of coal during pyrolysis at temperature in the range of 200-1200°C. On the basis of this behavior, boron was classified into 2 group: one group that released boron at temperatures below 900°C and the other group that released boron at temperatures above 900°C. No appreciable volatilization was observed for boron during gasification of pyrolyzed chars.

### Optimizing Coal Flotation Control Based on an On-Stream Analyzer

Xiao-ping Yang, Yan-ru Chen, Xiao-qiang Wang, China University of Mining & Technology, CHINA

The recent research advance about the coal slurry ash content online measurement makes it possible to automatically and effectively control the coal flotation. The basic method and principle to online analyze the coal slurry ash content is firstly introduced, and then the structure of the on-stream ash content analyzer is designed. The multi-stream measurement system based on the on-stream analyzer is presented. The process control of coal flotation has been designed by taking advantage of the multi-stream measurement system, the densimeter, the flowmeter and other sensors to measure the process parameters. The optimum control algorithm combines the feed forward control with the feed-back control. The feed forward system calculates the tonnage of coal in the feed entering the flotation system, and controls the reagent additions to the flotation feed according to the reagent consumption per ton of coal. And the feed-back system amends the reagent additions further with the fuzzy logic control strategy. The mutual control mode can increase the clean coal recovery and keep the minimum reagent consumption ensuring the ash content of the concentrate within the required specification.

### POSTER SESSION 1 COMBUSTION

#### Effective Direct Chemical Looping Coal Combustion with Using of Bi-Metallic Supported $\text{Fe}_2\text{O}_3$ -CuO Oxygen Carriers

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

The paper contains results of research work on a promising combustion technology known as chemical looping combustion (CLC). In CLC process, the concentrated  $\text{CO}_2$  stream can be obtained after water condensation without any energy penalty for carbon dioxide separation. The aim of this work was to prepare supported bimetallic  $\text{Fe}_2\text{O}_3$ -CuO oxygen carriers (oc) and to evaluate the performance of these for the CLC process with hard coal.

One cycle CLC tests were conducted with different  $\text{Fe}_2\text{O}_3$ -CuO oxygen carriers in an atmospheric thermo-gravimetric analyzer (TGA) utilizing hard coal as a fuel. Effects of oxygen carrier chemical composition, particle size, steam addition on the reaction rates were determined. The fractional conversions and reaction rates were calculated utilizing the TGA data. Oxidation reaction was significantly faster than the reduction reaction for all supported  $\text{Fe}_2\text{O}_3$ -CuO oxygen carriers. As shown, bimetallic oxygen carriers presented significantly improved reactivity comparing to standard mono-metallic Fe oxygen carriers. Also, the adding of CuO to  $\text{Fe}_2\text{O}_3$  well stabilized the oc's structure. Moreover, the thermodynamic analysis by HSC Chemistry v.7.0 software showed the only minor interaction with coal ash. That indicates that supported  $\text{Fe}_2\text{O}_3$ -CuO carriers are more resistant to ash compared to recently identified oxygen carriers. Reassuring, the TGA data showed that obtained oxygen carriers might be effectively used for direct coal CLC reaction.

Acknowledgement: Financial support of this work by Polish Ministry of Higher Education and Science (Contract No. 685/N-USA/2010/0.) is acknowledged.

#### Mercury Emission from Co-Combustion of Coal and Sludge in a Drop Tube Furnace

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

Co-combustion of coal and sludge is suggested as an effective method to dispose wastewater sludge and to reduce the use of fossil fuels. However, multiple air pollutants can be emitted from the co-combustion because wastewater sludge contains various toxic substances. We analyzed mercury contents in the sludge samples obtained from five sewage treatment plants and found 0.7 ~ 2.5 ppm Hg in the samples. This range of mercury content is significantly higher than that in coal which is reported to be approximately 0.1 ppm on average. In addition, significant amounts of inorganic substances such as chloride, iron and copper, which may affect mercury species in the flue gas, were found in the sludge samples. Mercury is therefore expected to have different behavior in the flue gas from co-combustion of coal and sludge. The objective of this study is to understand the behavior of mercury in the co-combustion flue gas. Each sludge sample was pre-mixed with coal at different ratios and combusted in a drop tube furnace at a temperature of 950 °C. The flue gas was sampled to determine elemental and oxidized mercury concentrations. The concentrations of other flue gases such  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{NO}_x$  were also recorded in a gas analyzer to monitor the extent of combustion. The drop tube furnace showed more than 80% combustion efficiency based on the percentage of  $\text{CO}_2$  in flue gas. Mercury emission significantly increased with an increase in the ratio of sludge in the sample. Although mercury oxidation increased with an addition of sludge, it increased slightly with an increase in the ratio of sludge in the sample.

### POSTER SESSION 2 GASIFICATION

#### Review of Techniques for Oxygen Separation from Air

Karen J. Uffalussy, Evan J. Granite, Henry W. Pennline, DOE/NETL, USA

Oxygen is extensively used in industry. In electric power generation with coal, oxygen is needed for gasification and combustion systems. Coal gasification is a strategy for utilization of abundant domestic coal in a clean and efficient manner. The higher thermal efficiency of coal gasification systems versus traditional combustion-based power generation results in a reduction in net carbon dioxide emissions. In integrated gasification combined cycle power generation, the gasifiers require large amounts of oxygen, and oxygen separation from air is a critical and costly step. In oxy-firing, coal is burned with near pure oxygen, and the resulting flue gas stream, after condensation of the moisture, is mostly carbon dioxide that can then be stored.

Methods for capture of oxygen can include techniques utilizing sorbents, solvents, chemical reactants, membranes, electrochemical facilitated transport, and commercially available cryogenic techniques. The underlying mechanisms for oxygen separations can include adsorption, absorption, chemical reaction, diffusion, ionic transport under the influence of an external electric field, and phase changes.

A literature survey for oxygen separation from air will be presented, with an emphasis upon solid sorbents. Areas for future research will be suggested, including classes of novel sorbents.

#### A Brief History of Oxygen Separation from Air

Michael Hajduk, Karen J. Uffalussy, Evan J. Granite, DOE/NETL, USA

Oxygen is extensively used in industry. In electric power generation with coal, oxygen is needed for gasification and combustion systems. Coal gasification is a strategy for utilization of abundant domestic coal in a clean and efficient manner. The higher thermal efficiency of coal gasification systems versus traditional combustion-based power generation results in a reduction in net carbon dioxide emissions. In integrated gasification combined cycle power generation, the gasifiers require large amounts of oxygen, and oxygen separation from air is a critical and costly step. In oxy-firing, coal is burned with near pure oxygen, and the resulting flue gas stream, after condensation of the moisture, is mostly carbon dioxide that can then be stored or utilized.

Methods for capture of oxygen have employed sorbents, solvents, chemical reactants, membranes, electrochemical facilitated transport, and cryogenic techniques. The underlying mechanisms for oxygen separations can include adsorption, absorption, chemical reaction, diffusion, ionic transport under the influence of an external electric field, and phase changes.

The history of humanity's efforts at oxygen separation from air is a fascinating story, going back to Joseph Priestley's discovery of oxygen in 1774 using mercury as a chemical reactant; the Brin Process of 1880 utilizing the thermally reversible reaction between barium oxide and oxygen to form barium peroxide; through current commercial and research efforts employing cryogenic, sorbent, membrane and electrochemical separations. It is also noted that oxygen is separated from air by nature. Various mineral oxides have been sequestering oxygen in the earth's crust for several billion years. Animals have been using a chemical scrubbing system for oxygen uptake and transport (blood and circulatory systems) for over five hundred million years. A literature survey for oxygen separation from air will be presented, with an emphasis upon the history of oxygen separations. Areas for future research will be suggested.

