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

Thank you,

Badie I. Morsi

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

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SESSION 1
Clean Coal Demonstration and Commercial Projects - 1

The Value of Fuel Flexible Circulating Fluidized Bed Technology

Robert Giglio, Antonio Castilla Oliver, Amec Foster Wheeler, USA

The use of Circulating Fluidized Bed (CFB) combustion technology is growing strongly in large utility power plant applications. It has now reached sizes and efficiency levels never imagined by many executives of utility power companies.

This paper will explore the market drivers and technology advancements which allowed CFB boiler technology to grow from small-scale industrial applications to large ultra-supercritical power plants in less than 20 years.

The CFB's fuel flexibility is the primary driver behind the decisions of many power company executives for selecting CFB boiler technology over conventional PC technology. This is due to a growing uncertainty in the global coal market and a trend of declining coal quality vs. attractive price discounts.

However, fuel flexibility means more than just being able to burn a wide range of coals and biomasses. It also means that plant reliability, maintenance, ease of operation, and stack emissions are not significantly impacted over the wider fuel range. Design features of Amec Foster Wheeler's CFBs will be reviewed and compared to conventional PC boiler technology showing how they contribute to high reliability, low maintenance, and cost effective designs.

This paper will also provide an updated review of some of the largest and most advanced CFB plants around the world. Examples would be Tauron's 460 MWe supercritical CFB Lagisza power plant in Bedzin, Poland successfully running since 2009 and the 2,200 MWe ultra-supercritical CFB plant in Samcheok, South Korea, scheduled to come on-line in 2016.

Finally, this paper provides a view for the value that CFB technology can bring to Africa as a valuable part of South Africa's IPP market.

Application Update of OMB CWS Gasification Process

Guangsuo Yu, Qinghua Guo, Xueli Chen, Yifei Wang, Zhenghua Dai, Haifeng Liu, Fuchen Wang, Xin Gong, ECUST, CHINA

Opposed Multi-Burner (OMB) coal-water slurry (CWS) gasification technology is a representative coal gasification technology. This gasification process adopts an entrained-flow OMB gasifier to produce syngas that mainly consists of carbon monoxide and hydrogen using CWS and pure oxygen under high pressure and high temperature operating conditions. With many technical advantages, OMB CWS gasification efficiency is very high, and the carbon conversion rate is normally higher than 98.5%.

Up to now, OMB CWS gasification technology has been licensed on 43 projects for a total of 118gasifiers. The design has coal capacity range from 750 to 3250 TPD for single gasifier and pressure range from 1.5MPa to 6.5MPa. The total capacity is over 140 thousand tons coal per day. There are 54 gasifiers on 20 different projects currently running smoothly in China with the largest one having a 3000TPD coal capacity.

In July 2015, the world biggest CWS gasification plant in Shanxi province China, which adopted 8 OMB CWS gasifiers, has started up. The syngas produced from this gasification plant is used for F-T synthesis process. Totally, there are 6 projects with 17 OMB CWS gasifiers commissioned in 2015.

In September 2015, the project with largest single capacity (3000TPD) of OMB gasifier in Inner Mongolia has passed the 72 hours continuous performance test, and this plant is now in stable operation state.

Ohio Valley University's Alternative Clean Energy Facility

Marcus Wiley, TCG Global, LLC, USA

West Virginia, a longtime leader in coal production is also going to be leading the world in demonstrating alternative clean energy production from coal. Coal production in WV has declined recently with huge losses in coal related employment, gross revenue and taxes due largely to the global war on coal.

Coal can be a clean alternative energy source and Ohio Valley University (OVU.edu) is doing something about letting the world know about it. The University - a faith based liberal arts school - located in Vienna, WV, is developing a commercial scale Alternative Clean Energy training center, (OVU-ACE). This is not only a research project, but a for profit venture, with the proceeds to be used to fund OVU operations with a goal of graduating their students debt free along with valuable life and career skills. The commercial scale facility scheduled to be operational in 2018 is designed to utilize approximately 600 tons of coal per day producing 2 to 3,000 barrels of liquids, hydrogen and by-product electricity along with carbon capture.

This project integrates multiple existing technologies into one facility to demonstrate to the world that clean energy from coal can be produced economically and is commercially viable. The project will make fuels, hydrogen, electricity and capture CO2. The facility is to be used as a training and education center for their students to excel in this new cleaner world. They offer a degree in Energy Management and Production Engineering, and students will intern at the facility for hands on experience. The university has retained Fluor Corporation (www.fluor.com) to provide technical engineering services in their development of the OVU-ACE facility. Fluor has prepared a feasibility study which includes a gasifier to be provided by TCG Global, LLC (www.tcgenergy.com) to produce a clean syngas from coal that will be converted into a mixed alcohol to be used as an octane booster for gasoline and diesel fuels as well as a slip stream of hydrogen for various markets including fuel cell cars and busses. One unique aspect of the Fluor process is the recycling and utilization in the process of CO2. Waste heat from the facility will be utilized to produce electricity as well. Carbon Dioxide capture will be demonstrated with various utilizations including a green house and Enhanced Oil Recovery. In addition, plans are underway to co-locate a lab with the WV Geological Survey for research and education in the recovery of Rare Earth Elements from coal ash sources, and EOR research using an old oil well located on the facility property.

SES SGT Commercial & Operation Plant Updates

Francis Lau, Synthesis Energy Systems, USA

Synthesis Energy Systems Inc. (SES) owns a commercially proven and competitively advantaged clean energy technology. SES will update its SGT Gasification Projects Status and Market Focus.

SESSION 2
Combustion Technologies - 1

CFD Simulation of an Industrial Wet Flue Gas Desulfurization Spray Tower: A Comprehensive Model with Special Attention Devoted to the Modeling of Absorption and Chemical Reactions

Raymond Everson, Arif Arif, Hein W.J.P. Neomagus, Dawie Branken, North-West University, SOUTH AFRICA

A complete CFD model for an industrial scale flue gas desulphurisation (WFGD) spray tower was developed and validated which included the hydrodynamics of the gas and droplet phases as well as the mass and heat transfer between the phases and the chemical reactions inside the slurry droplets. The model is capable of estimating the desulfurization efficiency, pH, enhancement factor and the concentration of chemical species in the slurry droplets.The mass transfer is based on the two film theory and the reactions in the droplets are assumed all to be at equilibrium. A non-isothermal operation was modeled with all parameters adjusted accordingly. The model was validated against plant results obtained from an industrial WFGD absorber which included the prediction of flue gas velocity, temperature and desulfurization efficiency. The dependence of the desulfurization efficiency on the enhancement factor and slurry pH obtained from the chemical model was found to be well aligned with the plant tests and literature results.

Optimization of Coal and Combustion Air Distribution for 500 MW Tangential Coal-Fired Plant

Kitae Kang, Korea Southern Power (KOSPO) CO., Ltd, KOREA

Recently aggressive reductions of greenhouse gas in coal-fired power plant emissions are mandated. So the electric utility industry has been moving toward improvement of plant efficiency. As the most cost effective means of improving efficiency in coal-fired power plant, the combustion modifications should be reviewed as the first step in any strategy.

The purpose of this project is to increase the plant efficiency through the optimization of coal and combustion air distribution in boiler.

The investigation of optimal operating condition through combustion test in fully operating boiler can be extremely time-consuming and expensive. The approach in this project was to use CFD to quantify the impacts of variations of burner fuel flow and secondary air flow on boiler operating parameters. And then based on CFD result, detailed optimum operating condition was derived by performing the combustion test.

Firstly, the impacts of variations of two operating parameters such as burner fuel flow and secondary air flow distribution were investigated using CFD with focusing on unburned carbon and NOx emissions. The following general conclusions were drawn from CFD. Unburned carbon reduced from 14.75% to 5.59% when secondary air flow to row C, D burner was increased by 3%. The added air is pulled from the other four rows proportional to the baseline secondary air flows of each burner. And unburned carbon also reduced from 7.17% to 6.95% when coal flow to row C burner was decreased by 15%. The removed fuel is the distributed between the other four rows proportional to the baseline fuel flows of each burner. And secondary air distribution has larger impact on unburned carbon than fuel distribution.

The CFD results mean that pulverized coal particles from row C burner contribute most to unburned carbon.

The coal from the middle burners (row C) tends to pass through the central fuel rich core of fireball, seeing very low concentrations of O_2 and experiences lower residence time than the bottom burners(row A,B). The coal from the bottom burners (row A, B) experience the most residence time for burnout. The coal from top burners (row D, E) circulates at larger radius, in close proximity to combustion air introduced through the row F, over fire air, seeing high concentration of O_2. Even though the coal from the top burners (row D, E) experiences lower residence times in the furnace, they experience higher oxygen concentration, critical for complete burnout.

And then combustion test was performed to derive the optimum operating conditions only about secondary air distribution especially air flow to row C and D, focusing on unburned carbon and NOx, furnace gas temperature, heat absorption rate. In the test, optimum rate of increase in secondary air flow to row C&D was investigated according to OFA (over fire air) damper position 10, 26, 53% (average of OFA #1~4 ports damper position). The added secondary air flow to row C&D is pulled from the other four rows. As a result of combustion test, the optimum rate of increase in secondary air flow to row C&D is each 1.8/ 6.1/ 14.4% at OFA damper position 10/ 26/ 53%. The optimum rate of increase in secondary air flow to row C&D is proportional to OFA damper position. At OFA damper position 10, 26%, unburned carbon decreases and NOx increases by increasing secondary air flow to row C&D. But at OFA damper position 53%, both unburned carbon and NOx decrease. Also it is possible to increase plant efficiency (0.13%p) and decrease cost of fuel ($330thousand/year) by optimization of secondary air distribution.

NLP/MINLP for Modeling and Optimization of Lignite Pyrolysis Process

Wengying Li, Yi Huang, Qun Yi, Minhui Gong, Guosheng Wu, Taiyuan University of Technology, CHINA

Lignite pyrolysis based polygeneration system is an efficient and clean way for lignite utilization. The polygeneration system integrated with different configurations and processes, which can realize reasonable conversion of element and cascade utilization of energy, thus improve the energy efficiency and economic benefits of the whole system and reduce the emission of pollutants. Pyrolysis process is core unit of the lignite pyrolysis based polygeneration system, and the main products from lignite pyrolysis are semi-coke, tar and gas, and the distribution of these products, especially the tar components distribution, has great influence on downstream processes. However, there have been limited studies available in the literature on the accurate modelling of the lignite pyrolysis with detailed information about the production distribution and energy requirement.

In this work, a Nonlinear Programming (NLP) model was established to describe the process of lignite pyrolysis, and the pyrolysis model was validated through comparing with the pilot or semi-industry technology such as Toscoal technology, Lurgi-Ruhrgas (L-R) technology, Dalian University (DG) technology, Advanced Coal Conversion Process (ACCP) technology, Coal Oil Energy Development (COED) technology and Shenwu (BJSW) technology. All of the results showed the good agreement with the actual production values, suggesting that the model can be as a universal one for simulation of lignite pyrolysis. On the basis of this model, the products distribution and energy penalty can be obtained in the condition of different coal and pyrolysis technologies. Further, a Mixed Integer Nonlinear Programming (MINLP) modeling was established to optimize the pyrolysis process to acquire the optimal comprehensive performance (efficiency, economy and environment) of the pyrolysis process, and as a result, the best production distribution and pyrolysis technology can be determined for different lignite coal.

SESSION 3
Carbon Management - 1

Status of the Carbon Capture International Test Center Network

Roxann Laird, Southern Company Services, USA

The Carbon Capture International Test Center Network (ITCN) is a consortium of world leaders in the research and development of CO2 reduction technologies. Through the cooperative exchange of expert knowledge and operational experience, the ITCN seeks to address the technical issues that challenge near-term commercial deployment of advanced CO2 capture processes for combustion power plants. ITCN membership includes operators of major CO2 capture test sites—E.ON's Wilhelmshaven power plant, Norway's CO2 Technology Centre Mongstad, SaskPower's Shand Power Station, Southern Company's National Carbon Capture Center (NCCC), and the U.K.'s Pilot- Scale Advanced Capture Technology facilities.

The ITCN was officially founded in November 2013 with commitments of support from the governments of Norway and the U.S.A. For the first two years of its existence, the network was headquartered at the Technology Centre Mongstad. Chairmanship was transferred in February 2016 to the NCCC in Alabama, U.S.A. The NCCC will operate the ITCN with the U.S. Department of Energy's Office of Fossil Energy for the next two years.

The shared knowledge of the ITCN is expected to contribute significantly to the development of cost effective, commercial CO2 capture technologies. With semi-annual workshops, ITCN members have tackled critical issues of post-combustion capture such as emissions and degradation of amine-based solvents; permitting requirements; and control of aerosol formation. Results of the in-depth studies conducted by the network will be published for public benefit. Accomplishments and future plans of the ITCN will be discussed in this presentation.

Status of Technology Development at the National Carbon Capture Center

Roxann Laird, Southern Company Services, USA

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

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

Operations at the PC4 have included more than 38,000 hours of bench- and pilot-scale technology evaluations with coal-derived flue gas, with over 2,500 hours under simulated natural gas flue gas conditions. Testing with the PC4's Pilot Solvent Test Unit has demonstrated near 100 percent mass and energy balance closures, and has allowed evaluation of advanced solvents from seven different technology developers. Other technologies tested at the center include independent processes employing solvents, membranes, enzymes, and sorbents.

For gasification and pre-combustion CO2 capture technologies, the center has accommodated more than 33,000 hours combined of developer technology testing since 2009. These technologies include water- gas shift, carbonyl sulfide hydrolysis, and Fischer-Tropsch catalysts; fuel cells; high-temperature mercury and CO2 sorbents; physical and chemical CO2 solvents; membranes for CO2 and hydrogen separation; pressure-swing adsorption; advanced instrumentation; and biomass co-gasification.

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

Performing a Push-Pull Test in a Shallow Aquifer to Assess Impacts of CO_2 and Impurities Leakage on Freshwater Quality

Stéphane Lafortune, Philippe Gombert, Zbigniew Pokryszka, INERIS, FRANCE;
Maria del Camino Martin Torre, Universidad de Cantabria, SPAIN

In 2015, INERIS has performed a push-pull test by injecting 3 m^3 of brine saturated with dissolved CO_2, containing impurities and tracers, in a shallow chalky aquifer. The objective was to simulate leakage from CO_2 storage and to assess impacts on groundwater quality. This test has been performed in the framework of the FP7 CO2QUEST research project, funded by the European commission from 2013 to 2016. This project addresses issues regarding the impact of impurities in CO_2 stream captured from power plants.

The push-pull test has been done at the experimental site located in Catenoy city, about 60 km north of Paris. The site was equipped with 10 piezometers (~20m-deep wells dedicated to water table measurement and groundwater sampling in the saturated zone) and 4 air-wells (~10m-deep wells dedicated to underground atmosphere measurement and sampling in the unsaturated zone).

During a previous research project (ANR CIPRES, funded by the French national research agency from 2011 to 2015), injections of food grade CO_2 dissolved in fresh water was performed in Catenoy in 2013 and 2014. Taking feedback from this previous experiment into account, a new injection has been carried out in 2015 during the CO2QUEST project. This third injection was done with CO_2 containing some impurities (Fe, Mn, Cu, As, Zn) and tracers (Li, He, uranine/$C_{20}H_{10}Na_2O_5$) dissolved in salted water. This salted water is similar to the brine contained in the deep saline aquifer where CO_2 storages could be done. 3 m^3 of salted water with CO_2, impurities and tracers were injected for 3 hours during the push phase. After 3.35 days, 580 m^3 of aquifer water were pumped for 95 hours during the pull phase. Between the end of the push phase and the beginning of the pull phase, we let the injected fluid migrate inside the aquifer and interact with groundwater and rocks.

Both saturated and unsaturated zones have been monitored during all the experiment. During the push phase, we observed concomitantly an increase of salinity and concentrations of impurities and tracers, and a pH decrease. Despite a high pumping volume during the pull phase, we didn't make equivalent observations, because of the combination of diffusion, gravity effects and chemical reactions. 1-D geochemical modeling helped us to better understand the behavior of CO_2, impurities and tracers during the test.

Authors will detail the design of the push-pull test and of the monitoring plan. They will also present results from monitoring and modeling to draw the conclusion that the impact of the experiment on groundwater quality was very limited. It would be useful to perform an extended injection test, to confirm the conclusion when leakage lasts longer.