#### Numerical Simulation of Coal Gasification in OMB Coal Gasifier

Jianliang Xu, Xueli Chen, Guangsu Yu, Zhenhua Dai, Haifeng Liu, East China University of Science and Technology, CHINA

A comprehensive model was used to simulate the multiphase reaction flow in entrained flow gasifier in this paper. The model of computation was based on gas-phase Eulerian balance equations and the realizable  $k-\varepsilon$  turbulence model was applied to close the Reynolds-averaged Navier-Stokes equation. The particle phase was described by Lagrangian equation of motion. The eddy-dissipation-concept model and unreacted-core shrinking model were used to simulate the homogeneous and heterogeneous reactions. The P1 radiation model was adopted to model the radioactive heat transfer in gasifier. The results show that the simulated carbon conversion, outlet gas concentration and temperature were agreed with the industrial performance data. The two phases flow field, temperature and species concentration distributions in gasifier were illustrated. The influences of gasifier pressure and  $\text{O}_2/\text{Coal}$  ratio on gasification performance were discussed.

#### Iron Mineral Changes of Two Coal Types Occurring During Gasification

F.B. Waanders, North-West University, SOUTH AFRICA

The amounts of the minerals pyrite, jarosite, troilite, pyrrhotite and non-sulphur containing minerals such as ankerite, illite and siderite vary considerably in coals from

diverse origin and the speciation of iron and sulphur in coals has been extensively studied by Mössbauer spectroscopy and is well established. Lignite, which accounts for almost half of proven coal reserves in the world, can be seen as an important primary energy sources and is generally characterised by a high moisture content, low heating values and low carbon content. Bituminous coals on the other hand have been used extensively over many years in the gasification process in South Africa and a large proportion of the liquid fuels produced in South Africa results from the gasification of the coal and subsequent further refining. These coals contain less moisture and have typically a higher heating value, compared to lignite.

The mineral matter associated with the coal undergoes various transformations during the coal gasification process and as an example the temperature of transformation of pyrite depends very much on the reducing or oxidizing conditions in the gasifier.

The principle aim of this investigation was to determine the changes that the Fe-containing minerals and mineral associations undergo during gasification of either a lignite or bituminous coal used for gasification purposes. Due to the complexity of the counter-current coal-gas process used, detailed studies were undertaken for both a gasifier run on lignite and one run on bituminous coal.

Representative samples from various heights in the gasifier operating on lignite and on bituminous coal, were taken after the whole gasifier had cooled sufficiently. Each sample was homogenized, riffled and split into equal quarters and subsequently analysed. The Mössbauer analyses were conducted on the powdered samples that were ground to  $-180\mu\text{m}$  in a ball mill. The powder was placed between Perspex plates and then irradiated with  $\gamma$ -rays from a 50 mCi  $^{57}\text{Co}(\text{Rh})$  radioactive source to obtain a Mössbauer spectrum. The Mössbauer spectra were obtained with the aid of a Halder Mössbauer spectrometer, capable of operating in conventional constant acceleration mode using a Xe-gas filled proportional counter. The samples were analysed at room temperature and data collected in a multi-channel analyser (MCA) to obtain a spectrum of count rate against source velocity. A least-square fitting program was used and by superimposing Lorentzian line shapes, the Mössbauer parameters of each constituent was determined with reference to the centroid of the spectrum of a standard  $\alpha$ -iron foil at room temperature. The amount of each constituent present in a sample was determined from the areas under the relevant peaks. The temperature inside the gasifier was determined according to the standard ISO 7404-5 vitrinite reflectance profile technique and was used to determine at which temperatures within the gasifier mineral changes occurred.

From the Mössbauer spectra it is clear that pyrite was the only abundant Fe-bearing component present in both the lignite and bituminous coal present and deformation started at  $450^\circ\text{C}$  (just over halfway through the gasifier) and it changed gradually to form, in conjunction with the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  present in the coal, a Fe-containing glass and hematite at the bottom, or ash grate of the gasifier. By means of Mössbauer spectroscopy the change in the Fe-bearing mineral pyrite was followed from the top of the gasifier to the ash grate. Mössbauer spectroscopy could thus be, amongst others, a valuable tool in the determination of mineral changes occurring in a gasifier and can help in optimization efforts of the gasifier.

#### **A Laboratory-Scale Entrained-Flow Reactor for Parameter Studies of Coal and Biomass Pyrolysis and Gasification**

Micah S. Jakulewicz, Jason M. Porter, Terence E. Parker, Colorado School of Mines, USA

A laboratory scale entrained flow reactor has been constructed to investigate the pressure and temperature regimes of coal and biomass pyrolysis and gasification. The facility was designed with the specific intent to have a compact footprint and minimize capital and operational costs. The system's size reduction was realized by reducing the feedstock particle size and in turn decreased the reaction residence time required for complete reaction of the fuel. The system is controlled using a Real-Time data acquisition system allowing for system-wide control by a single operator. The entrained flow facility has an operating pressure ceiling of 56 atm with a maximum operating temperature of  $1700^\circ\text{C}$ . Reactions of interest are contained by a 50 mm internal diameter silicon carbide reaction tube that runs 1 meter through four independently controlled heating zones and encased in a thermally stabilized pressure vessel. Aerodynamically pulverized coal or biomass sifted from  $100\mu\text{m}$  to  $25\mu\text{m}$  in 10  $\mu\text{m}$  bins is pneumatically fed using argon. The solid fuel is injected into the reaction zone with super-heated steam and oxygen. Viewports are located at three axial locations along the reactor tube, providing built-in functionality for future development of optical diagnostics. Preliminary test results from operation of the facility at 2.5 and 8.5 atm with Utah subbituminous coal are presented.

#### **A Parametric Study of Sorption Enhanced Steam Hydrogasification of Coal for In Situ Removal of $\text{CO}_2$ with Self-Sustained Hydrogen Supply**

Zhongzhe Liu, Chan S. Park, Joseph M. Norbeck, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, USA

The in situ removal of  $\text{CO}_2$  and the increase of energetic gas yield, including  $\text{H}_2$  and  $\text{CH}_4$ , during the sorption enhanced steam hydrogasification reaction (SE-SHR) were studied by varying parameters of gasification agents. The two key input parameters are hydrogen to carbon molar ratio ( $\text{H}_2/\text{C}$ ) and steam to feedstock mass ratio. Lignite was used in this investigation as the feedstock to the steam hydrogasification reaction

(SHR) with the fixed additional amount of quicklime as the sorbent. The experimental results showed that at each steam to coal mass ratio increasing the  $\text{H}_2/\text{C}$  molar ratio enhanced the outputs of  $\text{H}_2$  and  $\text{CH}_4$  and decreased the productions of  $\text{CO}$  and  $\text{CO}_2$ . This was mainly due to the improvement of hydrogasification. When the  $\text{H}_2/\text{C}$  molar ratio was fixed, with the increase of the steam to coal mass ratio, the yields of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CO}_2$  were raised. It was because of the domination of steam gasification in the SE-SHR. Especially, more  $\text{CO}_2$  could not be captured with higher steam input because the  $\text{CO}_2$  production was over the capacity of the little amount of sorbent. Furthermore, hydrogen yields could be guaranteed enough for recycle use at the  $\text{H}_2/\text{C}$  ratios of 0.5 and 1. Finally, the production of synthetic natural gas (SNG) and synthesis gas (SG) was simulated by Aspen Plus using the SE-SHR based output gas. The quality of SG and SNG was then evaluated.

#### **Small Scale Coal-Biomass to Liquids Production Using Highly Selective Fischer-Tropsch Synthesis**

Santosh Gangwal, Southern Research Institute; Arun Bose, DOE/NETL, USA

This project seeks to advance coal to liquids (CTL) and coal-biomass to liquids (CBTL) processes by demonstrating cost-effective, novel Fischer-Tropsch (FT) catalysts that selectively convert syngas derived from the gasification of coal and coal-biomass mixtures predominantly to drop-in gasoline and diesel, thereby eliminating expensive upgrading operations. The project also seeks to evaluate the impacts of adding moderate amounts of biomass to coal on liquid products, CBTL economics, and compare CBTL carbon footprint with petroleum based fuels production processes. This technology development effort is supported by the U.S. Department of Energy. Other project partners include Southern Company, Nexant, and Chevron Energy Technology Company.