Geological Carbon Sequestration and its Influence on Subsurface Microbial Diversity and Metabolic Carbon Cycling

Mariana Erasmus, Esta van Heerden, University of the Free State, SOUTH AFRICA; Tullis Onstott, Princeton University; Mary DeFlaun, Geosyntec Consultants; Tommy Phelps, University of Tennessee, USA

As an attempt to manage carbon resources more efficiently, South Africa will be storing anthropogenic CO_2 in geological formations. However, within these deep subsurface environments, it is well documented that diverse microbial communities can be found and the metabolic activities of these microorganisms are closely tied to the geochemical and mineralogical processes. Therefore, to define possible influences that the CO_2 could have on the diversity and ultimately carbon cycling, the interaction was studied between the sequestered CO_2 and the subsurface biome, as well as the geological environments. To define the current activity of the biomes *in situ*, the biogeochemistry for a study site, similar to proposed sites for carbon sequestration in South Africa, was characterized comprehensively using sampling techniques that were designed to maintain subsurface conditions with preservative addition for reliable analyses, including stable isotopic analysis to define current biogenic impacts. The diversity of a subsurface biome from the study site was characterized using DGGE and NGS analyses and was found to contain microorganisms belonging to the Archaeal, Bacterial, and Eukaryal domains, but was dominated specifically by Proteobacteria. A novel, continuous, high-pressure bioreactor was designed and used to evaluate the influence of the stored CO_2 on the subsurface microbial diversity and metabolic carbon cycling by simulating carbon sequestration conditions.

Due to the extreme conditions of the deep subsurface, most of these microorganisms have adapted to survive in extreme energy limiting conditions while lowering their metabolic activities. The research indicated that even though in most of the conditions tested the microorganisms were not able to multiply or to produce detectable amounts of expected metabolic products, they surprisingly remained viable, most likely due to the presence of biofilm formations that allowed for protection and resistance in these harsh conditions. However, a considerable decrease in the diversity was observed while the transcriptome data revealed that the selected subsurface metabolic activities like sulphur, nitrogen, and carbon were active. Diversity analyses of the bioreactor confirmed that microorganisms, utilizing these metabolisms, remained viable after six weeks under carbon sequestration conditions. These conditions, mainly due to the acidic environment created by the dissolved CO_2, allowed for significant leaching of metals from the sandstone, especially aluminium and iron, creating even more stressful environments, thus restricting the growth of the biome. This is the first study in South Africa that demonstrates the impacts carbon sequestration could have on the biogenic carbon cycling with additional considerations to changes in biogeochemical conditions to be considered in the ventures to capture and store carbon in terrestrial environments.

SESSION 4
Coal Science - 1

Physical and Chemical Characteristics of Coke by using Ash-Free Coal as Binder

Gyeong-Min Kim, Kevin Yohanes Lisandy, Jin-Ho Kim, Chung-Hwan Jeon, Pusan National University, KOREA

Coke strength can be increased by adding ash-free coal (AFC) binder. The effect of the AFC binder added during the development of coke on the physical and chemical properties of coke was experimentally investigated to understand the mechanism of increase in coke strength. In this study, two AFC samples extracted by the Indonesian low rank coal were used to understand the effect of binder. Further, the addition of a torrefied fuel produced from biomass along with the coal binders was also considered to realize a reduction in CO_2 emission in the steel making plants. The interface between the base coal and AFC was observed via Scanning Electron Microscope (SEM). And the coke strength was investigated by performing indirect tensile test and ^{13}C NMR analysis were used. To investigate the mechanism of increase in the coke strength, thermal coal (has no Free Swelling Index) that is used at power plant was bound with the AFC, and SEM analysis was performed. The results show that the indirect tensile test strength between the molecular structures, as determined by ^{13}C NMR analysis of the cokes, is proportionate to the average number of aromatic rings.

The Influence of K_2CO_3 on the Swelling and Caking Behavior of Large South African Coal Particles

S. Coetzee, H.W.J.P Neomagus, J.R. Bunt, North-West University, SOUTH AFRICA

The swelling and caking behaviour of large coal particles from the Waterberg (GG) region in South Africa were investigated. The main objectives were: 1) to qualitatively and quantitatively evaluate the swelling and caking behaviour of 10 and 20 mm GG coal particles, 2) and to investigate the influence of K_2CO_3 (at different concentrations) and varying heating rates on the degree of swelling and caking during devolatilisation.

Large coal particle swelling was quantified by means of a defined volumetric swelling ratio (SR_V), using mercury submersion measurements. It has previously been found that this method can be used to quantify the volumetric swelling of 5, 10 and 20 mm coal particles. Raw particles, and particles impregnated with a 5.0 M K_2CO_3-solution, were devolatilised from 100 to 700 °C. The influence of heating rate on the degree of swelling of 20 mm GG particles was investigated using varying heating rates (1, 3, 5, 7 °C/min) during devolatilisation. It was found that K_2CO_3-impregnation decreased the average SR_V by between 13 and 20 %, for 3, 5, and 7 °C/min heating rates. However, the raw and impregnated particles showed no significant difference in degree of swelling at 1 °C/min. Results also indicated that an increase in heating rate (from 3 to 7 °C/min) resulted in increased SR_V values, for both the raw and K_2CO_3-impregnated particles.

Coal caking, and the effect of K_2CO_3 thereon, was evaluated based on extent of caking, which was quantified using bridging neck size measurements. Bridging neck size was defined as the cross-sectional bond between two coal particles, as obtained from X-ray computed tomography scans. The influence of varying K_2CO_3 concentrations (1, 3, 5, 7 M) and heating rates (1, 3, 5, 7 °C/min) on the extent of caking was investigated using batch samples (30-40 particles) of 10 mm GG particles, devolatilised from 100 to 700 °C. Results showed that 1.0 M K_2CO_3 solution decreased caking by 40 %, while no significant difference was observed in the degree of reduction of caking for higher K_2CO_3 concentrations. The caking propensity of the coal particles was significantly influenced by heating rate, where an increase in heating rate resulted in increased caking.

Overall, it can be concluded that both K_2CO_3 and varying heating rate can be used to modify the swelling and caking propensity of a moderately swelling coal such as GG. The results show the viability of using an additive to reduce unwanted swelling and caking, specifically in coal utilisation processes where a reduction in heating rate will decrease process efficiency.

Time of Flight Secondary Ion Mass Spectrometry and High-Resolution Transmission Electron Microscopy/Energy Dispersive Spectroscopy: A Study of the Distribution of Hazardous Elements in Coal Ashes

Diego de Medeiros, Marcos L.S. Oliveira, Bianca D. Lima, Luis F. O. Silva, Centro Universitário La Salle, BRAZIL; Frans Waanders, North West University, SOUTH AFRICA

Relatively new techniques can help in determining the occurrence of amorphous and mineral species and the distribution of contaminants from coal ashes. The Brazilian coal ash was chosen because of its well-known sorption capability. The physico-geochemical characterization of ultrafine/nano-particles present in the ashes samples and their interaction with environment are the aim of this study. The methodologies applied for this work were field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FE-SEM/EDS), high-resolution transmission electron microscopy with energy dispersive X-ray spectroscopy (HR-TEM/EDS) and time of flight secondary ion mass spectrometry (ToF-SIMS). Some hazardous volatile elements, C, N, S and Hg contents were also determined in the studied samples. This study will serve as a basis for further scientific research on the soil retention of hazardous elements. New techniques such as spectroscopic imaging and transmission electron microscopy make it possible to check which coal ash components retain heavy metals, thereby contributing to propose effective measures for the remediation of contaminated soil. The EDS analysis coupled with the FE-SEM and HR-TEM observations of the fly ash particles with 100 to 0.1 nm demonstrates that these materials contain a small but significant proportion of encapsulated HVEs. In addition, the presence of abundant multi-walled carbon nanotubes (MWCNTs) and amorphous carbon particles, both containing hazardous volatile elements (HVEs), was also evidenced by the FE-SEM/EDS and HR-TEM/EDS analysis. A wide range of organic and inorganic compounds were determined by chemical maps obtained in ToF-SIMS analysis.

Investigation of Solvent Crystallization Process of Anthracene

Wenying Li, Xiaoxiao Ding, Cuiping Ye, Mingming Fan, Hai Mu, Jie Feng, Taiyuan University of Technology, CHINA

Anthracene is one of the most value-added components of coal tar, which is an irreplaceable chemical raw material in dye, pharmaceutical, and photoelectric industries. As a result of its low cost and energy consumption, simple technology, solvent crystallization is the most widely used in large scale to refine anthracene from crude anthracene. Crystallization is a complicated process combined mass and heat transfer. To obtain higher purity anthracene and determine the factor which influences the separation process substantially, the effects of solvent, cooling mode, temperature, stirring rate and impurity on the crystal size, crystal morphology, and purity were investigated in the solvent crystallization process of anthracene. Powder X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to explore the morphology and crystal size evolution of anthracene. The purity was measured by gas chromatography (GC). Meanwhile, the best crystal in good shape was obtained. The intact crystal particles were produced in N,N-dimethylformamide(DMF) with the initial temperature of 80 ^{o}C at the stirring rate of 450 r/min, when the cooling curve was controlled by a forced circulating system. In addition, the interaction mechanism between impurity and anthracene was analyzed.

Pyrolysis Product Evaluation and Prediction From Coals of Different Rank

Gustav Pretorius, J.R. Bunt, North-West University, SOUTH AFRICA; M. Gräbner, Air Liquide, GERMANY

Predictions of pyrolysis product yields based on only raw coal information (proximate- and ultimate analysis) with the help of existing pyrolysis models i.e. FLASHCHAIN and CPD (chemical percolation devolatilisation) can be helpful to easily determine which coals are more amendable to chemical production. These models were created for flash pyrolysis, but the validation of these models for slow pyrolysis can serve as early indicators for design purposes of fixed bed gasifiers. The aim of this study is to develop models for five coals of different rank (lignite A, subbituminous A and three high volatile C bituminous coals) in order to predict the char, tar, water and gas yields as well as the tar composition (oils and tars) when heated at slow heating rates (<10°C/min). A modified Fischer Assay setup, developed by the North-West University, was used in order to investigate pyrolysis at temperatures higher than that of the ISO 647 standard, for the pyrolysis experiments, i.e. final temperatures of 520, 720 and 920 °C. The effect of coal rank and pyrolysis temperature on the obtained product yields and compositions were evaluated experimentally and modelled. It was found that an increase in coal rank resulted in a decrease in total volatile yield, as expected. All coals showed a more significant increase in total volatile loss within the range of 520 to 720 °C than compared to the temperature range of 720 to 920 °C., which could be attributed mainly to H_2 release at higher temperatures. Pyrolysis product yield predictions, based solely on the proximate-and ultimate analysis, using FLASHCHAIN yielded parity plots showing very good agreement for all temperatures when compared to experimental data.

SESSION 5
Gasification Technologies: Gas Cleanup

Improving Response Rates of Acid Gas Absorber Columns

Chris Higman, Higman Consulting GmbH; Bernd Epple, Christain Heinze, TU Darmstadt, GERMANY; Jose Marasigan, EPRI, USA

Increasing penetration of intermittent renewable sources of electrical energy such as wind or solar into the energy mix places an increasing demand on the flexibility of other power plant, in particular fossil fuel-based units.

The suppliers of natural gas combined cycle equipment have been particularly successful in designing plants with increased ramp rates. In a recent review [1] EPRI has analyzed the potential for using such equipment to improve the ramp rates of IGCC power plant. The review concluded that this was certainly possible, and identified the limiting equipment to be the acid gas removal system. Experience with such units in chemical applications has shown that at faster ramping rates than about 3%/min. the design sulfur specification cannot be maintained and a short-term sulfur breakthrough occurs. In that review it was postulated that this could be attributed to reduced solvent flow in the lower part of the column, while the hold-up required for higher load operation was being built up.

Follow up work has been performed at the Technical University of Darmstadt to verify this hypothesis and propose mitigation measures.

A typical tray column using a physical solvent was modelled, initially in ASPEN Plus and then in ASPEN Plus Dynamics. The dynamic model was calibrated against typical performance of industrial plant. The initial hypothesis could be verified and further refined. A number of proposals for mitigation measures were investigated and evaluated. The understanding gained by this work will be applicable also to packed columns and chemical solvents, though in the latter case the model will need to be extended to include kinetic effects.

This paper describes the simulation work and the proposed mitigation measures. It also describes the proposed next steps to transfer these results to a physical setting.

Thermodynamic Possibilities and Constraints for the Regeneration of Spent Solid H_2S Sorbents Based on Ce-, La-, and Zn-Oxides

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Sorbents based on ZnO, Ce_2O_3, and $La_2O_3/La_2O_2CO_3$ can be used for deep, dry, medium/high temperature desulfurization of fuel gas or syngas. The spent solid sorbents from producer or syngas high/medium temperature desulfurization (sulfidation) processes can be regenerated generally by three methods: mild oxidation, reactions with steam (in fact the reverse sulfidation reaction) or by reactions with SO_2 leading to production of elemental sulfur. The problems in application of the oxidation reactions for spent sorbents include highly exothermic reactions, necessity to use higher temperatures to overcome formation of stable sulfates (e.g. $ZnSO_4$), oxy-sulfates (e.g. $La_2O_2SO_4$) and highly thermodynamically stable basic sulfates (e.g., $ZnO*2ZnSO_4$). Necessity to use relatively high temperature and precisely defined oxygen/sorbent molar ratio is usually a practical obstacle for highly selective conversion to reactive, reusable (non-sintered) oxide. In regeneration by steam, the highest conversions to H_2S are attained in regeneration of Ce-based sorbents due to formation of CeO_2. More advantageous regeneration reactions with steam are those with the decreasing number of moles of gaseous products, because in such a case the higher operation pressure in H_2S desorption has a beneficial effect. The thermodynamic analyses based on minimization of Gibbs energy for the systems are focused on suitable ways and conditions for regeneration of spent desulfurization sorbents from dry cleaning of producer gas in a temperature range 600 – 1200 K. Three sulfidic compounds (ZnS, Ce_2O_2S and La_2O_2S) were considered for regeneration to the corresponding oxides or oxy-carbonates by mild oxidation, reaction with SO_2 and reaction with water vapor or a mixture of water vapor and CO_2. Zinc sulfide can be regenerated practically only by mild oxidation either at O_2/ZnS molar ration around 1.5 at temperatures between approx. 950 and 1050 K or at temperatures over 1200 K at higher O_2/ZnS molar ratios. The temperatures of regeneration higher than 1100 K cause, however, sintering/changes of sorbent texture. At lower O_2/ZnS molar ratio (approx. below 1.4) and at temperatures above 1000 K, volatility of zinc (formation of Zn-vapors) is significant. The Ce_2O_2S-based spent cerium sorbents are advantageously regenerated by reaction with SO_2 at temperatures over 700 K (between 700 and 900 K). In this way CeO_2, elemental sulfur and small concentrations of S_2O are theoretically produced. Higher SO_2 concentrations in gas cause higher concentrations of S_2O formed in the regeneration process. If the spent Ce-sorbent contains also Ce-halides (e.g. $CeCl_3$), they are not decomposed by SO_2. In such a case regeneration by steam at temperatures over 800 K with formation of CeO_2 could be considered. The La-based spent sulfur sorbents (containing La_2O_2S) are preferably open to regeneration by reaction with CO_2 and H_2O vapor leading to formation of $La_2O_2CO_3$ and H_2S. The suitable operating conditions involve temperatures between 700 and 800 K and higher operating pressures (over 1 MPa). The regeneration of La_2O_2S by simple oxygen oxidation is complicated by formation of very stable oxy-sulfate $La_2O_2SO_4$. Regeneration of La_2O_2S by means of reaction with SO_2 is thermodynamically strongly limited.

Particle Fragmentation Behavior in a Bench Scale Entrained-Flow Coal-Water Slurry Gasifier

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Fragmentation behavior of coal char particles in an entrained-flow coal-water slurry gasifier is essential for the gasifier slag discharging process and the downstream syngas primary clean-up system. The phenomenon of particle fragmentation process occurring in the gasifier captured by a high speed video camera on a bench scale opposed multi-burner (OMB) gasifier illustrated that the secondary fragmentation behavior exists in the entrained-flow gasifier after the particles moving from high temperature impinging flame region to the gasification chamber outlet region. Particles larger than 200 μm in the impinging flame region have porosity structures with fragile shapes, while most of the particles smaller than 100 μm have spherical shapes. As long as the coal char particles move from the impinging flame region toward the gasification chamber outlet region, the primary fragmentation is almost finished in the impinging flame region and the secondary fragmentation is probably taken place as a result of percolative fragmentation and undergoing gasification reactions. The particle size distributions under different oxygen to carbon ratios (O/C) also indicate that there has a significant fragmentation when the particle size is larger than 200 μm.

SESSION 6
Coal Mining and Beneficiation - 1

The Product Yield Problem and the History and Future of Washability Analysis

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Most of the coal in South Africa is not of a high enough quality to use as raw coal domestically or as an export product. For this reason, coal in South Africa has been beneficiated since 1905 to produce useful products (Coulter, 1957; De Korte, 2010).