The project will implement a full coal and coal-biomass to liquids bench-scale FT synthesis reactor system to produce liquid transportation fuels. The project will use an existing air-blown transport gasifier (also known as TRIG<sup>TM</sup>) operated by Southern Company at its National Carbon Capture Center as the source of both coal and coal-biomass derived syngas. Southern Research will design and fabricate a bench scale skid mounted FT reactor system to produce liquid FT products. Southern Research will carry out a suite of analyses to characterize all liquids from the CTL and CBTL test runs and compare the property differences/similarities and product quality produced by coal vs. coal-biomass blends. A preliminary technical and economic analysis will be carried out to evaluate the relative economics of CTL and CBTL processes and cost reduction due to selective transportation fuel production, and to determine the potential of moderate biomass addition to coal for reducing the carbon foot print of the CBTL process compared to petroleum-based fuel production processes.

### **POSTER SESSION 3 SUSTAINABILITY AND ENVIRONMENT**

#### **Desulfurization Behavior of Turkish Lignite by Hydrogenation and Hydrothermal Processes**

Arzu Kanca, Deniz Uner, Middle East Technical University, TURKEY

Lignite is the major fossil fuel in Turkey. Lignite reserves have been widely spread across the country. Since it has very high amount of ash and has low calorific value, lignite is defined as a low quality coal. Additionally, high sulfur content in Turkish lignites has been considered as another primary drawback in utilization of this fossil fuel. The elimination of high sulfur content of Turkish coals was examined by hydrogenation and hydrothermal methods. Hydrogenation has been common and effective industrial application for sulfur removal. The main disadvantage of this process is the necessities of severe reaction conditions. The first hydrogenation experiments were completed in semi-batch reactor at temperatures between  $40^\circ\text{C}$  to  $800^\circ\text{C}$ , for 700 mg coal samples in quartz reactor. Total flow rate was adjusted as 50cc/min with different  $\text{H}_2$  concentrations. The gaseous products were passed through the glass fractures installed by adsorbents such as  $\text{ZnO}$  and  $\text{PbO}$  at  $0^\circ\text{C}$  and the transformation from metal oxides to metal sulfides has been observed by XRD at the end of the reaction test. The first results of the elemental analysis before and after hydrogenation process indicated that sulfur contents of lignite samples significantly reduced after hydrogenation. In the second part of the study, Turkish lignite will be desulfurized under steam flow and sulfur composition of coal will be analyzed by a LECO analyzer. As a result, the desulfurization reactivity will be investigated in the presence of  $\text{H}_2$  and steam flows in order to compare hydrogenation and hydrothermal desulfurization processes.

**A Field Study on Simulation of CO<sub>2</sub> Injection-ECBM Production and Prediction of CO<sub>2</sub> Storage Capacity in Un-Mineable Coal Seam**

Qin He, Shahab D. Mohaghegh, Vida Gholami, West Virginia University, USA

Studies have shown that, coal seam, an un-conventional reservoir, is considered as a promising option for CO<sub>2</sub> sequestration because of its large CO<sub>2</sub> sequestration capacity, long time CO<sub>2</sub> trapping and extra enhanced coal-bed methane (ECBM) production benefits. However, unlike conventional reservoirs, gas flow in the coal seam can cause the cleat permeability and porosity change during the injection/production process. In other words, for example, once gas is injected and adsorbed on coal matrix, the matrix will swell, and the cleat permeability and porosity will decrease correspondently. Because of its special features and the nature of gas retention in CBM reservoirs, simulating the production and injection will have more complexity compared to conventional resources.

In this paper, a real project is studied and is used to simulate the primary and secondary coal bed methane production and CO<sub>2</sub> injection. The key geological and reservoir parameters that are germane to driving ECBM and sequestration processes, including cleat permeability, cleat porosity, CH<sub>4</sub> adsorption time, CO<sub>2</sub> adsorption time, CH<sub>4</sub> Langmuir Isotherm, CO<sub>2</sub> Langmuir Isotherm, Palmer and Mansoori parameters, have been analyzed and varied within a reasonable range consistent with typical coal seam performance through sensitivity analysis. The final simulation results of the CBM/ECBM production and CO<sub>2</sub> injection show a perfect match with the actual data. The history matched model is selected thereafter to predict total CO<sub>2</sub> sequestration capacity in this field, which gives a very good approximation of the initial calculation by the company based on experimental results. Some predictive scenarios for CO<sub>2</sub> injection have been performed and the results are shown in the following sections in order to evaluate how much CO<sub>2</sub> can be injected in the next few years or, when the required CO<sub>2</sub> injection amount can be fulfilled. In the end, a suggestive simplified workflow for CO<sub>2</sub> sequestration-ECBM simulation is addressed.

**Modeling Analysis of CO<sub>2</sub> Sequestration in Saline Formation Using Artificial Intelligence Technology**

Vida Gholami, Shahab D. Mohaghegh, West Virginia University, USA

One of the most domineering environmental issues is the increase in atmospheric carbon dioxide (CO<sub>2</sub>) concentration ensuing from anthropogenic sources. Sequestration in geological formations is one of the proposed solutions for removing greenhouse emissions from the atmosphere.

Since aquifers are considered to be most widely available, there is high potential to find a suitable aquifer with large capacity or close to CO<sub>2</sub> source. The structure and the interconnection of the pores provide flow of gases or fluids through the bed and all these factors make aquifers the second largest, naturally occurring potential store for CO<sub>2</sub>.

Numerical reservoir simulators are conventionally used to build models of the CO<sub>2</sub> Sequestration process. The sequestration project deals with a wide range of uncertainties. Any comprehensive study or uncertainty analysis of the representative numerical reservoir models would be tedious and time consuming requiring high computational costs. Therefore, comprehensive analysis of such models is quite impractical.

This work presents a new artificial intelligence base technique known as Surrogate Reservoir Model (SRM) that can mimic the behavior of the commercial reservoir model with high accuracy in fractions of a second. Application of SRM to Mattoon field, located in the eastern three quarters of section 8 of Mattoon Township, Coles County, IL, is presented in this article.

Upon validation of SRM Key Performance Indicators (KPIs) of the simulation model are identified to help reservoir engineers concentrate on the most influential parameters on the model's output when studying the reservoir and performing uncertainty analysis. These indicators can be used so as to build a spatiotemporal model which can deliver dynamic properties such as pressure, water saturation and CO<sub>2</sub> mole fraction at each particular location of the reservoir in a specific time.

Unlike conventional geo-statistical techniques that require hundreds of runs to build a response surface or a proxy model, building an SRM only requires a few simulation runs, which saves a lot of man hour time and computational costs.

**Influence of Temperature and Moisture on Gas Permeability of Matrix Coal**

Jun Zhang, Jianli Yang, Yunmei Li, Hongxian Niu, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences; Feng Gao, Taiyuan University of Technology, CHINA

The sequestration of carbon dioxide (CO<sub>2</sub>) in unminable coal seams represents an option for long-term CO<sub>2</sub> geological storage to mitigate climate change. The injected CO<sub>2</sub> may enhance coalbed methane (CBM) recovery, which may partly offset the costs of the storage process. In short, this process is referred to as CO<sub>2</sub>-ECBM. The CO<sub>2</sub>-

ECBM technology is based on the relative affinity of CO<sub>2</sub> and CH<sub>4</sub> to coals under given pressure and temperature conditions. CO<sub>2</sub>-ECBM is not yet a mature technology, in spite of the growing number of pilot and field tests worldwide show its technical feasibility. There is a lack of knowledge on the mechanism of the CO<sub>2</sub>-ECBM process due to the complexity of the coal seam structure and the mixed fluid transport processes. The coal seams are characterized by a dual porosity structure including cleat and matrix pores. The transport process of gas and water in the cleats can be described as pressure-driven laminar flow and obeys Darcy's law while the flow of gas and water in the matrix may be considered as diffusive or a combination of diffusion and viscous flow. Darcy flow through face and butt cleats in coal seams is relatively fast and the primary role in the CBM/ECBM process, whose mechanism is well established. Transport within the coal matrix, which serves as the storage location of gas by adsorption, however, an important and rate-determining process in CBM/ECBM that is still poorly understood. This study is aimed to investigate the characteristics of the fluid flow in the coal matrix. An attempt will be made to establish the relationship between temperature, moisture, and permeability.