Mining companies and investors need to have confidence in the coal resource size, the amount of product that will be produced from the coal (the product yield), and how coal will perform in the beneficiation plant to enable appropriate plant design.

In recent years there have been examples where less than expected product yield was achieved, or where a plant could not produce the product it was meant to produce. In Moatize, Mozambique, product yield for coking coal was less than expected, one of the main reasons why a project, bought for about U$ 4 billion in 2011 was sold for about U$50 million in 2014. In 2013 it was reported in the press that a plant in the Limpopo coalfield, South Africa did not produce the expected coking coal product it was meant to produce.

Coal washability analysis or float and sinks analysis has generally been used to estimate if a certain coal quality can be attained soon after coal beneficiation started in 1905. Currently these analyses are extensively used as a standard method in the South African and worldwide coal industry to estimate coal quality and yield that may be attained from a raw coal. Coal float and sink analysis is a tedious (Leonard, 1979) time consuming process requiring at least one day to complete at a cost of around a US$1000 per simple analysis (Miller et al., 2001).

Recently, a method using X-ray computed tomography to determine coal washability online has been developed (Miller et al., 2001). This method is much faster and less costly than traditional float and sink analysis, and it has been proposed that if used online in plants it can help with the control of the plant and increase efficiency in product yield.

In spite of developments in float and sinks analysis the product yield problem (that is in practice obtaining less than expected product yield than was estimated by washability analysis from samples) frequently occurs. This paper will explore a more generalized definition of washability (Dorland et al., 2015) as well as a method to utilize this more general definition of washability to improve plant design information, as well as the prediction of product yield, especially within the South African context.

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Estimation of Moisture Dynamics within a Composite Coal Stockpile

Kyle Enslin, Chris van Alphen, Eskom; Walter Schmitz, University of Witwatersrand, SOUTH AFRICA

Justification of the project

The real, and unfortunately detrimental, effects wet coal can have on a power station first came to public light in 2008 when Eskom first started load shedding. Existing dewatering technologies such as mechanical and thermal driers are costly, thus, Eskom needs to investigate economical solutions to reduce the moisture content reaching its power stations. Coal stockpiles are seldom designed to be utilized as coal drying instruments. However, during times of wet coal this is often the case. Understanding the mechanisms that control coal moisture and coal stockpile drainage is crucial to better coal stockpile design, coal contract negotiation and coal stockpile operating. Taking advantage of a coal stockpile's natural drainage ability can afford Eskom cost savings by avoiding capital expenditure on dewatering technologies, reducing downtime and increasing efficiency.

Purpose

The purpose of this project is to investigate the factors controlling the moisture content and natural drainage characteristics of a composite coal stockpile. Better understanding what factors are at play and the effect these factors have on moisture content will aid Eskom in managing its coal stockpiles more effectively.

Theoretical framework

It is known in soil mechanics that a small amount of fines such as clay can greatly affect the permeability of a soil (Das, 2002). Williams and Whitton (2008) concluded that saturated and unsaturated soil mechanic principles can be applied to coals (ie: they behave similar to soils in terms of drainage and moisture retention). Sandamela (2014) also concluded that drainage rate and moisture content of a coal stockpile was controlled largely by fines content (-500micron). With this information the author endeavoured to establish a relationship between the fines content of a composite coal stockpile and its drainage rate and moisture content. The relationship was investigated by varying the fines content from 0% to 10% in 1% increments, saturating the sample with water, then allowing to drain. The drainage rate and moisture content (inherent, surface and total) was recorded for each test.

Results and conclusions

The inherent moisture, as expected, was fairly constant and varied between 1-2%. The total moisture increased as the surface moisture increased. The equilibrium total moisture varied between 4.08% and 7.27%. It was discovered that a linear relationship exists between surface moisture and fines content. For this particular coal it was discovered that 50% of the fines fraction (-500micron) consists of -50micron particles, meaning that just by removing the -50micron fraction the fines content would halve and result in a moisture content reduction of 1,5%. In conclusion, the fines content, just as in soils, is the leading control of drainage and moisture content. By being more intimately aware of the fines portion of a composite product coal, the potential drainage performance and moisture characteristics may be estimated.

Implications for Eskom and the power industry in Southern Africa

These results clearly show that by effective management of fines content the drainage and moisture retention of a composite coal stockpile can be improved. By utilising the natural drainage ability of a coal stockpile significant cost savings may be achieved by way of avoiding more common, expensive dewatering technologies and improving power station efficiency.

Seal Design Investigations for Omerler Underground Coal Mine in Turkey

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Western Lignite's Enterprises (GLI) under the branch of Turkish Coal Enterprises (TKI) located in Tuncbilek, Kutahya has been operated since 1940's. According to the current reserve estimation, the site has around 170 million tons of lignite. Annual production of the site reaches 4.2 million tons while 20% of that amount is met from underground mining. Omerler underground lignite mine producing around 1.000.000 tons of lignite from fully mechanized longwalls. Average thickness of lignite seams is 8 m to 9 m. Top caving system is used to produce 6-m thickness coal from the backside of hydraulic support system while the initial 3-m thickness of lignite produced from shearer. Seals are used to form a barrier to isolate abandoned working areas from the current production sites. 29 seals were constructed up to date for the underground mine. In this study, 29 seals were firstly classified based on construction material and cross-section area, and then classified seals were also evaluated based on seal thickness. 4 different types of seals were found in the underground mine while seal thicknesses were also changed as 45 cm, 50 cm, 70 cm, 100 cm. Reinforced concrete, brick, and aerated concrete blocks were used as construction materials. Engineering properties of construction materials as well as surrounding rock mass of the seals were also determined as a part of this study to evaluate the sufficiency of seals against collapse caused by explosion and/or in-situ stress-strain conditions. The following reasons are summarized to the requirement of re-design and evaluation of the existing permanent seals to protect the underground mine against any type of accidents. Excessive number of abandoned mining panels increases the stress over seals as well as the effect of depth that is around 150 m. The geological materials around the seals are mostly classified as poor or very poor. Space behind the seals were not filled up to 100 m for 21 number of the seals and that increases the risk of gas explosion or flood. The quality control of construction materials was not documented in the mine. Because of these, permanent seals designs were evaluated and re-designed in this study to protect the underground mine. The current design procedures proposed as per USA, UK, and German systems discussed in this study detailed were applied to evaluate the sufficiency of existing seals as well. As a result of this study, a new procedure to design permanent seals are proposed after evaluating and re-designing the existing permanent seals of Omerler Underground Lignite Mine.

SESSION 7
Clean Coal Demonstration and Commercial Projects - 2

The Future of Coal

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Coal has been the historic fuel for humans. The Romans started its use in 2nd century AD. For over 2000 years it met human needs from heating to cooking. It fueled the entire Industrial Revolution in Europe. In 1880 the British stretched its use to transportation, power generation, steel making and cement production. Every year around 1000M tons of Lignite coal is mined globally.

Environmental considerations have challenged the use of coal as a 21st century fuel. The slogan being: 'COAL WITH NO TOLL'. Mississippi Power has accepted this challenge by building the Kemper County Energy facility where state of the art Integrated Gasification Combined Cycle (IGCC) technology has been applied to produce 582 megawatt electric power, together with production of Sulphuric Acid and Anhydrous Ammonia while 65% of the emitted carbon dioxide will be captured and sold to the oil companies. Water will be recycled this will be the first coal plant with almost no emission which is expected to be in service in first half of 2016. Future of coal rests on the success of such technology initiatives. From 2nd century Rome to 21st century Mississippi coal as a fuel has come of age.

Status Update on the Kemper County IGCC Project

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

The Kemper County IGCC plant is a lignite-fueled 2-on-1 Integrated Gasification Combined-Cycle (IGCC) facility incorporating the air-blown Transport Integrated Gasification (TRIG™) technology jointly developed by Southern Company; KBR; and the United States Department of Energy (DOE) at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. The plant is owned by Mississippi Power Company (MPC) and has a calculated nameplate capacity of 830 MW with a peak net output of 582 MW. Incorporating advanced emissions-control equipment, the facility is designed to produce marketable products of ammonia, sulfuric acid, and carbon dioxide. Over 65% of the carbon dioxide will be captured and used for enhanced oil recovery (EOR), making the Kemper facility's carbon emissions comparable to those of a natural gas-fired combined cycle power plant. The Kemper County project team is currently completing startup/commissioning activities. The facility's Commercial Operation Date (COD) is set for the third quarter of 2016.

ITEA CCS Flameless Pressurized Oxy-Combustion: The Strategic Role of Intermediate Scale (50 MWth) Demonstration Units, Tailored on Local Quality and Low Rank Coals in Each Major Geographic Area, to Mature Technology in View of Industrial Exploitation

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

FPOC (Flameless Pressurized Oxy-Combustion) is gaining ground in coal-CCS competitive scenario thanks to its superior efficiency performance, flexibility, and favorable economics supported by figures of an industrial 350 MWe detailed engineering study.

No matter the demonstrated FPOC technology platform fuel flexibility at small scale (5 MWth) , the huge capital and apparent financial risk of a first-in kind industrial facility calls for intermediate scale demonstration units experience fully suited around the real case in re. In addition, FPOC validated small scale capability to manage low rank solid fuels requires specific, case by case direct demonstration experience to become bankable for industrial opportunities.

The intermediate scale demonstration facility is also the desirable field for helping OEMs and system manufactures to grow confidence of solution synergistic with the innovative FPOC technology, and to provide requested guaranties for future industrial units.

Therefore, the intermediate scale demonstration unit scope is not limited to a single units in the world which provides scalability data, but it becomes a tool specialized for local typical coals to serve the technology exploitation in a major geographical area.

Two FPOC intermediate scale demonstration unit initiatives are ongoing. Both are at feasibility study phase.

The one for European region is led by Sotacarbo-ENEA in cooperation with ITEA, with the support of Italian Government grants, to be located at Sulcis (Sardinia). Apart quality coal, the 50 MWth large pilot focus is for low ranking high sulfur, high ash content, coal, and for Polish lignite. Manifested interest in participating to the initiative have been already represented by Thermal Division-Institute of Power Engineering of Poland, and GE-NuovoPignone, at terms and condition to be defined within the feasibility study.

For North America, SwRI is leading the intermediate scale demonstration pilot initiative, teaming with EPRI and ITEA, potentially with the support of DOE grants for the feasibility study, for a location to be selected among the ones which already manifested interest in hosting the activity. The unit is specifically target to get evidence/validation of PRB, HV Illinois bituminous, Texas low&high Sodium lignite.

Process and technology set up of the two initiatives are presented, with focus on peculiar solutions for each case.

Shenhua Coal Refining Technology Development

Cliff Y. Guo, National Institute of Clean-and-low-carbon Energy, CHINA

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

The pilot plant was built in ShaanXi Yulin of China to demo the latest Coal Refining technology and ready for the test this fall. The successful demo of this technology will have significant impact on the clean and efficient utilization of LRC in China and world.

SESSION 8
Combustion Technologies - 2

Fuel Additive Efficient Coal Combustion Technology

Marc Ottolini, International Innovative Technologies Ltd.; William Nimmo, Syed Sheraz Daood, University of Sheffield, UNITED KINGDOM

High efficiency and low emissions from PF coal power stations has been the drive behind the development of present and future coal combustion technologies. Upgrading coal, capturing CO_2, reducing emissions of NOx, SO_2 and particulate matter, mitigating slagging, fouling and corrosion are the key objectives of these efficient coal technologies.

This study focuses on a newly developed fuel additive (Silanite™) technology, which addresses most of the aforementioned key points. Without the need to change the boiler installation this finely milled multi-oxide additive when mixed with pulverised coal has proven to increase the boiler efficiency whilst reducing NOx and particulate matter (dust) emissions and beneficiating the coal fly ash. This technology has been tested on a 233MW$_{th}$ water tube PF boiler as per EN BS 12952-15:2003. The fuel additive reduces NO emissions typically by 15%, improves combustion efficiency with up to 2%, reduces dust emissions by up to 20% and reduces the L.O.I of fly ash by 40%. This technology has also proven to be effective in combination with SNCR, taking the combined effect up to 50-65% NO reduction.

Based on the nature of the additive in theory it was expected that Silanite™ would have a neutral to advantageous effect on corrosion of the boiler. To validate this, the additive mixed with subbituminous coal fly ash was tested in a simplified yet effective corrosion test setup. The corrosion test facility with 6 silicon carbide electrically heated elements transversely placed in the top half of the furnace can modulate the temperature up to 1200^{o}C. A gas mixture skid supplied the humidified simulated combustion gas products (O_2: 3-4%, CO_2: 14-16%, HCl: 0.03-0.05%, SO_2: 0.13-0.15%, N_2: 75-78%, H_2O: 6-8%) inside the heated chamber. After surface preparation and having been coated with the base line fly ash and Silanite™ mixed fly ash T22 ferritic steel alloy (Cr: 2.25%, Mo: 1%) coupons were placed inside crucibles positioned in the heated compartment. These coupons were exposed to the simulated combustion gas environment for a (non-stop) duration of 1000 hrs. The preliminary rate of corrosion (mm/year) results using real fly ash samples from a full-scale PF boiler presented reference corrosion rates. This test showed that Silanite™ mixed coal fly ash coatings act as a protective layer in comparison with the base line coal fly ash coatings on a standard T22 alloy. The findings were reported based on the samples run in duplicate. The 94:06 coal fly ash to Silanite™ mass ratio coated samples produced corrosion rates of about 0.3-0.35 mm/y compared to 0.5-0.7 mm/y for the base line samples.

Impact of Biomass Co-Firing with Unreactive Coals in Pulverised Fuel

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Utilisation of coal in the global power generation market has been predicted to increase substantially over the coming decades, with higher efficiency production and clean technologies providing a low carbon energy market. An increase in coal combustion will lead to the necessity for burning more low rank and unreactive coals that result in high quantities of unburnt carbon within the waste ash. The potential to minimise the unburned carbon loss, by co-firing with biomass is an attractive option that would lead to lower emissions and higher energy outputs. The aim of this research is to determine to what extent additions of biomass can increase volatile yields, thus reducing ignition temperature, and improving char burn-out for a selection of unreactive bituminous coals.

This work has studied a range of industrially relevant biomass fuels which have been co-fired with unreactive coals in varied heating rate experiments at a blend ratio of 50:50 weight %. The biomass fuels were bagasse, eucalyptus, miscanthus, olive cake, wood and a steam exploded torriefied pellet, whilst the coal samples originated from South Africa and Wales. Under slow heating rates, experienced during Thermogravimetric Analysis (TGA), no synergistic effects were observed. In addition, ballistic heating rate experiments conducted in a TGA showed no synergistic effects. During the fast heating rate experiments, comparable to power generation conditions, achieved using a Drop Tube Furnace (DTF), variable synergistic effects were observed.

The slow heating rate experiments have been used as a baseline for which to quantify the effects observed during co-firing at the fast heating rates. The outcomes from slow heating rate experiments show an additive relationship with no catalysis occurring, whilst fast heating rates provide an increase in volatile matter yield compared to the predicted values. Further work is proposed to investigate the impact of varying blend ratio and temperature at fast heating rates.

Effects of Temperature on Physico-Chemical Characteristics Evolution of Rice Husk Char under Reburning Conditions

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Nitrogen Oxides (NO_x) and mercury are the major pollutants emitted from coal-fired power station, which leads to acid precipitation, photochemical smog, and heavy metal migration and transformation that impose a significant threat to the environment and human health. The combination of sorbent injection and flue gas conditioning bas been considered as a promising mercury emission control technology. However, the technology is not applied widely due to the limitation of sorbent cost and flue gas conditioning technology. Reburning has been considered as an economic and effective in-furnace NO_x control technology. Biomass fuels have been considered as ideal reburning fuels due to its renewable nature, CO_2-neutral character, and relative less contents of sulfur and toxic heavy metals (such as mercury), as well as relative abundant contents of AAEMs (Alkali and alkali earth metals, mainly K, Na, Ca, and Mg) and chlorine (Cl). It will form reasonable concentrations of AAEMs and Cl in the flue gas in biomass reburning process, which is benefit to promote NO reduction and mercury catalytic oxidation, and finally to achieve simultaneous control of NO_x and mercury in conventional air pollution control devices (APCDs). On the contrary, AAEMs and chlorine species bounded in biomass released during the thermo-chemical conversion process of pyrolysis, gasification and combustion may result in slagging and/or fouling problems for the operation of boiler heating surface areas and gas turbine blades in the gasification-based power generation cycles. Both biomass properties and pyrolysis conditions can affect the characteristics of element release and physico-chemical structure of biomass char. To our knowledge, there are few studies on physicochemical characteristics evolution under reburning condition. Therefore, it is necessary to understand the evolution of physico-chemical characteristics of biomass particles during reburning process.

In this paper, several biomass including cotton stalk (CS), maize stalk (MS), rice husk (RH), sunflower stalks (SS) and wheat stalks (WS) were pyrolyzed in an entrained flow reactor under reburning condition. The physico-chemical properties of pyrolyzed biomass (biomass char) were characterized by scanning electron microscopy - energy dispersive spectrometer (SEM-EDS), specific surface area and pore size analyzer, X-ray diffraction (XRD), X-ray fluorescence spectrometer (XRF), and Fourier transform infra-red (FTIR) spectroscopy, respectively. The effects of biomass species, reaction temperature in the reburning-zone, stoichiometric ratio in the reburning zone (SR2), residence time and the initial oxygen content in the simulated gas on evolution of physico-chemical characteristics of biomass char was analyzed. The mechanism of element release of biomass particles was discussed. The results indicated that release fraction of AAEMs of WS and RH is the largest, followed by MS and SS, and CS is the smallest. The release of AAEMs bound in rice husk (RH) is ordered as Na>K>Ca>Mg and there is a little change on all four AAEM species (Na, K, Mg and Ca) as the reaction temperature increasing from 850°C to 1050°C. Over 80% of Na and K and more than 90% of chlorine is released during biomass pyrolysis under reburning condition while reaction temperature is at 1150°C. The obtained results demonstrates there is a coupling effect on the release of AAEMs and chlorine. The specific surface area increases significantly with increasing the reaction temperature of 850-1150°C and micro pore fraction of biomass char is larger than 70% at temperature of 1150°C. The residence time has significant effect on pore structure parameters, the specific surface area of RH char increases from 13.35 m^2/g to 112.56 m^2/g while residence time increase from 0.5 s to 1.0 s. The surface area of CS char also increases with increasing the initial oxygen concentration in the flue gas. The functional groups decrease significantly with increasing the reaction temperature which indicates poor adsorption capability.

Low NO_X Coal Burner Temperature Profile Evaluation

Dewan Smit, Sandile Peta, Eskom; Walter Schmitz, Reshendren Naidoo, University of Witwatersrand, SOUTH AFRICA

Stringent worldwide emissions legislation, the drive to lower carbon emissions, together with the ever increasing demand to preserve the environment has led to a considerable demand for cleaner and more efficient coal combustion technologies. A primary technology for the reduction of emissions of oxides of nitrogen (NOx) is the installation of low NOx coal combustion burners. Extensive research into various burner characteristics and in particular the aerodynamic characteristics required to improve combustion performance of low NOx coal burners has been extensively undertaken and is ongoing.

In South Africa, the recent power supply and funding constraints limit the opportunity to perform utility-scale online coal burner analysis to make sensible adjustments. Computational fluid dynamics (CFD) is a definite tool to aid with analysis, design and development of pulverized coal combustion burners. This method is capable of providing detailed information on the distributions of temperature and chemical species and the behaviour of pulverized coal particles over the entire combustion spectrum that cannot easily be obtained by experimental or other means. CFD modelling offers a substantially lower cost solution and more importantly zero risk to production loss.

In this work the aerodynamic behaviour of a full scale, aerodynamically staged, single low-NOx coal burner was numerically investigated. The objective of the study was to develop a single low NOx burner CFD model in Ansys Fluent, to better characterize and understand the flame shape in terms of temperature profile, species distribution and ignition point. This could serve as a tool to assist with plant optimization, design proposals and occurrence investigations.

To have confidence in the single burner coal combustion CFD model, the results was compared to experimental data obtained from an operational low NOx coal burner during a pre-defined load condition. To improve on the single burner combustion CFD model results, drop tube furnace (DTF) experiments have been done to calculate the specific South African coal's single rate Arrhenius kinetic parameters (pre-exponential factor, activation energy) for the coal devolatilization and char burnout stage of the combustion process.

SESSION 9
Carbon Management - 2

Acid Gas Control by Dry Sorbent Injection in Air and Oxy-Fuel Combustion

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To reduce the impact of anthropogenic greenhouse gas emissions on the earth's climate, CO_2 capture and storage/utilization (CCS, CCU) technologies for coal-fired power generation were developed to concentrate the CO_2 for processing and sequestration/utilization. Oxy-fuel combustion is one of these CCS/CCU technologies. In oxy-fuel operation, coal is burned with a mixture of O_2 and recirculated flue gas, instead of air. The mixing of O_2 with recirculated flue gas is, among other issues, necessary to lower the temperature in the furnace which otherwise would exceed the limits of construction materials of the boiler. Due to the lack of flue gas dilution by airborne N_2, the concentrations of flue gas components such as CO_2, SO_2 and H_2O under oxy-fuel fired conditions increase considerably by a factor of around 4. Also the concentrations of HCl and of SO_3 that is formed by an oxidation of SO_2 were found to be increased in oxy-fuel combustion. Acid gas components are responsible for certain fouling problems and hot (e.g. superheater) and low temperature (e.g. air preheater, recycle lines) corrosion in power plants and due to their higher concentrations require careful attention in the oxy-fuel process. In oxy-fuel combustion, acid gas components ultimately need to be removed from the flue gas to produce a clean CO_2 product for transport and storage. Dry sorbent injection (DSI) for acid gas removal may be particularly interesting for the application within the oxy-fuel recycle loop, since it can avoid energy losses caused by excessive cooling of the recirculated flue gas in wet scrubbers and at the same time can remove the acidic gases that otherwise would condense and form corrosive solutions in the flue gas recycle line. DSI can be used as a measure to control the level of acid gases in an oxy-fuel boiler and recycle system and therefore can allow the application of high S and Cl fuels while operating the system within tolerable acid gas concentration limits. The presented experimental results aim to demonstrate the applicability of dry sorbent injection to control SO_2, SO_3 and HCl in oxy-fuel fired combustion processes. Also limitations of the application of the dry sorbent injection technology in oxy-fuel operation will be discussed.

Different mostly Ca-based sorbents have been injected at various locations in a 20 kW_{th} and a 500 kW_{th} pilot scale pulverized coal combustion test rig of Institute of Combustion and Power Plant Technology (IFK) of the University of Stuttgart. The sorbents limestone, different qualities of calcium hydroxide and Trona were tested in the two combustion test rigs that were fired with a high sulfur (2.7 wt%, daf) and high chlorine (0.3 wt%) US coal. Depending on sorbent and impurity to tackle, the sorbents were co-injected with the fuel, injected into the furnace at approx. 1100°C, or injected before an ESP or fabric filter. For the different experiments, SO_2, SO_3 and HCl abatement performance at various sorbent to impurity injection stoichiometries were determined. The tests have been performed under air and oxy-fuel fired conditions, allowing a comparison of the performance in these two combustion regimes. The presentation will focus on results from pilot scale (500 kWth) testing, but will also relate to results from smaller scale (20 kW_{th}) testing. All sorbents achieved good HCl and SO_2 removal performances. Particularly, in oxy-fuel operation, high SO_2 and HCl removal efficiencies were observed. For example, in-furnace injection of calcium hydroxide at a molar Ca/S ratio of 1 could remove approx. 60% of the SO_2 in the flue gas, while under air-fired conditions this was only about 40%. Also a good SO_3 removal performance was observed with capture efficiencies higher than 90% with a moderate sorbent injection amount. This shows that DSI techniques can be a means to control sulfur oxide concentrations of an oxy-fuel process to technologically tolerable levels.

Introduction to the Wyoming Integrated Test Center

Jason Begger, Wyoming Infrastructure Authority, USA

The creation of the Wyoming Integrated Test Center (ITC) was authorized in 2014. With the support and encouragement of Governor Matthew H. Mead, the Wyoming State Legislature allocated $15 million in funding to construct a post-combustion test center to study the capture, sequestration and management of carbon emissions from a Wyoming coal fired power plant. An additional $5 million commitment from private industry was required under the legislation, which has since been secured from the Tri-State Generation and Transmission Association in addition to $1 million pledged from the National Rural Electric Cooperative Association. Basin Electric is providing the host site as well as many additional in-kind contributions including engineers and construction management services.

The ITC will provide space for researchers to test CCUS technologies using 20 MW of coal combustion flue gas. Along with testing capture technologies, additional research will look at taking flue gas and turning it into a marketable commodity. The research at the ITC will lead to new opportunities in petrochemicals as well as other commercial uses of carbon dioxide. Research at the facility will help ensure the viability of the coal industry, which supports jobs, local and state economies and keeps electricity prices low for millions of people around the world.

In October 2015, Governor Mead announced that the ITC would be built at Basin Electric Power Cooperative's Dry Fork Station near Gillette, Wyoming. The Dry Fork Station is a state of the art coal-fired power plant operated by Basin Electric Cooperative. Pre-construction engineering and design work started in 2015 and the first phase of construction occurred in Spring 2016 to take advantage of the power plant's regularly scheduled maintenance shutdown. Additional engineering is ongoing with site preparation and other construction work to begin in the Fall of 2016. The ITC is scheduled to be completed in the Summer of 2017.

The Wyoming Infrastructure Authority is managing entity of the project.

Adsorption Characteristics of Bituminous Coal Seams in Zonguldak Basin

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Zonguldak Coal Basin, located on the Black Sea coast, is the main part of the Upper Carboniferous bituminous coal basin of Turkey. Much of the bituminous coal mining has thus been concentrated in the Zonguldak Basin. The estimated coal reserve, carried to 1200 m under sea level, is about $1.32x10^9$ tons of coal in this basin. 57 coal seams have been identified and 38 are workable with their thickness varying from 0.7 - 10 m and dips from 0 - 90°. The most important coal seams are the Cay and Acilik seams having average thickness of 6 and 4.5 m, respectively. Furthermore, the Sulu, Hacimemis, Domuzcu and Buyuk seams having an average thickness ranging from 1.5 m to 2.5 m are the other coal seams which are regarded as important for coal production. The aim of this study is to determine the gas adsorption characteristics of coal seams in the Zonguldak Basin. A number of samples were collected from 8 different seams. The adsorption characteristics of samples were measured and attempts made to correlate the results with different coal properties determined with the help of proximate analyses. Methane adsorption isotherms were measured at constant temperature of 25°C at different gas pressures up to 50 bar and the results were discussed in relation to the gas capacities of coal seams. Langmuir equation was used to interpret the adsorption isotherms. Results of the interpretation of the adsorption isotherms indicate that Langmuir (monolayer) adsorption capacity of coal seams varies between 10.3 m^3/t and 18.2 m^3/t. Although the respective data are highly scattered, a certain correlation could be defined between different coal properties and the adsorption capacity. The most apparent correlation is observed between the ash content and the gas adsorption capacity. The trends between Langmuir adsorption capacity and ash content are generally in accordance with the trends observed in other coal basins.

SESSION 10
Coal Science - 2

Determination of Rare Earth Elements (REE's) in Coals and their Associated Ash Products from Selected Localities in South Africa

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There is an increase in international demand for a variety of rare earth elements (REE's) (i.e. Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Th, Yb, and Lu) in modern electronic and related components. This has led to a desire to broaden extraction from both previously productive locations, such as China, and to expand extraction to new sources, possibly including coal and its ash products. The extraction of REE's from coal and/ or coal ash depends on a number of factors, one of the most important being the concentration of the elements in the feed coal and derived ash. Thus, it is vital to physically and chemically characterise coal that was used to generate coal ash which is believed to be a potential source of REE's.

The aim of the study is to determine the levels of REE's in three South African coals and their associated ash products, with the intention of identifying the viability of commercial extraction of these REE's from these base materials. Coal and coal ash were analysed using a variety of routine and advanced techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma-mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA).

Results obtained from XRD analysis show that coal samples were mainly composed of quartz (SiO2) and kaolinite [Al2Si2O5(OH)4], a minor amount of calcite (CaCO3) and muscovite [KAl2(Si3Al)O10(OH,F)2], and a trace amount of pyrite (FeS2), carlinite (Ti2S), nitranite (NaNO3) and nacrite [Al2Si2O5(OH)4]. The associated ash products were mainly composed of quartz (SiO2) and mullite (3Al2O3•2SiO2), a minor amount of albite (NaAl.Si3O8) and hematite (Fe2O3), and a trace amount of anorthite (CaAl2Si2O8), cristobalite (SiO2) and sillimanite (Al2SiO5). Results of REE's concentration in the coals and their associated ash products using SEM, ICP-MS/OES and INAA are pending.

Rare Earth Elements from Coal and Coal By-Products

Mary Anne Alvin, DOE/NETL, USA

Rare earth elements (REEs) are critical materials used in a broad range of technologies significant to national security, energy, medical, and consumer products. The Department of Energy's (DOE) Office of Fossil Energy (FE) and National Energy Technology Laboratory (NETL) have identified opportunities and benefits of recovering REEs from coal processing facilities, coal ash at power stations or haul-back sites, and by-product materials associated with coal deposits. Challenges are being addressed with respect to the development of technically feasible and economically viable separation processes, *in-situ* sensing and monitoring equipment, and environmental sustainability of recovery during the REE separation and extraction efforts.

NETL/FE's R&D program is focused on validating by 2025 one or more pilot-scale separation processes for recovering REEs from coal and/or coal by-products in forms that range from mixed metal pre-concentrates (2% or higher), to REE mischmetal (rare earth mixed alloy, near 100% purity), and readying potential co-production processes for commercial deployment. This paper provides an overview of the NETL/FE's REE separations program, describing efforts currently being conducted in collaboration with industry, university and National Laboratory participation.

Multifaceted Nanominerals and Ultrafine Particles in Phosphogypsum: A By-Product of Coal Cleaning Rejects

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Phosphogypsum ($CaSO_4{\cdot}2H_2O$), a by-product of phosphate rock processing, contains a large amount of impurities such P_2O_5, F, radioactive elements, organic substances, secondary nanominerals, and ultrafine particles (UFP) enriched in metals and metalloids. In this study, we examined phosphogypsum (PG) collected from abandoned fertilizer industry facility in south Brazil (Santa Catarina state). The fragile nature of nanominerals and UFP assemblages from fertilizer industry systems required novel techniques and experimental approaches. The investigation of the geochemistry of complex nanominerals and UFP assemblages was a prerequisite to accurately assess the environmental and human health risks of contaminants and cost-effective chemical and biogeological remediation strategies. Particular emphasis was placed on the study and characterization of the complex mixed nanominerals and UFP containing potentially toxic elements. Nanometer-sized phases in PG were characterised using energy-dispersive X-ray spectrometer (EDS), field-emission scanning electron microscope (FE-SEM), and high-resolution transmission electron microscopy (HR-TEM) images. The chemical composition and possible correlations with morphology of nanominerals and UFP, as well as aspects of nanominerals and UFP, were discussed in the context of human health exposure, as well as in relation to management of the nanominerals and UFP in PG environments.

Briquetting of Disk-Pelletized Fine Coal

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Forming wet coal fines into spherical pellets in a pan pelletizer before drying and briquetting can offer potential advantages over direct briquetting of the fines. These advantages include an agglomerate that is amenable to thermal drying on a conveyed bed, a more flowable feedstock for briquetting, and improved briquette durability stemming from a more consistent feed rate and/or more uniform blending of coal and binder. Accordingly, the work to be presented focuses on a comparison of briquettes made from air-dried coal fines, air-dried coal pellets, and thermally-dried coal pellets with the latter being briquetted both while hot and after cooling. Results for briquettes made with thermally-activated binders as well as the co-briquetting of biomass with the fine-coal pellets will also be discussed. These evaluations and comparisons demonstrate that improvements in the durability of coal or coal-biomass briquettes can be obtained with hot, thermally-dried coal pellets versus otherwise equivalent coal fines or coal pellets dried at ambient temperature.

SESSION 11
Gasification Technologies: UCG - 1

UCG – Unlocking Southern-Africa's Coal Potential: Update on the Africary's Theunissen Underground Coal Gasification (TUCG) Project in South-Africa

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African Carbon Energy (Africary) is putting South Africa at the forefront of Underground Coal Gasification (UCG) by developing a one billion-tonne coal deposit at Theunissen in the Free State to fill a vital gap in the country's electricity supply. Working to register as an Independent Power Producer (IPP) with the Department of Energy, Africary is championing a technique that had been commonplace several decades ago, and one which holds several advantages over conventional coal mining which has now become the mainstream.

Why UCG? Underground Coal Gasification is a mining method that extracts previously stranded coal reserves in-situ, through a gasification process by constructing at least two horizontal boreholes, where one borehole is used to inject air/oxygen to convert the coal into syngas and another to bring the syngas to surface. It is an economically and environmentally viable option for mining deep reserves (200 metres or deeper), and with two thirds of the planet's coal unable to be mined through conventional techniques it is the most promising technology for the future.