Yangquan anthracite originating from the northern part of the Qingshui basin, which contains gas-rich coals in China, was selected in this study. In order to avoid the visible cleats in test samples, the small and cylindrical sample plugs (6-10 mm diameter; 8-19 mm length) were used in the experiments. The gas breakthrough tests on the coal matrix plugs were conducted in a test system, in which adsorption, porosity and permeability can be measured simultaneously under near zero stress. The sample plugs were fixed in the sample compartment by special glue. The gas permeability and porosity of air dry coal plugs to He under different gas pressure and temperature conditions were investigated.

It is expected that different sample plugs with the different porosities result in different breakthrough behaviors. The variation of permeability coefficients of the plugs from the same coal lump is apparent due to the heterogeneity of the coal. The connectivity of the pores may be an important factor to be considered. The breakthrough curves of coal plugs with respect to He were found to vary with pore gas pressure (0.5-0.8MPa) and temperature (30-60 °C). It was found that the structure of the coal plugs varies during the test. The permeability coefficients increase with the increase of the porosity of coal plug.

**Characterization and CO<sub>2</sub> Sorption Properties of Materials for CCS Applications**

Jiajun He, Erik C. Rupp, Jennifer Wilcox, Stanford University, USA

Carbon capture and sequestration (CCS) has become an important option for mitigating CO<sub>2</sub> emission and global climate change by capturing CO<sub>2</sub> from large point sources and sequestering it underground. However, the feasibility of CCS is mainly limited by the high cost of carbon capture, and to be more specific, the enormous energy requirements during the regeneration of aqueous amine solutions. To overcome this limitation, micro and mesoporous sorbents have become promising candidates. A considerable variety of sorbent materials have been investigated for the application of CO<sub>2</sub> capture, including metal organic frameworks, zeolites, carbon nanotubes and mesoporous silicas, including SBA-15 and MCM-41. However, the CO<sub>2</sub> sorption capacity and kinetics under realistic flue gas conditions remain unclear. In this study, a variety of potential sorbents are investigated by several characterization techniques to gain insights into the relationship between sorbent properties and adsorption performance under flue gas conditions.

Breakthrough experiments are performed in a temperature-controlled packed-bed reactor with small amounts of sorbent (<250 mg). Experiments are performed with a resolution of 0.1 mmol CO<sub>2</sub> per gram of sorbent using an Extrel MAX300-LG quadrupole mass spectrometer downstream of the packed bed. The inlet gas is either a mixed gas (CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O) for testing under ideal conditions or a simulated flue gas created by burning methane in air, with potential contaminants such as SO<sub>2</sub>, HCl and NO<sub>x</sub> doped in at part per million levels post-combustion. The breakthrough experiments provide an understanding of CO<sub>2</sub> uptake, sorbent repeatability and impact of flue gas contaminants on capture. In addition, a Quantachrome Autosorb iQ2 automated gas sorption analyzer is used to determine surface area, pore volume and pore size distribution of the tested CO<sub>2</sub> sorbents.

The sequestration of captured CO<sub>2</sub> is the other key aspect of CCS. Enhanced natural gas production in gas shale formations using captured CO<sub>2</sub> may help offset the costs associated with CCS. The composition of gas shale (primarily clay minerals with small amounts of kerogen) has non-negligible effects on the interaction of a particular shale and injected CO<sub>2</sub>, which may affect the extent of sequestration and enhanced gas recovery. In this study, we investigate the compositions of various shale formations, including the Barnett, Eagle Ford, Haynesville and Fort St. John formations. X-ray photoelectron microscopy is used to analyze the atomic composition of the samples while Fourier transform infrared spectroscopy is utilized for the characterization of functional compounds in the samples. Knowledge of the physical and chemical properties of these materials will provide insight into the surface-CO<sub>2</sub> interactions that take place in these systems.

## **Fracture Model, Ground Displacements and Tracer Observations: Fruitland Coals, San Juan Basin, New Mexico, CO<sub>2</sub> Pilot Test**

Tom Wilson, Matt Weber, Hema Siriwardane, West Virginia University/DOE/NETL;  
Art Wells, DOE/NETL; Bill Akwari, ConocoPhillips; George Koperna, Advanced Resources International; Jim Bennett, Schlumberger, USA

This study incorporates observations from some of the experiments conducted on the Southwest Regional Partnership (SWP) for Carbon Sequestration's San Juan Basin pilot test site. This enhanced coalbed methane recovery/carbon sequestration test was conducted in the thick coals of the Fruitland Formation in the high rate production fairway of the San Juan Basin. The pilot test was funded by the U.S. Department of Energy and managed by the National Energy Technology Laboratory. The SWP in collaboration with ConocoPhillips injected approximately 16,700 metric tons of CO<sub>2</sub> into the Fruitland coals from July 23<sup>rd</sup> of 2008 through August 14<sup>th</sup> of 2009. 3D seismic data from the site revealed that the seismic response of the Fruitland Formation is recognizable as a well defined seismic sequence and that individual coal zones in the formation are generally detectable. 3D seismic data also revealed that structures in the Fruitland Formation and overlying Kirtland Shale are more complex than anticipated. Analysis of well log data revealed that the Fruitland Formation coal zones throughout the area surrounding the site consist of two coal beds, each separated by a shale parting. This observation indicates that the coal reservoirs consist of six separate coal beds rather than three. Perfluorocarbon tracer monitoring revealed early arrival of tracer in a direction roughly orthogonal to that anticipated prior to CO<sub>2</sub> injection. Tiltmeter derived ground surface displacements revealed subsidence across the area rather than uplift. The additional information obtained from the studies conducted at the site during its multiyear duration provide the opportunity to revise our models of the reservoir and sealing strata and to obtain new insights into observed reservoir responses to CO<sub>2</sub> injection. A model discrete fracture network (DFN) is developed for the Fruitland coals that incorporates results from this multiyear study. Fracture sets incorporated in the model are derived from FMI log observations. Attributes derived from the 3D seismic data over the site are analyzed to obtain insights into larger scale reservoir architecture that may control flow in the vicinity of the CO<sub>2</sub> injection well. These attributes are combined with ground displacements observed during CO<sub>2</sub> injection to guide the distribution of fracture intensity through the reservoir. Properties of the DFN including porosity, permeability and fracture storage volume are upscaled into a gridded model of the reservoir. The aerial distribution of reservoir parameters derived in this study will improve our understanding of Fruitland coal reservoirs; help develop more effective strategies to enhance coalbed methane recovery combined with CO<sub>2</sub> storage; and, help guide future flow simulations of Fruitland coal CO<sub>2</sub> floods in this region of the high rate production fairway.

## **Recent Advances in Carbon Dioxide Capture with Sorbents for Power Generation Point Sources**

Henry W. Pennline, DOE/NETL, USA

Carbon sequestration may be a viable technique to reduce the greenhouse gas carbon dioxide (CO<sub>2</sub>) from large point sources, such as coal-fired combustors that are used in electricity production. Simplistically, it is a two-step process where the carbon dioxide is captured from the exiting plant flue gas and then permanently stored in a geologic formation. The capture step is the more costly of the two. Although monoethanolamine wet scrubbing has been proposed and accepted as a baseline CO<sub>2</sub> capture technology, certain solid sorbents can offer a significant advancement in the capture technology area. Various sorbent systems have been investigated, but rigorous process development has not occurred with some sorbents because of inherent deficiencies. An effort was devoted to zeolites, specifically 13X and others, but because of their strong attraction for moisture, a component in most gas streams of interest that contain CO<sub>2</sub>, the research concluded. Alkali/alkaline earth compounds were also investigated, but poor energetics, such as high heats of reaction and large temperature differences between absorption and regeneration conditions, ended further investigation. Activated carbons, although relatively cheap, typically suffer from poor selectivity to CO<sub>2</sub>, since other components in the gas to be decarbonated will also be readily adsorbed. More recent work with metal organic frameworks, or MOFs, has been reported. For post-combustion applications, these sorbents have very low CO<sub>2</sub> capacities at ambient pressures and can be sensitive to moisture. Pre-combustion application for MOFs could be more relevant. Although there can be some candidates from these families of sorbents that could be serious contenders as post-combustion sorbents, the recent sorbent development work at NETL-ORD has concentrated on amine-enriched sorbents. The advantages of these types of sorbents will be outlined. Realizing the link between sorbent development and the process development, one can determine the information that is pertinent to the process. The relationship between the sorbent properties and sorbent reactor design will be described for an amine-enriched sorbent. Energetics will be detailed along with recommendations/suggestions for future investigations in the sorbent capture area.

## **U.S. Geological Survey Geologic Sequestration Assessment – 2012 Project Update**

Margo D. Corum, Peter D. Warwick, U.S. Geological Survey, USA

The U.S. Geological Survey (USGS) has a successful history of conducting scientific investigations and impartial, robust, quantitative, probabilistic geologic-based assessments. The Energy Independence and Security Act of 2007 authorized the USGS to conduct a national assessment of potential geological storage resources for carbon dioxide (CO<sub>2</sub>) in consultation with the U.S. Department of Energy (DOE), the U.S. Environmental Protection Agency (EPA) and State geological surveys.

The primary objective of the project is to assess the CO<sub>2</sub> sequestration capacity of both buoyant and residual traps in saline formations within the major sedimentary basins of the United States. In 2008, the USGS developed a probability-based assessment methodology that was extensively reviewed by experts from industry, government and university organizations (Brennan et al., 2010). The probabilistic methodology is currently being used to assess CO<sub>2</sub> geologic storage resources at the basin scale. Individual storage assessment units (SAUs) for each basin are defined on the basis of geologic and hydrologic characteristics outlined by Brennan et al. (2010). As of April 2012, preliminary geologic models have been developed to estimate CO<sub>2</sub> storage capacity in 36 basins within the United States and a total of 203 SAUs have been identified. The results of the assessment are not of total in-place resources, the results are estimates of the technically accessible storage resources based on present-day geological and engineering technology related to CO<sub>2</sub> injection into geologic formations. During 2012, probabilistic ranges of the technically accessible CO<sub>2</sub> storage resource of the SAUs will be generated.

In support of these assessment activities, CO<sub>2</sub> sequestration related research is being conducted by members of the project. Results of our research will contribute to current and future assessments conducted by the USGS and elsewhere. Research topics include: (a) geochemistry of CO<sub>2</sub> interactions with subsurface environments; (b) subsurface petrophysical rock properties; (c) enhanced oil recovery and the potential for CO<sub>2</sub> storage; (d) storage of CO<sub>2</sub> in unconventional reservoirs (coal, shale, and basalt); (e) statistical aggregation of assessment results; and (f) potential risks of induced seismicity. Ultimately, the complete national assessment, summary geologic descriptions of the evaluated basins and SAUs, and complementary research results will be released as USGS publications that will be available on-line at <http://energy.usgs.gov> and via the DOE National Carbon Sequestration Database and Geographic Information System (NatCarb) mapping portal <http://www.natcarb.org/>.

Reference:

Brennan, S.T., et al., 2010, U.S. Geological Survey Open-File Report 2010-1127, <http://pubs.usgs.gov/of/2010/1127>.

## **Results of USGS Workshop on CO<sub>2</sub> Sequestration in Unconventional Reservoirs**

Kevin B. Jones, Margo D. Corum, U.S. Geological Survey, USA

The U.S. Geological Survey (USGS) held a workshop titled "CO<sub>2</sub> Sequestration in Unconventional Reservoirs" in March 2012 with 36 participants from academia, industry, and government. This workshop was part of the USGS National Geologic Carbon Sequestration Assessment Project, which is currently estimating potential subsurface storage volumes in the existing pore spaces of sandstones, limestones, and dolostones [1]—alternate lithologies, such as coal, organic-rich shale, basalt, and ultramafic rocks, are not included. These alternate lithologies can store CO<sub>2</sub> by mechanisms (sorption or mineralogic reaction) different than the buoyant and residual trapping mechanisms currently being assessed by the project [1]. The goals of the workshop were: 1) to determine the current state of laboratory, modeling, and pilot projects in unconventional reservoirs; 2) to discuss the feasibility of CO<sub>2</sub> storage in unconventional reservoirs; and 3) to build a set of recommendations that could be used to underpin a USGS methodology to assess CO<sub>2</sub> storage potential in unconventional reservoirs, if such storage proves feasible. The attendees delivered 20 oral presentations, participated in group discussions, and formed two working groups to address issues specific to CO<sub>2</sub> sequestration in 1) coal and organic-rich shale and 2) basalt and ultramafic rocks. Here we address the findings of the coal and organic-rich shale group.

The coal and organic-rich shale working group addressed the feasibility of long-term CO<sub>2</sub> storage primarily by sorption, and reviewed several current pilot projects involving CO<sub>2</sub> injection into coal and organic-rich shale. The group produced several recommendations regarding a potential CO<sub>2</sub> storage assessment methodology, including: 1) Coal and organic-rich shale should be assessed separately from each other, although their mechanisms for CO<sub>2</sub> storage are similar. 2) Storage potential should be assessed in all coal rather than only in "unmineable" coal, because coal mineability depends on changeable economics and technology rather than on geologic characteristics. 3) Sealing formations should be present above any potential storage formations to reduce the risk of leakage to overlying formations or venting to the surface as much as possible, even though CO<sub>2</sub> sorbed into or onto organic material is immobile and no seal may technically be necessary. 4) The minimum depth for assessment should be 900–1000 m, because at greater depths, CO<sub>2</sub> is a supercritical fluid at typical pressures and temperatures, allowing greatly increased storage capacity. 5) Storage potential should be assessed in formations of all thicknesses. 6) Storage potential should be assessed in two tiers based on groundwater salinity restrictions on CO<sub>2</sub> injection from the U.S. Environmental Protection Agency: 3,000–10,000 mg/L total dissolved solids (TDS) and greater than 10,000 mg/L TDS. 7) Storage potential should be assessed in all shales with vitrinite reflectance > 0.5% and total organic content > 1%. Several other factors may not directly influence methodology development, but were considered necessary by the participants for a full

understanding of CO<sub>2</sub> storage potential in coal and organic-rich shale formations. These factors include enhanced gas or oil recovery using CO<sub>2</sub> injection, matrix swelling with a corresponding decrease of permeability and injectivity as a result of CO<sub>2</sub> injection, and whether shales have been hydraulically fractured to allow hydrocarbon extraction.

At the end of the workshop, the participants recommended that the USGS proceed with development of a methodology for assessment of CO<sub>2</sub> storage potential in coal and organic-rich shale. This methodology development depends, of course, upon USGS-specific priorities. For more information, please visit <http://energy.usgs.gov/HealthEnvironment/EnergyProductionUse/GeologicCO2Sequestration.aspx>.

Reference: [1] Brennan, S.T., et al., 2010, U.S. Geological Survey Open-File Report 2010-1127, <http://pubs.usgs.gov/of/2010/1127>

## POSTER SESSION 5 COAL-DERIVED PRODUCTS

### Preliminary Study of Hydrothermal Extraction of Direct Coal Liquefaction Residue

Xingjia Jiang, Jianli Yang, Wenzhong Shen, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, CHINA; Hong Cui, University of Hawaii at Manoa, USA

Direct coal liquefaction residue (DCLR) contains valuable organic components which are proved to be important precursors for preparing high value-added coal materials. In this work, subcritical water (SBCW) was used as potential green solvent to extract hydrocarbons from DCLR. The influences of extraction time, extraction temperatures, and mass ratio of DCLR to water on extraction efficiency of hydrocarbons were investigated and the optimized conditions were discussed. The extracts were characterized by elemental analysis, FT-IR, constant-wavelength synchronous fluorescence spectrometry (CWSFS) and high performance liquid chromatography (HPLC). The results show that some hydrocarbons can be extracted, and the possible mechanism involved in the extraction process of DCLR is proposed.