Africary Holdings (Pty) Ltd (Africary), is planning to establish an underground coal gasification (UCG) project in the Free State, South-Africa. The company has acquired prospecting rights for coal over an area of more than 300 square kilometres and has identified potential target areas for the establishment of a UCG project at a site located about 24 km north-north-west of Theunissen and 27 km south-south-west of Welkom in the Free State Province. The company has expertise in mining, gasification and power generation project development, specifically based on UCG and conventional coal mining.

The average annual selling price of local electricity has risen >60% from 2010 to 2015 and is set to rise further in the years to come, making power generation from gas produced by UCG competitive. The current project will involve gasification of ±5 million tons of in-situ coal over 20 years under an area of about 150 hectares and will generate >50 MW (nett) clean electricity to the grid from an installed gross capacity of ±77 MW (or ±31t/hr coal flow, ±2400 kmol/h wet gas and ±53kNm^3/h equivalent or >80 000kg/hr). The UCG process will operate with an average of 35% oxygen enriched air as agent feed to produce a clean Syngas with a heating value of >7MJ/m^{3}n at gas-engine intake.

Africary may become the world's first commercial UCG operator to supply electricity for base load power supply. The product of this application will transform the face of coal mining and electricity production in South-Africa to new future perspectives and heights. The project will be able to compete with coal-fired power generation without the need for any rebates, and with the increase in tariffs makes electricity generation with UCG cost competitive.

Once UCG is seen to be commercial acceptable, opportunities will arise for poly-generation, using the syngas to make diesel, fuels or chemicals. UCG not only turned out to be safer, but also more economical and more efficient.

The Queensland Underground Coal Gasification Pilots 2008-2016 – Evidence Based Assessment and Lessons in Government and Public Relations

Cliff Mallett, Carbon Energy Limited, AUSTRALIA

UCG trials commenced in late 1999 in Queensland when Linc Energy ignited a vertical well design at Chinchilla. By 2008 there were three active UCG companies, Linc Energy with new controlling ownership, Cougar Energy, a new company set up by the former principal of Linc Energy, and Carbon Energy, a company spun out of the national research organization CSIRO based on new technology CSIRO developed. All three companies held government mining licenses to conduct UCG activities.

This period coincided with a massive expansion of coal seam gas projects operating under petroleum licenses in the same coal deposits being used for UCG. Simultaneous development of UCG and CSG on the same coal deposit is not possible as UCG requires groundwater pressure to be present in the coal, and CSG extracts the water to lower groundwater pressure to release methane from the coal. Overlapping tenures for UCG (mining) and CSG (petroleum) were in conflict. Coal seam gas projects were promising investment of up to $60B, and exerted significant influence on government policy. In 2008 the Queensland government effectively placed a moratorium on commercial UCG by announcing UCG Pilots would be assessed on their environmental performance before a policy for commercial UCG would be promulgated. An Independent Scientific Panel (ISP) was appointed to assess the performance of the UCG Pilots. All three UCG companies participated in the pilot program necessitating selection of sites before exploration programs had been completed to identify optimal site conditions.

The Cougar site became the focus of local activists groups after an erroneous monitoring well sample result became public. The government responded to activists concerns and subsequently forced closure of the site. Aspects of the government's actions were strongly criticised in a subsequent investigation by the office of the Queensland Ombudsman. Cougar never reported to the ISP. Cougar initiated legal action against the Queensland government which was later abandoned for lack of funds, but has always maintained that it had caused no environmental harm.

The ISP reviewed reports on operations of Linc Energy and Carbon Energy and based on this evidence concluded that in principle UCG can be operated in an environmentally acceptable manner, but noted that neither operator had fully decommissioned or completed rehabilitation planning for their site. The government extended the review period and requested the two remaining Pilots to demonstrate decommissioning and rehabilitation planning. Carbon Energy completed the requirements of the ISP and submitted Decommissioning and Rehabilitation reports in 2014. These detailed the decommissioning of the Panel 2 cavity, cleaning the cavity with removal of 92% of pyrolysis products from the cavity, comprehensive investigations of the contamination remaining in the cavity and surrounding rocks, and a rehabilitation plan to restore organic contaminant levels to non-detect. No response has been provided by the government to these reports.

Linc Energy has not reported on decommissioning and rehabilitation yet. The government has launched a prosecution against Linc Energy claiming environmental harm. Court action is pending but Linc Energy has denied causing environmental harm. In April 2016 the Linc Energy company went into administration, and a week later without any industry consultation the government announced a ban on UCG in Queensland. In the press release it made reference to difficulties with Cougar Energy and Linc Energy, neither of which have yet been confirmed by disputed court proceedings. There was no comment on the apparently successful operations of Carbon Energy.

Leaching of Metals from Post-Underground Coal Gasification Cavity Residues

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Underground coal gasification process is accompanied by the generation of organic and inorganic waste therefore the threat of ground water pollution is the dominant environmental concern during and after UCG technology implementation. The potential environmental problem have been reported in the 1980s and 1990s as well as recently by Queensland Government, Australia. In the post-reaction cavity formed as a result of the underground coal gasification a part of the solid products remain as ash residue or carbon chars. Particularly little is known about inorganic pollutants so research on metal elution from the cavity residues seems to be necessary for understanding a possible water contamination.

The aim of this study was to examine whether water entering the post-reaction area after underground coal gasification (UCG) leaches metals from the post-processing waste in the cavity to such a degree that it can pose a threat to the environment.

The work presents a comparison of chosen metal elution from cavern residue after underground coal gasification and from the ash obtained during combustion of the same samples of coal in a boiler. The influence of coal rank (hard coal and lignite are compared) on metal leaching behaviour is demonstrated. Also the influence of the range of water mineralization on metal elution is shown. The usefulness of the data for metals spreading in modeling works is proposed.

It has been found that the major and trace metals present in coal after the completion of the UCG process may be eluted after gasification by incoming groundwater. The majority of tested elements tend to be leached in a stronger degree from ash residues than from chars. Metals present in the ash derived from burned coal (B, Al, Cr, Co and Mo - with the exception of brown coal ash) exhibited a greater affinity for the aqueous phase than did the metals present in the ash from UCG. In comparison with the residues from hard coal, the residues of gasified lignite show the higher relation to the water phase.

The presence of such elements as Cr, Pb in eluates may suggest that toxic metals are able to leach to water from the residues of the gasification process and that there might occur a non-negligible risk of environment contamination.

Based on the results of this study, one can conclude that the intensity of metal elution from gasification residues depends not only on the degree of coal conversion and the type of structure into which the metals are bonded (mineral and organic coal matter) and the volatility of the various metals but also on the gasification (combustion) conditions, such as the gasifying agent used, temperature and operating pressure.

Coupled Thermo-Chemical-Mechanical Modelling of Cavity Growth and Farfield Geomechanical Assessment in Underground Coal Gasification

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This paper will present the recent findings of an EU 7th Framework Programme funded international research project, which is aimed at integrating field, laboratory and numerical modelling approaches in order to address a number of technology gaps in the field of Underground Coal Gasification (UCG). An integrated simulation methodology, which considers the thermal, chemical and geomechanical processes taking place during UCG cavity growth is developed and implemented. The cavity growth model results are then used in modelling the geomechanical behaviour of the roof/floor strata in a coalfield. A number of geologically representative UCG scenarios modelled aim at evaluating potential impacts on local hydrology and surface subsidence, as well as determining the optimal panel sizes for different coal types, thicknesses and panel depths below the surface.

The simulation methodology is based on coupling two industry standard simulators, Advanced System for Process ENgineering (ASPEN) Plus, used for the thermo-chemical simulation, and FLAC3D^{TM}, which enables the thermo-mechanical simulation of the UCG process. The coupling of the two simulation tools is achieved through sequential interchange of data. Principally, the Aspen Plus model simulates the chemical processes taking place in the coal seam and focuses on the thermodynamic, mass and heat transfer modelling components in order to calculate the amount of produced heat, as well as gas under restricted Gibbs minimisation and equilibrium conditions. In addition to the different chemical reactors that constitute the Aspen Plus model constructed, calculator blocks written in Fortran code were introduced to regulate modelling performance in line with experimental data, which is provided by the laboratory experiments carried out by Central Mining Institute (GIG) in a large scale high pressure UCG reactor capable of testing 0.4x0.4x3.5m coal blocks at up to 1,600 ^{o}C and 5.0 MPa. The FLAC3D^{TM} model is designed to reflect the realistic 3D spatial features of a gasified coal seam underground. Using input data computed in Aspen Plus, the FLAC3D^{TM} code produces the resulting thermo-mechanical stress distributions on the coal seam and the surrounding strata, taking account of both mechanical failure and coal spalling effects, heat transfer rates within the cavity and the surrounding strata, and provide updated input parameters which are returned to the Aspen Plus model. The cavity growth modelling results include the extent and the growth rate of the developing UCG cavity given the specified operational parameters such as the coal characteristics (e.g. composition, formation thickness, depth), the composition of reagents injected (i.e. air, oxygen, steam) and the feed rate, the pressure, the gasification and the combustion temperatures. Based upon the cavity geometries obtained for different coal seam and operational scenarios, large-scale (including the whole overburden) geomechanical modelling is carried out to evaluate strata behaviour and its impact on UCG panel designs and the environment.

SESSION 12
Coal Mining and Beneficiation - 2

Avdan Lignite Mine Open Pit Planning and Design Studies for Thermal Power Plant

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Sustainability of a thermal power plant shall be conditioned by a well-planned coal mine production. According to thermal power plant capacity, annual production target should be decided based on the quality of coal deposit. Average lower calorific value of coal deposit can be used to calculate the annual production target. Once the target is resolved, mine planning and design studies can be initiated, and the first selection must be performed between open pit and underground mining production. In this study, Avdan lignite site located in the western part of Denizli, Turkey was selected as a case study area. Average lower calorific value is modelled based on the geostatistical applications and determined as 1,719 kcal/kg while resource and reserve calculations were also performed by using integrated mining software and found as 30.5 MTon and 26.4 MTon, successively. The capacity of the thermal power plant is decided as 150 MWe, so annual lignite production target is selected as 1.5 MTon/year based on the thermal plan capacity assumptions that will be discussed in this paper in detail. Open pit mine is selected as production method due to the depth and economic reasons. Firstly geotechnical and slope stability investigations were applied at the site to design bench and overall slope geometrical properties such as bench height, width, angle, and overall slope angle related with the production depth. Once the stability studies are completed, planning and design studies then can be commenced. Optimization should be performed to select the most suitable place for initial production location minimizing the stripping ratio especially in the early years of the production to reduce the duration for returning on investment earlier. Design and planning studies although it is involuntarily is like a trial-and-error method to lower the stripping ratio that is the most important factor for unit cost of a production as well as investment amount. After a series of trial-and-error studies based on optimization techniques, open pit mine planning projects were performed annually for the first 5 years of the production, and the rest of the production planning projects were performed based on 5 years' production target. According to the reserve and production target, open pit mine will serve to the thermal power plant nearly for 18 years. Final open pit limit and design was also performed in the study as a main output of this research. Target and designed production amount as well as annual and cumulative stripping amount were determined according to all open pit mine planning and design studies. Finally, 26.4 MTons of coal will be produced after stripping 380 Mm^3 overburden and 50 Mm^3 interburden materials in 18 years that makes this project will be important open pit mine project in the western part of Turkey to supply coal for the 150 MWe capacity thermal power plant.

Modelling a Multi-Layer Coal Mine Deposit: A Case Study of Avdan Lignite Site in Denizli, Turkey

Mohammad Lashgari, Murat Ozkan, C. Atilla Ozturk, Selamet Ercelebi, Istanbul Technical University; Mustafa Darici, Anadolu Mining Co., TURKEY

Coal is one of the most important sources for energy production in all over the world. Sustainability of energy production from a thermal power plant should be correlated with reserve quality and quantity of coal deposit. Reserve quantity and quality must be determined from innovative approaches to decrease risk arising from ore body modelling. Geological formation of the coal deposit can be assumed as the initial stage for coal deposit research. Coal deposit can be found as vein, lake, or delta types based on the location, geological background and evolution. Understanding the geological background of coal deposit is useful for estimating possible development of coal deposit based on the location. Vein type coal deposits are the easiest to model due to the continuity while delta types are the most complex structures. Interburden defined as the material separating coal seams within strata is also continuous for vein type coals while several interburdens can be found randomly in coal band alternation for delta type deposit. Different veins in a single coal deposit can be correlated based on whole coal dating however it is hard to correlate the several different coal bands in a single delta type coal deposit. Avdan lignite mine deposit is located in the western part of Turkey. This deposit is important to supply coal for a 150 MWe capacity thermal power plant located close to the mine site nearly for 25 years. The lignite mine will be operated by open pit mining based on the feasibility project carried out for thermal power plant. The deposit is delta type that was a challenging study for modelling ore body. A database was formed from 103 drill logs in the study area for modelling the coal deposit. Maximum distance between the drill logs is prevented to exceed more than 250 m to obtain coal deposit reserve classification as per measured coal resource. Border of the coal deposit was defined from the database based on the geological structure. Cut-off values for minimum coal thickness and lowest calorific value are selected as 40 cm and 950 kcal/kg during the coal deposit modelling. These values were selected as per production method as well as thermal power plant technology. Afterwards, database was used to model the coal structures in the lignite zones. Two main coal structures that are named as Sekkoy and Yenidere Coal Zones were derived from the investigations. Due to the impossibility of correlations among the coal bands, coal zones were defined for these two main coal structures. Coal zone definitions that are the most innovative aspect of this research would be useful to determine the quantity of the coal reserve for the different coal zones in the study area. Hence, although it was not possible to correlate coal bands from one drill log to the other, it is possible to design the coal zones as well as the coal thickness that must be required for reserve estimation. On the other hand, the quality of the deposit based on calorific value, humidity, ash, and sulphur was also determined for each coal zone from geostatistical research. Thereby, quality distribution maps as well as calorific value and reserve estimation graph were also designed for the study area. Integrated mining software packages were used to model delta type coal deposit as well as geostatistical applications to obtain quality distribution maps.

Mineral Matter in Coals from the Soutpansberg Coalfield, South Africa

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This paper aims to study and characterize mineral matter that is found in samples from the Soutpansberg coalfield, Limpopo Province, South Africa. An understanding of the mineral matter abundance and composition is of importance, as studying these can indicate the sedimentological and geochemical history of peat and coal forming environments. Studies done on the mineral matter can provide knowledge that can also be used to assess how different coals behave when undergoing utilization processes (Ward, 2002).

Samples were collected from Coal of Africa‘s Makhado project areas in the Soutpansberg coalfield. Petrographic analyses, proximate, total sulphur, X Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and electron microprobe analyses were conducted on these samples. The studied coals were characterized by relatively high ash, total sulphur, volatile matter contents, and low moisture and calorific values. The coal is Medium Rank C and is very rich in vitrinite. Petrographically, three different mineral groups were identified: silicates, carbonates, and sulphides. The mineral in the coal samples show evidence of both syngenetic and epigenetic mode of occurrence.

Petrographic studies using a Zeiss Axio Imager M2M retrofitted with Hilgers Diskus Fossil system microscope indicates that the silicates are mainly clays and quartz, with the clay minerals occurring as mainly as aggregates, cell and cavity infilling the vitrinite macerals. The clay minerals were identified as kaolinite by XRD. The quartz is sub-rounded to rounded and it occurs bound within the maceral matrix. Different types of pyrite were identified: infilling cell or pore structures, massive, framboidal, euhedral, infilling cracks, and replacing siderite nodules. The first four types mentioned indicate a syngenetic origin, whereas the last two types indicates an epigenetic origin. Framboidal pyrite with concentric ring formations have also been determined in some samples. From the SEM analysis, the concentric rings are still pyrite but have a slightly lower Fe content than the framboidal pyrite centre, and Ni was detected.

The carbonates present are siderite and calcite. The siderite occurs as nodules which could possibly be syngenetic in nature, and the calcite infills cracks in vitrinite (thus being epigenetic in origin). There are some siderite nodules that are being replaced pyrite, with some grains totally replaced and some still preserving the siderite. XRD and SEM studies showed the presents of dolomite and ankerite. Ankerite mineral is found associated with the concentric rings surrounding framboidal pyrite in cleats, as identified by the electron microprobe.

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Assessing Risks Related to Stimulation of Firedamp Drainage Boreholes in Order to Recommend Prevention Measures and Monitoring Methods to Help Early Risk Management during Design of Future Drainage Projects

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Coal mining in Europe is extending to deeper and deeper levels, facing ever increasing coal seam methane contents and much higher methane emissions at production districts. Methane emissions raise a serious safety problem but also limit production advancement rates. Current drainage and pre-drainage methods applied in European coal mines are not sufficiently effective to face growing risks related to methane emissions. Therefore, in order to improve safety and increase production rates, it is essential to develop new gas control and drainage techniques.

The Research fund for coal and steel of the European commission funds the GASDRAIN project between July 2014 and June 2018. The main objective of this project is to investigate stimulation techniques to improve drainage efficiency by increasing the permeability in the vicinity of firedamp drainage boreholes. As all stimulation techniques cannot be appropriate to all coal seams and mining conditions, 4 techniques are investigated by GASDRAIN partners. They are: hydraulic fracturing, open or cased hole cavitation, high pressure water jet slotting and use of explosives.

Application of these stimulation techniques induces risks during stimulation process but also later during mining of stimulated/fractured coal seams or rock strata. For instance, self-heating of coal and spontaneous combustion are possible risks due to penetration of oxygenated air within coal seams or rock strata through fractures created by stimulation.

Thus, a detailed risk analysis related to the use of the 4 stimulation techniques has thus been carried out. Firstly, all relevant incidents associated with stimulation of firedamp drainage boreholes have been identified through a bibliographical review and by collecting feedback from partners of the project through a questionnaire. Then, a core set of relevant risk scenarios has been defined and was represented with a bow-tie diagram (or event tree). Best practice measures to prevent and mitigate the risks (i.e. safety barriers) have also been selected.

Authors will detail results from the detailed risk analysis (relevant incidents, bow-tie diagram) and present recommendations on prevention measures or monitoring methods which can help early risk management during design of future drainage projects in European coal mines.

SESSION 13
Clean Coal Demonstration and Commercial Projects - 3

Illinois Industrial Carbon Capture and Storage Project

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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_2 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_2 is in north central Illinois. Because of the excellent regional geology and access to industrial scale quantities of CO_2, 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_2 emissions into the Mount Simon; safely, permanently, and economically for hundreds of years.

Illinois Basin - Decatur Project (IBDP), (Status- Post injection site monitoring). This project is led by Illinois State Geological Survey (ISGS), under the Midwest Geological Sequestration Consortium (MGSC) Regional Carbon Sequestration Program, and is a large-volume, saline reservoir sequestration test that injected 333,000 tonnes/yr of CO_2 for three years reaching its storage target of 1.0 million tonnes in November 2014. The project is currently conducting post injection site monitoring and data analysis.

Illinois Industrial Carbon Capture and Storage Project (IL-ICCS), (Status-Commissioning/Injection Authorization). This project is led by ADM and expands the sites CO_2 injection and storage capability to that of a commercial-scale operation with the ability to capture, inject, and store over 1.0 million tonnes per year. In December 2014, ADM received the nation’s first Class VI Underground Injection Control permit. This permit classification was specifically developed for the subsurface storage of CO_2 within the United States. In September 2015, the project completed all construction activities and is working with the USEPA on their review of the completion reports and evaluation of the pre-injection test data needed to finalize the permit’s five year operating and monitoring conditions. Start-up is expected during the first half of 2016. The focus of this presentation will be to update the status and report the results from these first generation, commercial scale, carbon dioxide capture and storage projects.

Process Optimization and Solvent Reclaiming Enhanced the Operation and Production of an Existing 800 Tonnes Per Day Plant Capturing CO_2 From Flue Gases of a Coal-Fired Power Plant

Ahmed Aboudheir, Lionel Kambeitz, HTC Purenergy, CANADA

A rate-based model has been formulated to predict the actual behavior and performance of the existing 800 tonne per day carbon dioxide (CO_2) capture plant. This plant is using 20 wt% monoethanolamine solutions (MEA) to capture CO_2 from flue gases of a coal-fired power plant. The CO_2 capture process configuration is a two train configuration: two absorbers and two strippers with a common surge/make-up amine tank. This CO_2 capture plant is in operation by Sealers Valley Minerals (SVM) for more than 35 years in Trona, California, USA. Due to the symmetry of the two trains, the model is built to simulate one train of the CO_2 capture plant using actual plant equipment constraints and operating parameters, such as the flue gas rate/composition, solvent rate/composition, HSS content in the solvent, steam supply and conditions of steam, etc. Comprehensive material and energy balances were produced using the HTC’s Process Design & Optimization modeling tools, PDOengine™. The average absolute deviation of the predicted parameters from the actual measured parameters is less than ± 7%.

The model is also used to plan the operating conditions for optimum utilization of the resources; such as material, utilities, and production capacity. The four main findings of improvement for the plant without major extra capital expenditures or modification for the plant equipment are: (1) Increasing the MEA concentration to 25wt% from 20wt% will reduce the solvent circulation rate by 7% and decrease the reboiler steam consumption by 5%; (2) Relaxing the solvent loading approach will reduce the reboiler steam consumption by additional 5%; (3) Reducing the flue gas temperature from 136 °F to 113 °F will improve the plant water balance, reduce the solvent circulation rate by 12%, and reduce the steam consumption by 14%; (4) Changing the existing packing from 2 inches plastic Pall Ring to metal IMTP #40 will improve the working capacity by 56%, reduce circulation rate by 30%, and reduce reboiler steam consumption by 21%.

Having an effective online solvent reclaiming unit within the process of CO_2 capture from flue gases produced at coal-fired Power Plants will contribute to the safe and cost-effective operation of the CO_2 capture plant. Applying the online solvent reclaiming process maintains the CO_2 capture plant's production capacity and assists in minimizing operational problems, such as corrosion, foaming, and fouling. Minimizing these problems will reduce the operating costs and the long-term plant deferred maintenance. Most of the chemical solvents used in the CO_2 post combustion capturing process require reclaiming in order to maintain the solvent absorption efficiency and to minimize some operation problems caused by degradation products, heat stable salts and other impurities accumulated in the solvent. Delta Purification designed and manufactured a unique Solvent Reclaimer that can remove all high-boiling degradation products, ionic species, impurities and fine suspended solids from the chemical solvents. The Delta Solvent Reclaimer™ process is proven to be less capital cost, less operating cost, less waste for disposal, and less utility consumption. It is simple to operate and maintain, has high recovery rates of solvent, it reclaims efficiently singe & mixed alkanolamines, and formulated solvents.

The advantages of using the Delta Solvent Reclaimer can be seen from the results and findings of our operations at this 800 tonnes per day capturing CO_2 from coal-fired power plant flue gas. The Delta Solvent Reclaimer is able to reclaim contaminated solvent even under excessively contaminated conditions with a recovery rate as high as 98% and restore the solvent to near its original purity; colorless, 17 wt% MEA, and minimum HSS. The average consumption of low pressure, saturated steam at 40 psig, is 1.0 lb steam per lb of recovered amine. The concentrated waste was periodically collected while the reclaimer process was in continuous operation. Concentrating the waste is the approach that contributed to the huge reduction of the quantity of the waste collected for disposal.

Optimization of an Existing 130 Tonnes per Day Plant Capturing CO_2 From Flue Gases of a Coal-Fired Power Plant

Ahmed Aboudheir, Lionel Kambeitz, HTC Purenergy, CANADA

An optimization study has been conducted on an existing 130 tonne per day carbon dioxide capture plant. The CO_2 technology implemented in this plant that has operated for over 15 years is based on a conventional process configuration using 16-17 wt% MEA solvent.

A slipstream of 5-6% of the flue gas is being taken from the coal power plant and sent to CO_2 capture plant through two blowers operating at 60% capacity. The flue gas enters the CO_2 recovery facility at the flue gas scrubber in order to reduce the sulfur dioxide (SO_2) concentration to less than 10 ppmv. The flue gas is further cooled to 40 ºC before entering the amine absorber column. The major equipment in the plant include SO_2 scrubber, flue gas cooler, CO_2 absorption column, solvent stripper column, solvent reclaimer, and filtration system. The captured CO_2 is then sent to the purification and liquefaction package for food grade applications.

A rate-based modelling approach is used to simulate the performance of the CO_2 capture plant using actual plant process flowsheet and operating parameters. Comprehensive material and energy balances were produced using the HTC's Process Design & Optimization modeling tools, PDOengine™. The average absolute deviation of the predicted parameters from the measured parameters is within ± 8%.

The developed rate-based model is then used to plan the operating conditions for optimum utilization of the resources. Based on the results obtained from the process optimization, it is possible to minimize the operating cost and enhance the production capacity of the CO_2 capture plant at minimum additional investment. The four main findings of improvement for the plant without major extra capital expenditures or modification of the plant equipment are:

(1) For the current CO_2 production capacity, the optimum solvent rate is 128.3 m^3/hr instead of 159 m^3/hr while maintaining the same production capacity. This can be achieved by increasing the solvent working capacity from 0.301 to 0.361 mol/mol. This will reduce the specific steam consumption from 3.17 to 2.59 kg/kg and the power requirement of re-circulating pumps by 19%. No additional capital expenditure is required to achieve these benefits.

(2) Changing the solvent concentration from 16 to 20 wt% will reduce the solvent circulation rate by 40% and steam requirement by 21%. This will significantly reduce the operating expenses of the plant without any additional capital expenditure.

(3) As the blowers are operating at 60% capacity, increasing gas flow rate up to 30% within the hydraulic capacity of the absorber will increase the production capacity by 28 TPD.

(4) Changing the absorber column packing from 2-inch pall ring to high performance IMTP40 and increasing flue gas rate by 30% will increase production capacity by 38 TPD and reduce reboiler steam consumption by 22% from the base case.

The U.S. Department of Energy's Current Portfolio of Major Fossil Energy Demonstration Projects

Thomas A. Sarkus, Diane Madden, Theodore J. McMahon, Anthony Zinn, Sai Gollakota, Venkat Venkataraman, Nelson Rekos, DOE/NETL, USA

The U.S. Department of Energy's National Energy Technology Laboratory is funding four active major demonstration projects aimed at proving CO_2 capture and geologic storage technologies at commercial scale. Taken together, these four projects are demonstrating a suite of commercial-scale CO_2 capture systems and geologic storage regimes. They carry a combined total value of approximately $8.6 billion, with DOE's cost share being approximately $1.0 billion (or 12%).

- Petra Nova's 240 MWe Post-Combustion CO_2 Capture & Sequestration Project at NRG Energy's W.A. Parish Station in Thompsons, Texas, will become the world's largest CO_2 capture and storage project retrofitted onto an existing coal-fired power plant when it enters commercial service in early-2017. *CO_2 capacity:* 1,400,000 metric tons/year; *Total est. cost:* $1 billion; *DOE cost share:* $190 million (or 19%); *Status:* Construction; *Anticipated Commercial Operations:* Early-2017.
- Southern Company's 582 MWe (net) Kemper County Integrated Gasification Combined-Cycle (IGCC) plant near Liberty, Mississippi is a lignite-fueled IGCC power plant based upon the air-blown Transport Integrated Gasification (TRIG™) technology. *CO_2 capacity:* 3,000,000 metric tons/year; *Total est. cost:* $6.97 billion (including new lignite mine & CO_2 connector pipeline); *DOE cost share:* $407 million (or 6%); *Status:* Construction; *Anticipated Commercial Operations:* Late-2016.
- Air Products & Chemicals' Demonstration of Steam Methane Reforming (SMR) with CO_2 Capture has been operating on two commercial SMR units for over 3 years in Port Arthur, Texas. *CO_2 capacity:* 925,000 metric tons/year; *Total est. cost:* $431 million; *DOE cost share:* $284 million (or 66%); *Status:* Operational (nearly 3 million metric tons of CO_2 captured and stored, to date); *Commercial Operations Date:* Dec. 16, 2012.
- Archer Daniels Midland's (ADM's) demonstration of CO_2 Capture from Biofuels Production & Storage into the Mt. Simon Sandstone involves a 2,000 ton/day CO_2 collection, dehydration and compression facility at ADM's biofuels plant in Decatur, Illinois, which will supplement a 1,000 ton/day facility that operated from 2011 to 2014 under a separate DOE-funded research and development project with the Midwest Geological Sequestration Consortium. *CO_2 capacity:* 900,000 metric tons/year; *Total est. cost:* $208 million; *DOE cost share: $*141 million (or 68%); *Status:* Construction/Permitting; *Anticipated Commercial Operations:* Early-2017.

All four projects represent major engineering accomplishments in terms of demonstrating clean energy technology. Because the Kemper IGCC and ADM projects will be presented separately, this presentation will summarize those two projects and focus mainly on describing and updating the Petra Nova and Air Products SMR demonstration projects.

SESSION 14
Combustion Technologies - 3

Vapor Phase Chemical Looping Combustion of Coal

Tomasz Wiltowski, Debalina Dasgupta, Kanchan Mondal, Quan Zhang, Southern Illinois University, USA

Chemical looping combustion is one of the most promising technologies that can efficiently utilize fossil fuel while capturing CO2 with a lower energy penalty and thus a lower cost. In general, pure or mixed metal oxides are used as the oxygen carriers and looped. When using gaseous or liquid fuels, this method is quite effective except for the longevity of the solid. However, when used with a solid fuel like coal, issues of slow kinetics, oxide-ash separation as well as oxide longevity have to be resolved. Chemical Looping Oxygen Uncoupling materials are now being considered to recreate the gas-solid reaction system with some success. Nonetheless, the carrier-ash separation and carrier robustness are still significant hurdles. The authors have conceptualized the "Vapor Phase Chemical Looping" combustion technology that would obviate the hurdles of traditional chemical looping. Here, the oxygen carrier is a metal oxide which is in the vapor phase under the fuel reactor conditions but the reduced for of the metal oxide is a solid under the same conditions. Thus, in the fuel reactor, the metal oxide vapors and the coal react as in a gas –solid reaction, thereby ensuring fast kinetics. The reacted metal oxide in its reduced form precipitates on the ash. The ash-reduced carrier is then moved to the air-reactor where the carrier is re-oxidized. The ash-carrier is then moved to a third separation chamber where the solids are heated to produce the metal oxide vapors that are fed to the fuel reactor. This simple act of heating separates the ash from the metal oxide completely. Finally, it must be noted that the metal oxide is in its vapor form, i.e. molecular form, and issues, such as pore structure and surface activity, that affect the carrier longevity are nonexistent. The authors have identified a few candidate materials and have experiments on one of the candidates have already proven successful. The conceptual design, the materials and energy balance, as well as some preliminary results from the proof of concept studies will be presented.

Copper-Based Chemical Looping with Oxygen Uncoupling: Process Development, Reactor Scale-Up, Pilot-Scale Studies and System Modeling

Kevin J. Whitty, Matthew A. Hamilton, Kirsten M. Merritt, Kyle O'Malley, Shakar Ali, Emir Rahislic, Andrew R. Fry, JoAnn S. Lighty, The University of Utah, USA

The University of Utah has been researching and developing chemical looping with oxygen uncoupling of coal since 2007, focusing on copper-based carriers and a system configuration based on two interconnected circulating fluidized bed reactors. R&D has combined fundamental experiments with operation of CLOU reactor systems at various scales and computational simulations for performance evaluation and reactor scale-up. Development has progressed from small lab scale through bench scale with a 10 kW dual bed research reactor, to semi-pilot scale with a recently-inaugurated 220 kW chemical looping combustion process development unit (PDU).

One of the challenges of scaling up copper-based CLOU technology is acquiring enough oxygen carrier material to support operation in larger reactor systems. The Utah CLC PDU, for example, requires 150-200 kg of inventory, so the oxygen carrier must be readily available in large quantities at comparatively low cost. Because no supplier has been identified that can affordably deliver 1+ tons of copper-based oxygen carrier material, an inexpensive oxygen carrier material has been developed in-house and the carrier production process has been scaled to produce large quantities of material sufficient for the 220 kW PDU.

This presentation describes development of the CLOU process at the University of Utah, including evaluation of fundamental processes key to performance of CLOU, modeling and scale-up of the process, large-scale production of copper-based oxygen carrier material and experience to date operating the world's largest dedicated CLOU reactor.

A Study on the Mineral Liberation and Transformations During Pulverised Bituminous Coal Combustion

Laurence Silvester, Cheng-gong Sun, Colin Snape, Hao Liu, Ofonime Udoudo, University of Nottingham; William Livingston, Doosan Babcock Energy Limited, UNITED KINGDOM

Ash deposition is a major cause of reduced boiler efficiency and unscheduled shutdowns from induced blockage, corrosion and erosion in pulverised coal fired boilers[1, 2]. A detailed understanding of the ash formation mechanism due to the inorganic minerals in coal is the first step in predicting the ash deposition behaviour on convective heat transfer surfaces. This study investigates the mineral liberation and transformations of six pulverised bituminous coals during devolatilisation and subsequent combustion at 1450℃ in a laboratory-scale drop tube furnace (DTF). The mineral properties of the coals and derived chars and ashes will be examined with mineral liberation analysis (MLA) to identify mineral transformation, morphological and particle liberation changes. X-ray diffraction (XRD) will be used to qualitatively validate the coal mineral phases. The physical changes due to devolatilisation and combustion will be determined through digital image analysis for particle size distribution and shape factor data. The combustion residues obtained from DTF tests and those collected from the convective boiler sections of four power plants will be compared in terms of their mineral distribution and physical properties, particularly the presence of particle agglomerates. Preliminary results suggest that the coals contain the major minerals quartz, kaolinite, illite and pyrite with minor minerals montmorillonite and calcite. Electron micrograph images of the power plant fly ashes show large agglomerating particles, with one fly ash showing unburned char particles, indicating an oxygen deficient boiler environment.