### Coal-Derived Humic Acid Intercalated Zn-Mg-Al Layered Double Hydroxides: Preparation and Application in Coal Fire Prevention

Anning Zhou, Bo Liu, Xuemei Jia, Xi'an University of Science and Technology, CHINA

In this paper, coal-derived humic acid (HA) intercalated Zn-Mg-Al layered double hydroxides (LDHs-HA) were prepared by the co-precipitation method, aiming to improve the fire prevention efficiency of the pristine Zn-Mg-Al-CO<sub>3</sub>-LDHs (LDHs-CO<sub>3</sub>). The obtained samples were characterized by X-ray diffraction (XRD), infra-red spectroscopy (IR) measurements and TG-DTA/DSC analysis. The diffraction peak by the basal planes (003) was found at 8.48° for LDHs-HA, which indicated that HA partly intercalated LDHs (the basal spacing  $d_{003}=1.04$  nm) were formed. The interaction between carboxyl COO<sup>-</sup> of HAs and hydroxyl OH<sup>-</sup> of LDHs was the main reason for the HA partly intercalated structure. The endothermic stages of LDHs-CO<sub>3</sub> were found to coincide with the exothermic stages of HAs, and LDHs-HA exhibited highly thermal stability. When 10% LDHs-HA were added in coal with 5% LDHs-CO<sub>3</sub>, the ignition temperature of coal was improved from 394.98° for raw coal to 437.64°, much more than that 417.57° when only 15% LDHs-CO<sub>3</sub> were added, which suggested the fire prevention effect of LDHs-CO<sub>3</sub> can be improved greatly by the organic HA modified LDHs.

### Performance of Coal/Polyaniline Composites in Epoxy for Corrosion Resistant Coatings

Anning Zhou, Kun Zhang, Shanxin Xiong, Jia Chu, Xi'an University of Science and Technology, CHINA

In recent years, conducting polymers such as polyaniline (PANI) in integrated organic coatings are used to protect carbon steel from corrosion due to formation of a good passive oxide layer on the steel surface. Here we report on the synthesis of a polyaniline (PANI)/coal/epoxy coating and its application in the corrosion protection of carbon steel. The synthesis of PANI/coal composites with different PANI contents and preparation of epoxy based coating system containing PANI/coal composites are described here. Coal was crushed into fine powder and ultrasonicated with a mixture of aniline monomer and ammonium persulfate to form PANI on its surface by in situ polymerization. The formation of PANI in PANI/coal composite material was characterized by SEM, XRD, FTIR and DSC. It was found that the PANI adsorbed on the coal surface. The comparative corrosion protection performance of the coatings containing epoxy with PANI/coal composites on carbon steel was tested in an aqueous solution of 3.5% NaCl and 0.1M HCl. The anti-corrosion performance of PANI/coal

/epoxy-coated carbon steel samples was evaluated by electrochemical corrosion measurements. The results show that the carbon steel coated with PANI/coal/epoxy films has more excellent corrosion protection than that with PANI/epoxy films. Based on the results of different techniques, it is found that PANI/coal/epoxy coating is effective in corrosion protection of carbon steel in acid and neutral media. We expect that this study opens a novel way for developing new doped PANI/epoxy materials for anticorrosion and other functional purposes.

### Integrated Process of Coal Pyrolysis and Methane Activation for Improving Tar Yield

Haoquan Hu, Lijun Jin, Jiahe Liu, Xinfu He, Pengfei Wang, Xun Zhou, Shengwei Zhu, Dalian University of Technology, CHINA

Hydropyrolysis is regarded as an attractive method for improving tar yield, but the high price of hydrogen limits its commercial use. Methane, as the main composition of natural gas, coal-bed gas and the main composition in coke-oven gas could be a low-cost hydrogen substitute in hydropyrolysis. Due to its perfect symmetry, methane has the most stable C-H bonds, thus, the activation of C-H bond of methane needs relatively higher temperature or the presence of catalyst. Since 2004, we put forward an integrated process to combine the methane activation process with coal pyrolysis. The main purpose is to utilize the active molecules, free radicals and hydrogen from methane activation process to stabilize the free radicals from coal pyrolysis, thus to enhance the coal tar formation in coal pyrolysis. In our project, several integrated processes of coal pyrolysis with methane activations including CO<sub>2</sub> reforming of methane (CRMP), partial oxidation (POMP), methane aromatization (MAP) and dielectric barrier discharge (DBD) plasma, were carried out. The results indicated that higher tar yield can be achieved in integrated process with a fixed-bed reactor consisting of upper catalyst layer and lower coal layer than that in coal pyrolysis under N<sub>2</sub> or H<sub>2</sub>. The tar yield in CRMP of Pingshu coal from Shanxi province is 32.2 wt%, about 1.6 and 1.7 times as that in coal pyrolysis under H<sub>2</sub> and N<sub>2</sub>, respectively, when the Ni/Al<sub>2</sub>O<sub>3</sub>-MgO catalyst with MgO content of 8 wt.%, calcination temperature of 800 °C and reduction temperature of 850 °C was used. The main problem in CRMP is the high water yield of 30.7 wt.%. The tar yield of Shenmu coal from Shaanxi province in MAP over Mo/HZSM-5 catalyst at the optimum conditions of 700 °C pyrolysis temperature, 25 mL/min CH<sub>4</sub> flow rate, 4 wt.% Mo loading and 30 min holding time is 7 and 6 wt.% higher compared with those in the pyrolysis of coal under N<sub>2</sub> and H<sub>2</sub>, respectively. The result of integrated process to combine coal pyrolysis with CH<sub>4</sub>/CO<sub>2</sub> activation by DBD plasma show that the tar yield of Shenmu coal under optimum condition is about 2.0 and 1.8 times as that under N<sub>2</sub> and H<sub>2</sub> at 400 °C, respectively. The problem is the unstable of the DBD plasma at high temperature, then it is difficult to operate the integrated process at the optimum temperature for highest tar formation of coal pyrolysis (normally at between 500 to 600 °C). The experiment was also carried out in a 10 kg/h continuous apparatus including a lower fixed-bed catalyst layer and fluidized-bed coal layer reactor. The result shows that the tar yield of Shenmu coal is about 1.4 times as that in coal pyrolysis under H<sub>2</sub>.

### Catalytic Hydrogenation of the Various Coals with Hydrogen over Molybdenum-Contained Catalyst for the Production of Liquefied Hydrocarbon Fuels

Cheol Jin Jeong, Gi Bo Han, Jung Hee Jang, Changsik Choi, Yongseung Yun, Institute for Advanced Engineering; Tae Jin Lee, Yeungnam University, KOREA

The fuel production process for the supply to meet the demand of liquid fuels should be developed because the demand of the liquid fuel dramatically increases and the oil reserves and its supply are restrictive and its price steeply increases, recently. Therefore, the various direct and indirect liquefaction processes using the various resources such as coal, biomass with the exception of oil for the renewable energy production have been investigated. Direct coal liquefaction is an efficient technology to produce liquefied hydrocarbon fuels with the combined cracking and hydrogenation of coal composed of carbon under high temperature and pressure. In this study, the various coals having the various organic and inorganic compositions of fixed carbon, volatile matters, ash and moisture were used for direct coal liquefaction and the reaction characteristics of coal hydrogenation was investigated to obtain the effect of the varied reaction conditions on the hydrogenation of coals. And then the reaction conditions such as the temperature, pressure, the amount of catalyst and hydrogen and reaction time were varied for the hydrogenation of coal. Also, the physic-chemical properties of the coals and catalysts before and after the reaction were analyzed by gas chromatography-mass, x-ray diffraction, proximate analyzer, elemental analysis, FT-IR etc.