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Combustion Properties of Bamboo When Blended with a South African Coal

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South Africa is economically vulnerable to climate change because its economy is powered by electricity generated from coal fired power stations. There is a need to reduce the reliance on fossil fuel energy not only because of greenhouse gas emissions but also energy security. Bamboo is touted as a renewable energy source, however, like other woody biomass material, it has poor physicochemical properties and low energy densities. Bamboo samples were subjected to thermal pre-treatment methods to establish their combustion and physicochemical properties. Bamboo samples of 1, 3 and 4+ years old were used, and each was tested raw and when subjected to torrefaction at 250°C and 280°C and low temperature carbonisation at 350°C and 400°C. A standard HGI method was modified to establish the grindability of the raw and treated bamboo material. The fuel properties and combustibility of these raw and thermally treated bamboo material were then studied using thermogravimetric analyses.

The raw bamboo samples exhibited calorific values (CVs) ranging from 17 MJ/kg to 18 MJ/kg whereas the torrefied and carbonised samples exhibited CVs ranging from 25 MJ/kg to 28 MJ/kg and 28 MJ/kg to 30 MJ/kg, respectively. The 4 year old bamboo carbonised at 400°C provided the highest CV of 30.24 MJ/kg. The fixed carbon content in the same sample increased from 16 to 74%. The energy yields ranged from 48 to 74% for the torrefied samples and 44 to 54% for the low temperature carbonised samples. At the torrefaction temperatures tested, the 4 year old bamboo had the highest mass and energy yield whereas at carbonisation temperatures, 3 year old bamboo had the highest. Both raw and thermally treated bamboo had higher reactivities, and lower ignition and burnout temperatures compared to that for coal.

The activation energies of the individual fuels ranged from 56 to 289 kJ/mol, using the Ozawa model. Bamboo samples carbonised at 400°C had the highest activation energy of all the bamboo samples tested, irrespective of age.

Thermogravimetric analyser (TGA) tests indicated that blending coal with bamboo (raw and thermally treated) increased the reactivity of coal during co-firing. When varying proportions of coal were blended with raw and thermally treated bamboo samples, biomass was always found to devolatilise at lower temperatures than coal but this appeared to aid the ignition of coal in the lower temperature ranges. As the percentage of coal in the blends increased, there was less interaction or influence of biomass. When carbonised, biomass was found to exhibit combustion profiles and behaviour closer to that of coal.

In summary, this study showed that torrefied bamboo samples exhibit lower ignition and burnout temperatures relative to carbonised bamboo samples, a factor which might support the application of torrefied bamboo as a source of fuel in low-temperature industrial boilers such as fluidised beds. The carbonised 4 year old bamboo forms, on the other hand, appear to be more suited to, and possibly the preferred alternative source of fuel for, firing alone or co-fired with coal in pulverised coal boilers such as those used in large scale power generation in South Africa.

An Experimental Study of Nitrogen Oxides Formation of Pulverized Coal in O_2/N_2 and O_2/CO_2 Atmospheres

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

Efforts to reduce the emissions of greenhouse gas form an irreversible trend in the modern world and oxy-fuel combustion is promising technology that can be applied to coal fired plants. As the regulations and standards of air pollutant emission are being tightened, nitrogen oxides (NOx) exhaust is important when the oxy-fuel combustion technology is applied for reduction of greenhouse gas emission. Several researchers who had tried to investigate the difference between NOx formation under oxy-fuel conditions and under conventional conditions reported that the tendency of nitrogen release in pyrolysis under CO2 was dissimilar from that under N2. The purpose of this study is to understand the effect of nitrogen release on NOx formation under oxy-fuel conditions. Thermogravimetric analyzer and drop tube furnace were used for observing the devolatilization and gasification characteristics with increasing temperature under CO2 and N2 atmosphere. Combustion experiments for measuring NOx concentration under O2-CO2 and O2-N2 atmospheres were performed using the drop tube furnace by varying the temperature and stoichiometric ratio. As a result of the thermogravimetric experiments, water evaporation and devolatilization occurred and the trends of these processes were very similar. However, under CO2 atmosphere at temperatures higher than 800°C the rate of weight loss increased during the weight loss under N2 which was uniform as gasification occurred. This trend can also be seen in the results of experiments carried out by drop tube furnace. The apparent volatile yields under CO2 atmosphere exceed that under N2 around 1300°C. In combustion experiments, the measured NOx concentration tended to increase as the temperature and stoichiometric ratio increased under O2-CO2 and O2-N2 atmospheres. However, the total amount of NOx under O2-CO2 atmosphere at all conditions was lower than under N2-CO2 atmosphere.

SESSION 15
Carbon Management - 3

Monolithic Amine-Grafted Sorbents for Post-Combustion CO_2 Capture

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Amine-based solid sorbents have been widely studied for CO_2 capture. The amine functional groups on the solid sorbents bind CO_2 through acid-base interactions. Our in situ infrared spectroscopic studies have revealed that the strength of acid-base interactions can be fine-tuned by controlling amine density and polyethylene glycol additives, allowing CO_2 to adsorb at temperatures below 55 °C, and to desorb at 100 °C. The differences in the CO_2 adsorption and desorption temperature as well as the sorbent's heat capacity govern the operating cost of the CO_2 capture process. The key challenges in scaling up the process of amine-based sorbents are lack of resistance to oxidative degradation and sulfur-poisoning as well as low rates of heat transfer. Development of an effective and stable sorbent requires a fundamental understanding of CO_2-O_2-amine and CO_2-SO_2-amine interactions. Our in situ infrared study revealed that the low stability of amine-grafted sorbents can be attributed to (i) the attack of reactive oxygen species on the C-H and N-H groups of the amine sites and (ii) interactions of amine functional group with SO_2, a contaminant in flue gas. The results of CO_2 capture study in a 5 KWe scale fluidized bed revealed that heat transfer is the rate-limiting step for the thermal swinging CO_2 capture process. We found that the rate of heat transfer can be significantly increased by depositing amine-grafted sorbents on a monolithic structure. This presentation will also discuss issues related to the development of cost-effective pilot scale CO_2 capture processes and compare process economics of various post combustion CO_2 capture approaches.

Mathematical Modeling of Adsorption Behaviour of SOD-ZMOF/Chitosan Adsorbent During Post-Combustion CO_2 Capture

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CO2 is one of the greenhouse gases (GHG) that cause global climate change. Therefore, it is necessary to reduce CO2 emission into the atmosphere to mitigate climate change. Carbon dioxide capture from industrial processes like coal-fired power plants is a very important step towards reducing CO2 emission [1]. In this context adsorption technology is envisaged to be a viable technology for CO2 capture. Effectiveness of adsorption technology depends on the presence of high CO2 adsorption capacity adsorbent and several adsorbents have been synthesized and tested for CO2 capture [2]. An example of such adsorbents is Sod-ZMOF/Chitosan composite adsorbent. In addition, understanding the behavior and performance of this adsorbent during post combustion CO2 capture is very essential to the design of an adsorption bed for CO2 capture and mathematical modeling is a very useful tool to investigate this. Furthermore, it is imperative to develop mathematical models that will sufficiently describe the CO2 adsorption behavior of Sod-ZMOF/Chitosan during post combustion CO2 capture. The mathematical model that describes the behavior of the adsorbent sufficiently can then be used for material design, optimization and design of an adsorption system for CO2 capture using Sod-ZMOF/chitosan as an adsorbent. The objective of this study is the prospective modeling of the adsorptive post-combustion capture of carbon dioxide in power generation systems based on integrated gasification combined cycle using new materials.

Against this background, this study investigated the adsorption behavior of Sod-ZMOFs/Chitosan during post combustion CO2 capture using a mathematical modelling approach. Five existing mathematical models for gas-solid adsorption were explored in this study to describe the behavior of this adsorbent. The models tested were Thomas model [3], Bohart-Adams model [4], Yoon-Nelson model [5], Wolborska Model [6] and the Clark's model [7] and the model results were compared with experimental results obtained at similar conditions at which the models were simulated. The experimental data were obtained at an operating pressure of 200kpa, gas flow rate of 2.1ml/s and a temperature of 41oC. The amount of the adsorbent was 1.1g and the N2/CO2 mixture of the ratio 9:1 was used to mimic the composition of the flue gas from coal-fired power plant. The kinetics of the adsorption was very fast and equilibrium was attained after 35 seconds. The CO2 adsorption capacity obtained experimentally at equilibrium point was 33.81 gCO2/Kg adsorbent while the CO2 adsorption capacities obtained from the models were; Thomas, 62.54 gCO2/Kg adsorbent; Bohart-Adams, 36.56 gCO2/Kg adsorbent, Yoon-Nelson, 36.750 gCO2/Kg adsorbent; Wolborska, 15.73 gCO2/Kg adsorbent; and Clark, 19.78 gCO2/Kg adsorbent. Bohart-Adams model seem to describe closely the CO2 adsorption behavior of the adsorbent with a percentage error of 8.13% and may be suitable for material design and optimization of an adsorption system for CO2 using Sod-ZMOFs/Chitosan as an adsorbent. The little deviation could be attributed to the operating conditions used during experiment and simulation of models. Using the Bohart-Adams model, effects of operating parameters such as temperature, CO2 inlet concentration, flowrate, pressure and mass of adsorbent on the adsorption capacity of the adsorbent were also studied. A decrease in operating temperature resulted in a longer breakthrough time. The adsorption capacity of the adsorbent also decreased at elevated temperatures. Increasing the inlet concentration of the gas accelerated the breakthrough point because the adsorbent got saturated much faster due to larger concentration gradient while an increase in the feed flow rate decreased the retention time of the gas molecules in the adsorption bed resulting in a decrease in the adsorption capacity of the adsorbent. These observations are in agreement with those reported in literature [8, 9]. In conclusion, the Bohart-Adams model showed excellent fittings for the examined range of breakthrough curves in this study.

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Synthesis of Chitosan-Impregnated SOD-Zeolite Metal Organic Frameworks (SOD-ZMOF) for CO_2 Capture: A Preliminary Investigation

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South Africa is amongst the top countries in the world emitting large amount of carbon dioxide (CO2) gas to the atmosphere. This is explained in that its energy resources mostly rely on coal. Several investigations have revealed that CO2 is a major greenhouse gas and, as such it contributes to about two-thirds in aggravating the greenhouse effect. Due to the aforementioned problems, much effort is being devoted to reduce CO2 emissions through the development and evaluation of cost effective methods for capturing and storing CO2. The amine-based absorption using monoethanolamine (MEA) is the most common and mature techniques for CO2 capture [1]. However, problems associated with this process are huge energy required for solvent regeneration and corrosiveness of the piping [1]. This calls for efficient alternative adsorption process for CO2 removal.

Adsorptive CO2 removal by solid adsorbents is a promising way. Besides being less energy intensive, this process has the ability of operating in moderate temperature and pressure [2]. Adsorptive CO2 removal using solid adsorbents has shown to be very effective. There are a number of solid adsorbents used for CO2 capture, but metal organic frameworks (MOFs) have drawn much attention over the past decade [2]. This is explained in that MOFs have large surface area, adjustable pore sizes, open metal sites and less energy for regeneration. A recent study reported in the literature is application of zeolite-like metal organic framework (ZMOF) developed by Chen *et al.* [2] for CO2 capture. The material displayed a relatively high CO2 adsorption capacity as compared to other types of MOFs. However, the properties of this MOF can be enhanced by incorporating in it with other materials through grafting, impregnation and ion exchange to improve its CO2 adsorption capacity. Against this background, this research aimed at optimizing ZMOFs (sod-ZMOF in particular) through structural modification or formation of composite material for enhanced CO2 adsorption. Sod-ZMOF was impregnated with chitosan after which the composite adsorbent was characterized and evaluated for CO2 adsorption.

Sod-ZMOF was synthesized by mixing 4.5-imidazoledicarboxylic acid, indium nitrate hydrate, DMF, Acetonitrile, imidazole, nitric acid and heated as described elsewhere [2]. The sod-ZMOF crystals produced were impregnated with chitosan. Chitosan was extracted from chitin. Chitin from crabs was first sieved and then demineralization, deproteinization and deacetylation were done in order to extract chitosan. Chitosan was impregnated onto sod-ZMOF by first dissolving it into acetic acid and stirred to obtain chitosan solution. Then sod-ZMOF was added to the aforementioned chitosan solution and stirred. The suspension mixture was then filtered and allowed to dry.

The synthesized sod-ZMOF and sod-ZMOF-chitosan was characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Thermo gravimetric analysis (TGA). XRD patterns showed that sod-ZMOF is crystalline. TGA analysis showed that sod-ZMOF is thermally stable up to temperature of 250OC and this is consistent to the results obtained by Chen *et al* [2] From FTIR analysis; functional groups that are present in the organic linker (4.5-imidazoledicarboxylic acid) are also present in sod-ZMOF. The functional groups in 4.5-Imidazoledicarboxylic acid are alkenes, alkanes, amine (HN), carboxylic acid (O-H), and aromatics. These functional groups were also identified on the FTIR spectra of sod-ZMOF. FTIR spectra of sod-ZMOF chitosan showed the presence of functional groups (N-H, C-O and aromatics). These functional groups are also present in organic linker and chitosan. However FTIR spectra of sod-ZMOF showed a decrease in t of O-H (carboxylic acid) band as compared to that in sod-ZMOF. When Chen *et al.* grafted amine on sod-ZMOF, the FTIR spectra of amine grafted sod-ZMOF also showed a decrease in the presence of O-H group as compared to just sod-ZMOF. Chen *et al.* [3]

explained the decrease in O-H band could be as a result of carboxylic acid being transformed to amide groups [3].

Performance evaluation of the material was carried out with an adsorption set-up using CO2/N2 gas mixture with 10% CO2. The evaluation was conducted on the sod-ZMOF without chitosan and sod-ZMOF impregnated with chitosan for comparison. For the adsorption experiments, which were conducted using an adsorption bed with 0.1 g of the adsorbent, temperature of 41, pressure of 200 kPa and flow rate of gas 126 ml/min were used. The highest adsorption capacity obtained at these conditions was 48.72 mlCO2/g adsorbent and 41.58 mlCO2/g adsorbent for sod-ZMOF and sod-ZMOF chitosan, respectively. The impregnation of chitosan on sod-ZMOF resulted in a decrease in adsorption capacity of the material. It is expected for sod-ZMOF-chitosan to have a higher adsorption capacity than sod-ZMOF as chitosan has amine groups with high affinity for CO2. The decrease in adsorption of sod-ZMOF-chitosan could be attributed to the occupation of the pore volume of the sod-ZMOF by some impurities which were not completely rid of during the drying. However, the adsorption kinetics of the sod-ZMOF-chitosan was faster than that of the sod-ZMOF. The faster kinetic of the chitosan impregnated sod-ZMOF could be attributed to the presence of the chitosan in the ZMOF. Since this is a preliminary investigation, efforts are on-going to unravel the problem behind the results that fell below expectation.