### Simulation of a Commercial-Scale Slurry Bubble Column Reactor for Fischer-Tropsch Synthesis using Cobalt Catalyst

Laurent Sehabiague, Badie I. Morsi, University of Pittsburgh; Rachid Oukaci, Energy Technology Partners, LLC, USA

A user-friendly simulator based on a comprehensive computer model for Slurry Bubble Column Reactor (SBCR) developed in our laboratory by Sehabiague et al. [1] was used to predict the performance of a conceptual commercial-scale (9-m ID and 50-m height) SBCR for syngas conversion using Fischer-Tropsch (F-T) synthesis in the

presence of cobalt catalyst. Newly developed correlations for predicting the hydrodynamic and mass transfer parameters and three different kinetic rate expressions for cobalt catalyst taken from the literature were incorporated in the simulator. The effects of operating conditions, including catalyst concentration, pressure, temperature, H<sub>2</sub>/CO ratio, and superficial gas velocity on the SBCR performance were predicted using the simulator. The predictions showed that the performance of the SBCR was strongly dependent on the kinetic rate expression used. At low catalyst concentration, the reactor operated in a kinetic-controlled regime with increased syngas conversion and catalyst productivity, however, increasing catalyst concentration drove the reactor to operate in a mass transfer-controlled regime with decreased syngas conversion and catalyst productivity. The transition from kinetic-controlled regime to mass transfer-controlled regime occurred at different solid concentrations depending on the kinetic rate expression employed. High H<sub>2</sub>/CO ratios in the inlet gas stream to the SBCR led to high syngas conversion. Increasing the superficial syngas velocity in the reactor decreased the gas residence time which decreased the syngas conversions. High operating temperature always resulted in high syngas conversion. Also, increasing reactor pressure resulted in low or high syngas conversion depending on the kinetic rate expression used.

[1] Sehabiague, L., et al., Modeling and optimization of a large-scale slurry bubble column reactor for producing 10,000 bbl/day of Fischer-Tropsch liquid hydrocarbons. Journal of the Chinese Institute of Chemical Engineers, 2008. 39(2): p. 169-179.

### Storage of Volatile Renewable Energy in the Gas Grid Applying 3-Phase Methanation

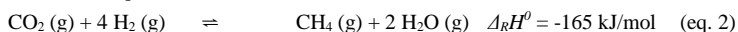
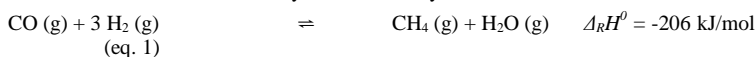
Manuel Götz, Rainer Reimert, Siegfried Bajohr, Karlsruhe Institute of Technology (KIT), GERMANY

#### Problem

In order to face the enormous challenges considering the climate change and the rising energy demand of the world, the expansion of renewable energies is necessary. Thereby, wind power and photovoltaic have the biggest potentials. However, the production of electric energy out of wind power and photovoltaic is volatile. Therefore, in times of surplus electricity-production a part of the electric energy has to be stored. For 2050, a required storage capacity of about 16 TWh is assumed for Germany. Unfortunately, for those quantities of electric energy and for storage durations of several days or weeks available technologies are sparse. Technologies like "pumped storage hydro power station" with a total capacity of 0.04 TWh in Germany and "compressed air energy storage" have individual disadvantages which will be discussed more in detail in the proposed poster. A reasonable alternative to store high amounts of electric energy is the conversion to chemical energy carriers like hydrogen or methane. While hydrogen can be added to the gas grid especially in high pressure grids the generation of SNG (substitute natural gas) seems to be interesting for storage of surplus energy from photovoltaic power in regional and rural distribution grids. The worldwide storage capacity in the gas infrastructure (underground storage) for methane is about 3700 TWh (Germany: 230 TWh) of chemical energy. The only disadvantage is the poor efficiency of about 63 % from electricity to stored SNG.

#### Approach to solution

During times of surplus electricity-production the excess energy can be used to produce hydrogen via PEM-electrolysis (proton exchange membrane-electrolysis). The PEM-electrolyser is more flexible to volatile electric power than the more common alkaline electrolyser. Hydrogen from electrolysis and CO<sub>2</sub> from biogas or other CO/CO<sub>2</sub>-sources can be used to synthesize CH<sub>4</sub> by methanation:



Therefore, a new methanation process with increased flexibility to variable hydrogen-flows than the established 2-phase-reactor systems like fixed-bed and fluidized-bed reactors has to be developed. Caused by the high heat capacity of the liquid phase, a 3-phase-reactor system (e.g. slurry bubble or flooded fixed-bed reactor) is able to store the heat of reaction of the methanation step in order to buffer the effect of fluctuating feed streams. Other advantages of the 3-phase-system are an easy temperature control and an easy removal of the reaction heat by external heat exchanger systems.

In a joint research project of the DVGW-Forschungsstelle at the EBI of the KIT and 6 other partners from industry and science (EnBW, Outotec, IoLiTec, h-tec, Fraunhofer ISE and Engler-Bunte-Institut) the described process chain will be researched and developed.

### POSTER SESSION 6 COAL SCIENCE

#### Chemometric Studies on Relationship Between Fly Ash Elemental Composition and Collecting Equipment Rows

Bruno Valentim, Helena Ribeiro, Universidade do Porto, PORTUGAL; James C. Hower, University of Kentucky Center for Applied Energy Research, USA

During the University of Kentucky Center for Applied Energy Research's (CAER) 2007 survey of coal combustion byproducts of Kentucky utility power plants, major oxides and minor and trace elements were determined on fly ash (FA) from several power plants at the. Considering the large amount of data, and the fact that FA samples were collected directly from the hoppers, these results are conducive to chemometric studies.

Analysis of variance (ANOVA) and post-hoc tests (Tukey and LSD) were applied in order to verify if there is significant variability in FA major oxides between three different ESP units and the individual ESP rows from the same power plant. Also a principle components analysis (PCA) was in order to further evaluate the associations between the elements separated along the combustion line and the different deposition line. All the calculations were performed using the SPSS 19.0 software.

Preliminary chemometric results indicate that when all the three units of the chosen power plant were considered together only CaO, P<sub>2</sub>O<sub>5</sub>, and SO<sub>3</sub> can indicate a possible row differentiation. Yet, comparing each element concentration pattern between each of the three units (not taking in consideration the rows) major differences are found in Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SO<sub>3</sub>, and TiO<sub>2</sub>.

Considering the power plant units separately: in unit 1 (equipped with a two-row ESP) CaO, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, and SO<sub>3</sub> are the only oxides showing statistical different amounts in rows 1 and 2; in unit 2 (also equipped with a two-row ESP) CaO, K<sub>2</sub>O, MgO, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, and SO<sub>3</sub> show statistical different amounts in rows 1 and 2. Thus, three more oxides provide resolution in unit 2 than in unit 1. In unit 3 (equipped with a five-row ESP; only four rows could be sampled) much more oxides differentiated, and only Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and TiO<sub>2</sub> did not exhibit significant differences in their concentrations along the four rows. After the post hoc tests, this unit revealed that the main differences were observed between the rows 1 and 2 and the rows 3 and 4.

#### Effects of Nitrogen and Sulfur on Coal Fluidity During Carbonization

Yuuki Mochizuki, Naoto Tsubouchi, Hokkaido University; Yohei Ono, Mitsubishi Chemical Corporation; Kazuya Uebo, Sumitomo Metal Industries, Ltd., JAPAN

To examine the effects of nitrogen and sulfur on coal fluidity, the evolution of HCN, NH<sub>3</sub> and H<sub>2</sub>S during carbonization at 3°C/min of seven coals (LL, GY, NW, GA, TR, SI and GC) has been studied with a flow-type fixed-bed quartz reactor. The carbon, nitrogen and sulfur contents of the coal samples range 80-88, 1.2-2.3 and 0.57-1.8 mass%-daf, respectively. The maximum fluidity (MF), determined by the Gieseler plastometer method, appears around 450°C with all coals, and the values range from 1.1 to 4.1 log(ddpm) and increase in the order of NW < SI < GC < LL < GA < TR < GY. The evolution of HCN and NH<sub>3</sub> from the coal samples starts at about 400°C, and each rate profile observed provides the main and shoulder peaks around 450 and 670°C, respectively, irrespective of the kind of N-species. H<sub>2</sub>S starts to evolve between 200 and 350°C, and the coal samples exhibit two distinct peaks at 450 and 550°C. The MF value tends to increase with increasing total amount of HCN or NH<sub>3</sub> evolved up to 450°C. Such a trend is also observed between total amount of H<sub>2</sub>S evolved up to 450°C and the MF value. It may thus be possible that the nitrogen and sulfur present in coal affect the MF value upon carbonization.

#### Dynamic Swelling Behavior of Pretreated Coal in Solvent

Lei Chen, Hang Gao, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, CHINA

To better understand the coal swelling mechanism in solvent, the dynamic and equilibrium swelling behavior of pretreated coal was measured by a so-called linear variable differential transformer (LVDT) deformation transducer apparatus. Utilization of coal pretreatment techniques, including thermal pretreatment and solvent extraction pretreatment, has been investigated to determine the effect of these procedures on the swelling behavior of coal in solvent. Pretreatment and swelling experiments have been carried out using bituminous Coal-1. Ethanol was used as swelling solvent in isothermal dynamic swelling experiment and pure tetralin (THN) was used as the test solvent in non-isothermal equilibrium swelling experiment. For isothermal swelling experiment, the swelling isotherm of 150 °C char in ethanol was similar with raw coal. The swelling rate and ratio of 350 °C char in ethanol were lower than raw coal. No significant swelling in ethanol was observed for the char obtained by thermal treatment of Coal-1 at 550 °C. The results on the swelling of coals pre-extracted in tetrahydrofuran (THF) and n-hexane were shown that THF-extracted coal in ethanol swelled faster and more significantly than raw coal, oppositely for n-hexane-extracted coal. For non-isothermal swelling experiment, the swelling ratio of 150 °C char in THN increased as the increase of the temperature and peaked at 300 °C, which was consistent with raw coal. The swelling ratio of 350 °C char in THN was lower than raw coal and peaked at 350 °C, higher 50 °C than raw coal. However, the swelling ratio of 550 °C char decreased with the increase of the temperature. The effect of solvent extraction pretreatment on non-isothermal swelling experiment was similar with that in isothermal swelling experiment. The swelling ratio of THF-extracted coal in THN was higher than raw coal and peaked at 300 °C. By contrast, the swelling ratio of n-hexane-extracted coal was lower than raw coal and peaked at 300 °C. The swelling behavior of pretreated coal was very much dependent on the thermal treatment temperature and the pre-extraction solvent characteristic.



## Effect of the MagMill on Coal Grindability and Coal Abrasiveness

R. R. Oder, EXPORTEch Company, Inc., USA

With the advent of modern dry coal cleaning technology, preparation of specification coals is feasible. Coarse dry cleaning technology such as air jigs is used at the mine site to reduce moisture and remove rock. Final cleaning can be done at the point of use by combining existing dry size reduction methods and new dry coal cleaning technology. This can have the effects of reducing both capital and operating costs while offering the fuel purchaser a wider choice of suppliers. This paper will show examples of beneficiation at the point of use which efficiently improve coal quality, increase throughput of the milling operation, and lower abrasiveness without sacrificing power plant grind, nominally 70 – 80 % finer than 200 mesh. This is accomplished by removing the hard, abrasive and difficult to grind minerals from the inside of the size reduction operation before they are over-ground.

We will review tests of pre-combustion dry beneficiation of bituminous, sub-bituminous and lignite coals employing a MagMill, a novel method of pulverizing where recirculation of pyrites and detritus inside the mill is minimized by removal of the coarse fractions of the gangue from the mill. A 1-1/2 TPH ring/roller pulverizer and a 3 TPH CE Raymond bowl mill were used in the testing. In this configuration of the MagMill, relatively coarse gangue and detritus are withdrawn directly from the internal circulation of the pulverizer and processed outside of the pulverizer through a two stage dry magnetic separator. The separator reject is discarded and the cleaned coal is returned to the pulverizer for additional grinding.

We will present results showing that the ash and sulfur levels of the MagMill beneficiated products of the ring/roller mill are not degraded and product particle size is not affected within the limits of power plant grind when the mill feed is increased up to two times. Results of bowl mill tests will be used to illustrate 50% reductions in product abrasion.

## Predictions of Voidage in a Packed Bed of Large Coal Particles

Gavin S. Deas, Roelof Coetzer, Adam Luckos, Sasol Technology, SOUTH AFRICA

The Ergun equation is widely used to predict pressure drop across packed beds of fine particles in a variety of applications especially in catalytic reactors. To the authors' best knowledge an extension of this equation to beds of large coal particles that are used in combustion, gasification and metallurgical processes has not been developed and tested experimentally.

According to the Ergun equation the pressure drop across a packed bed is strongly influenced by the bed void fraction (voidage). Voidage in the bed can be affected by several factors including average particle size, particle sphericity and the particle size distributions (PSD). In this study the voidage was measured, using the water displacement method, for coal beds with five different Sauter mean diameters in the range 5.7–32.0 mm and three different PSD compositions for each diameter. Two correlations describing the voidage as a function of particle diameter, particle sphericity and a dimensionless PSD factor have been developed. The two different dimensionless PSD factors for each of the correlations include a quantitative relation between the PSD width and the Sauter mean diameter (0.33–2.20) and a qualitative relation between the weighted mean diameter and Sauter mean diameter (1.00–1.40). These correlations describe the experimental values of packed bed voidage with standard deviations of  $8.96 \times 10^{-3}$  and  $8.99 \times 10^{-3}$  respectively. These correlations will be used to develop a modified version of the Ergun equation that can describe the pressure drop in the beds of large coal particles.

## Flotation of Fine Coal Using Cavitation Venture Tube for Pico and Nanobubble Generation to Improve Collision/Attachment

Felicia Peng, Yu Xiong, West Virginia University, USA

For successful froth flotation of coal and mineral particles, the key mechanisms of the flotation include the probabilities of collision, attachment, and detachment between the air bubbles and hydrophobic particles. Thus, the high or excess numbers or concentration of air bubbles in the flotation column/cell is highly desirable. However, this has not been achieved by the most commonly used bubble generators such as high pressure sparger, static mixer, etc. Those types of the bubble generators can only generate the mil size and micro size bubbles. While those bubble generating units might serve for most of purposes, the high dosages of frother and collector are required. Use of high quantity frother often causes the problem of downstream product dewatering operations. Additionally, the probability of collisions and attachment between air bubbles and hydrophobic particles are depending on the numbers or concentrations of air bubbles in the flotation column/cell due to limiting numbers of air bubbles can be generated in the column/cell. In recent development, the properly designed cavitation venture tube can be used to generate the air bubble sizes in the ranges of pico and nano bubbles. This means that the flotation column/cell full can be filled with high density of those pico and nano bubbles. The advantage of high density of tiny air bubbles in the flotation/cell is that, the flotation rate is no need to dependent upon on the numbers of tiny air bubbles for attachment. It is because the density of the pico and nano bubble generated by the cavitation venture tube are so high, the flotation rate due to the collision can be consider as the zero order of the concentration of the pico and nano bubbles (have very high probability of encounter between air bubbles and particles). In practical sense, this means the whole froth flotation column/cell are

filled with froth. It has been known, the pico bubbles and nano bubbles are less mobile than the mil size and micro size bubbles. They have much relative higher affinity and tendency to precipitate on the hydrophobic particles. The advantage of this is to increase in the probability of the collision and attachment, and decrease in the probability of detachment of particles from air bubbles, as well as selectivity. In this study, we have the experiment results of froth flotation of bituminous coal from Northern Appalachian region, using cavitation venture tube, to improve the probability of collision and attachment, and reduce the detach probability, which are the keys fundamental mechanisms of froth flotation as described above. A 50 cm diameter and 160 cm height of flotation column equipped with static mixer and one special configured cavitation venture tube were used for the coal flotation, by using MIBC as frother and kerosin as collector. The results show that combustible material recovery of 85-90% at clean coal product of 6-7% ash are produced from the feed with ash content of 22-27%, using 50% or less of the reagent dosages used in conventional flotation. The major operation parameters including, feed rate, water and air flowrates, solid concentration, reagent dosage effects on the combustible material recovery and separation efficiency are presented and discussed.