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Nanocomposite Architecture Hydroxy Sodalite/α-Alumina Membrane for CO_2 Capture

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The continuous anthropogenic carbon dioxide (CO_2) emission into the atmosphere in the past decades with its associated global climate changes and other environmental disasters has received substantial attention worldwide. Other greenhouse gases (GHG) such as methane are likewise emitted but research findings indicated CO_2 as the major pollutant, requiring urgent attention to combat climate change. Thus mitigating the climate change through reduction of CO_2 emission constitutes a technological and scientific challenge [1]. However, numerous technologies (absorption, adsorption and membrane technology) for CO_2 capture from power plants have been proposed and evaluated. Presently, the most advance and mature technique for CO_2 capture is absorption technology using monoethanolamine (MEA), but this technology is considered cost and energy inefficient and the amine solvent (monoethanolamine) possesses low stability at elevated temperature [1]. The development of superior and advance materials with considerable lower energy and cost penalty is essential. Therefore one of the promising candidate is membrane technology and zeolite based membrane systems prove to handy and useful than the traditional processes [2] . Zeolite membranes have found tremendous uses in the industry for separation and purification application. For instance, hydroxy sodalite (SOD membranes are known to possess high chemical and thermal stability up to 450^{o}C) [3]. However, commercial applications of zeolite based membranes are hampered by high cost of support and poor reproducibility. Moreover, zeolite membrane with zeolite coating on the support (i.e. thin-film supported zeolite membranes) are susceptible to abrasion and thermal shock at high temperature due to temperature mismatch caused by difference in thermal expansion of the zeolite material and the support, making them to lose selectivity very fast. On the contrary, nanocomposite architecture membranes obtained via pore-plugging hydrothermal synthesis protocol are more thermally stable and membrane defects are controlled [4, 5]. In this work, a nanocomposite architecture hydroxy sodalite membrane with zeolite crystals embedded within an α-alumina tube was synthesized using the pore-plugging hydrothermal synthesis technique and characterized. The as-prepared membrane was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM). The results obtained from these characterization techniques reveal that sodalite crystals were indeed grown within the porous structures of the support. In addition, the XRD analysis reveals the formation of sodalite crystals within the support. In addition, Small Angle X-Ray Scattering (SAXS) confirmed structural information such as particle size, shape and internal structure of SOD crystals. Since the average cage dimension of hydroxy sodalite is 0.265 nm, similar to the molecular size of an H_2 (0.27 nm), the successfully synthesized membrane will be evaluated for removal of H_2 from H_2/CO_2 mixture, a mixture that is obtained from pre-combustion after gasification in an Integrated Gasification Combined Cycle (IGCC) during power generation.

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SESSION 16
Coal Science - 3

Prediction of Spontaneous Combustion in Coal by Use of Thermogravimetry

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The self-heating of coals is a complex problem which has been occurring for centuries. This problem has been fatal to coal miners, an economical challenge to coal mines and a health risk in a release of greenhouse gases to the public in general. Therefore, everyone is affected by the self-heating of coal, which leads to spontaneous combustion when the ignition temperature is reached.

There are many test methods that have been used to test spontaneous combustion in coal, but all have one common factor or disadvantage of requiring long periods of time before a conclusion can be deduced. This then creates a need for a rapid and reliable method to test the liability of coal to self-heat in the coal industry and thus the motivation for this project.

The thermogravimetry analysis (TGA) method was selected to test the liability of coal to self-heat due to its short analytical duration. The Smith-Glasser oxidation test was selected to validate the TGA results obtained. The main aim of this project is to investigate the reliability of the TGA method to predict the propensity of coal to self-heat.

29 samples from different regions of South Africa were used, prepared to 250 µm for all the analyses and self-heating tests. All samples were analysed for proximate, calorific value, sulphur and petrographic properties before the spontaneous combustion liability tests began.

The TGA method followed two tests: 1) the O_2 adsorption and 2) the Ignition test. Five different heating rates (3, 5, 7, 10, and 20) °C/min were run in order to obtain five derivative slopes which would be used to obtain the TG_{spc} index. The oxygen adsorption test studies the mass increase at low temperature under exposure of air between the temperature ranges of 100 – 300°C.

The Smith-Glasser oxidation test method studies the reaction of coal with O_2 and calculates the O_2 absorbed per amount of coal tested. The Smith-Glasser test results collaborated with most of the other analytical results, and with the TGA results to a certain extent.

The TGA spontaneous combustion liability test requires additional analytical work to back up its results because the results do not appear as accurate as the Smith-Glasser oxidation test. It also requires repeatability tests to ensure the integrity of the results.

Mechanical and Thermal Characterization of Briquetted High Ash South African Coal Fines Using Low Density Polyethylene as the Binding Agent

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Over the years, mining techniques have become progressively higher throughput, resulting in the production of vast quantities of waste coal fines. In order to effectively utilize this waste coal, continued research has focused on determining both the mechanical and combustion characteristics of various briquetted fuel products derived from coal, municipal solid waste, sludge, biomasses, and combinations of these. In particular, the effective recycling processes for plastic waste represent a major challenge in the protection of the environment and natural resources. This is due to the descending credibility of the recycling processes and escalating operational costs. Consequently, alternative techniques, which incorporate plastic waste into existing industrial processes as raw materials or partial blends with other materials such as coal, have attracted research interest in recent years. Co-pyrolysis techniques in particular, have been widely investigated because they provide an attractive way to dispose of and convert polyolefins and coal into higher value fuel. In contrast, very few research papers report on plastic wastes as minor components, acting as binding agents, in coal blends. The current research entails the evaluation of various materials as potential coal fine's binders; understanding the chemical interactions between fine coals and the selected binder in order to produce robust coal briquettes. In this study, low density polyethylene (LDPE) was investigated as a potential binder during the briquetting of inertinite-rich South African coal fines. LDPE is abundant in plastic waste streams (constitutes approximately 63%) and possesses desirable energy, waterproofing, and binding characteristics. Laboratory scale briquettes were prepared using an LRX Plus pressing machine and cured at varying temperatures. Briquetted fuels were characterized for their mechanical properties using standard techniques including compressive strength measurements, attrition testing and thermogravimetric (TG) analysis. The effects of binder concentration and curing temperature on the mechanical properties of the blends were investigated. TG analysis data was used to evaluate the kinetics parameters such as the activation energy, pre-exponential factors, and the reaction orders, applying a model fitting approach. The results indicate a positive influence of the LDPE, suggesting the presence of an interaction between LDPE and the coal fines.

Evaluation of a Domestic-Use Low-Smoke Fuel Produced via the Pyrolysis of Lump Coal

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An estimated 3 million tons per annum of coal is used in approximately 1 million South African households as the primary heating and cooking energy source as electricity and electrical appliances are considered unaffordable by the low-income residents. Domestic use of coal in the Gauteng Province contributes an estimated 65% of the local air pollution and approximately 48% of the quantifiable particulate emissions in Johannesburg alone, and the treatment of the resultant air pollution related illnesses has been reported to cost the Government approximately R1,2 billion (approx.. 78 million US$) annually. It is thus of importance to develop a competitive alternative for coal as a household energy source. In this paper the evaluation of a low-smoke fuel (LSF), produced via the pyrolysis of lump coal and intended for household use is reported. The fuel was produced under an inert atmosphere at 450, 550, 650 and 750°C. Evaluation of the LSF performance was divided into: (1) practical performance (ignition time, time taken to boil a litre of water, space heating and combustion efficiency) and, (2) pollution reduction: where the reduction (as compared to the untreated raw coal sourced from merchants in the Kwadela township near Secunda) in the emission of gases (SO_2, NO_X, CO, CO_2), particulate matter and volatile organic compounds (VOCs) was considered. The experimental evaluation was conducted using a fully instrumented coal stove (Union™ 7) setup akin to those currently in use in coal-burning households. Results showed that the benefits of LSF included: reductions of approximately 80, 90 and 35% in particulate matter, volatile organic compounds and sulphur dioxide emissions respectively when compared to the raw coal.

Research of the Masking Effect of Surfactants on O-Containing Functional Groups in Low-Rank Coals

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Pingshuo long flame coal and Shengli brown coal, which are quite different in metamorphic grade and are of low impurity content, were chosen as test samples in this experiment. The samples were surface modified with three kinds of surfactants, which are CTAB, SDS and Span-80. The surface modified samples were taken into floatation experiment. Masking effect of the surfactants on the main oxygen containing functional groups in coal under different modifying conditions(dosage of surfactants and stirring conditions) was researched. The relationship between floatability of coal and its oxygen containing functional group content was also researched. Results of the experiment showed that masking effect of surfactants altered as the surfactant type or modifying conditions changed. The adsorption of surfactants on coal surface could decrease the content of carboxyl groups and phenolic hydroxyl groups effectively and improve the floatability of low rank coals.

SESSION 17
Gasification Technologies: General - 1

Soot Gasification in Syngas Atmosphere

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Soot and other undesired by-products are formed by radical polymerization reactions at process conditions characterized by low oxygen concentration and temperatures above 1200°C, typical for entrained flow gasification (EFG). Soot formation especially accompanies liquid feed gasification where the incomplete mixing of oxygen with vaporizing fuel droplets creates local areas of low oxygen concentration. The most common liquid feedstocks in EFG are residual oils. However, the gasification of low rank biomass derived fuels; e. g. bio-syncrudes originating from flash pyrolysis is currently in focus.

The removal of soot particles from syngas creates considerable capital and operational expenditure of an EFG plant. Washing, either by water-quench cooling or in washing towers is the conventional way to remove the soot particles from the raw synthesis gas. The make-up of the wash water, including soot removal and post treatment, involve most of the additional effort and expense. Furthermore, the syntheses gas which was cooled down by the washing process has to be heated up again to be processed in the downstream catalytic process units, which is energetically unfavorable.

A more convenient way is the cleaning of syngas at temperatures above those of the downstream process units, in order to avoid costly equipment for cooling and reheating and efficiency losses. Solid particles, composed of fly ash and carbonaceous residues (soot), can be removed by hot gas filtration.

New ways of reducing soot particle loading in raw synthesis gas could be the targeted conversion of soot particles in the gasifier´s post flame zone, or on hot gas filtration filter candles. For both measures knowledge about the gasification reactions (kinetics and mass transfer) of soot particles is essential.

The presented work contributes to the identification of kinetic parameters for soot conversion reactions in synthesis gas environment. Special attention is directed to changes of the soot structure and chemistry due to tempering and its influence on conversion reaction rate.

In an experimental set-up consisting of an electrically heated ceramic tube reactor, soot was produced from a mixture of propane and nitrogen by pyrolysis. Downstream of the pyrolysis zone soot was captured in a randomly packed bed of alumina particles of 0.5 - 1 mm diameter. CO_2 was inserted directly upstream of the soot laden filter bed to the gas stream to convert the soot partially to CO. The inlet and the outlet gas compositions were continuously monitored allowing calculation of the soot conversion by carbon balancing. In order to determine the influence of the soot's age on its gasification activity two types of experiments were performed. First, soot was produced and gasified downstream simultaneously, and second, the soot was caught in the filter and consecutively gasified after stopping the propane pyrolysis. Furthermore, soot was analyzed regarding its structural and chemical characteristics by means of elemental analysis, transmission electron microscopy and gas adsorption measurements. By means of the obtained analysis data the influence of mass transport in soot aggregates on reaction velocity could be calculated.

Comparison Study on Gasification of Long-Flame Briquette Coal with CO_2 and H_2O

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Long-flame coal, a low rank coal, is normally used for power-station and coal chemical industry. However, it is easily to produce a large number of fine particles through long-distance transport, which brings serious environmental pollution problems and also reduces the economic benefit. In the present study, a typical Chinese long-flame coal was made into three kinds of briquette coals (FH, JW and PM) as feed for gasification, by addition of different binding agents. Gasification experiment with three briquette coals was studied in a fixed bed reactor with CO_2 and H_2O and compared with the raw lump coal. The briquette and raw lump coals were firstly put into the reactor under N_2 atmosphere, and heated from room temperature to 500 ℃ by heating rate 10 K/min, 500 to 1000 ℃ by heating rate 5 K/min. After the temperature reached to 1000 ℃ for 30 minutes, the gas was shifted from N_2 to CO_2 (1 L/min) or H_2O (1.5 g/min), to carry out the gasification experiments for 1 hour. The gaseous products during the gasification process were collected in a gas holder and analyzed by a gas chromatography every 20 minutes. For gasification experiment with CO_2, the results showed that the raw lump coal had the highest carbon conversion (22.02%) and briquette JW owned the lowest value (11.66%). The carbon conversion in sequence was consistent with that for CO_2 reactivity test of samples: raw>FH>PM>JW. However, for gasification experiment with H_2O, the carbon conversion in sequence was inconsistent with that for CO_2 reactivity test of samples: FH>PM>JW>raw. The reason for the different was illustrated in the present study, which was mainly related to fracture of samples under different atmosphere and different additive formula. For both CO_2 and H_2O experiments, FH briquette owned best reactivity and good shape, which was a good feed for fixed bed reactor.

Experiments of Coal Partial Gasification on a Circulating Fluidized Bed

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As one kind of clean and efficient technology, gasification is used for converting carbonaceous fuels into valuable energy products. Nowadays, the most widely used gasification technology is entrained-flow gasification technology of which the pressure and temperature are very high. The cost of equipment and operation are high because of extreme furnace condition. This paper presents one novel gasification technology which is named coal partial gasification. The coal first partially gasified into syngas in the circulation fluidized-bed gasifier, and the ungasified char can be used for combustion. In this paper, one kind of Chinese lignite is gasified in a bench-scale circulating fluidized-bed gasifier. It is composed of circulating fluidized-bed gasifier, coal feed system, air feed system, steam generation system, gas-solid separation system, measuring system, and material returning system. The furnace is made of ceramic whose height is 2600m and diameter is 120mm. It is surrounded with heat strips. Oxygen and steam are adopted as gasification agents. Oxygen is from oxygen cylinder, and steam is from steam generator. Huating coal is chosen as experimental coal of which size is between 0.35mm and 0.9mm. Yellow sand is adopted as fluidizing agent of which size is between 0.35mm and 0.45mm. The experiments are conducted under atmospheric pressure while gasification temperature ranges from 890℃ to 980℃. The oxygen coal ratio and steam coal ratio for each experimental condition are 1.14 and 0.79, 1.05 and 0.36, 0.49 and 0.36, 0.37 and 0.38, 0.46 and 0.31, respectively. The experimental results showed that the ratio of effective gas ($CO+H_2+CH_4$) can reach ~65%. As gasification temperature increases, the ratio of effective gas decreases due to gas combusting. The content of tar decreases as gasification temperature increases.

Catalytic Reduction Mechanism Investigation of K_2CO_3 Modified Iron-Based Oxygen Carrier by Carbon

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It is almost infeasible to directly reduce iron oxide oxygen carrier only by coal char due to the slow reaction rate in the temperature ranges of chemical looping combustion (CLC). With alkali metal catalyst addition, however, this reduction can be significantly increased, which makes this direct reduction feasible in coal direct CLC. Because of the complexity of the reduction, the mechanism has not been explained in detail. This work tries to investigate this mechanism with K_2CO_3 decorated iron based oxygen carrier by activated carbon. The results show that K migrated from oxygen carrier to activated carbon at the initial stage of reduction. A possible migration mechanism can be summarized as following: firstly the K_2CO_3 on oxygen carrier decompose to K_2O; then the K_2O melt to the contact point of iron oxide and carbon; K_2O react with C to produce K, and some K volatilized and absorbed on carbon. The migrated K could then directly catalyze the $C\text{-}CO_2$ reaction. Besides the catalytic effect of K, a remarkable autocatalysis of iron oxide itself was also observed. Moreover, this autocatalysis seems to be related with the K addition. K_2CO_3 could also improve the reduction step of iron oxide by CO, however, this improvement is far lower than that of the whole reduction.

SESSION 18
Coal Mining and Beneficiation - 3

Development of a Condition Monitoring Philosophy for a Pulverised Fuel Vertical Spindle Mill

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The quantity and particle size distribution of pulverised coal supplied to combustion equipment downstream of coal pulverising plants are critical to achieving safe, reliable and efficient combustion. These two key performance indicators are largely dependent on the mechanical condition of the pulveriser. This study aimed to address the shortfalls associated with conventional time-based monitoring techniques by developing a comprehensive online pulveriser condition monitoring philosophy. A steady-state Mill Mass and Energy Balance (MMEB) model was developed from first principles for a commercial-scale coal pulveriser to predict the raw coal mass flow rate through the pulveriser. The MMEB model proved to be consistently accurate, predicting the coal mass flow rates to within 5 % of experimental data. The model proved to be dependent on several pulveriser process variables, some of which are not measured on a continuous basis. Therefore, the model can only function effectively on an industrial scale if it is supplemented with the necessary experiments to quantify unmeasured variables. Moreover, a Computational Fluid Dynamic (CFD) model based on the physical geometry of a coal pulveriser used in the power generation industry was developed to predict the static pressure drop across major internal components of the pulveriser as a function of the air flow through the pulveriser. Validation of the CFD model was assessed through the intensity of the correlation demonstrated between the experimentally determined and numerically calculated static pressure profiles. In this regard, an overall incongruity of less than 5 % was achieved. Candidate damage scenarios were simulated to assess the viability of employing the static pressure measurements as a means of detecting changes in mechanical pulveriser condition. Application of the validated pulveriser CFD model proved to be highly advantageous in identifying worn pulveriser components through statistical analysis of the static pressure drop measured across specific components, thereby demonstrating a significant benefit for industrial application.

Measurement and Prediction of Coal Flow Rates in Pulverised Fuel Pipes

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Justification of the project

The first step in improving combustion efficiency is to balance flows in the pulverised fuel (PF) pipes, which pneumatically transport coal from the mills to the burners in coal fired power plants. A critical activity in balancing the flows with respect to mass flow and particle size distribution is Isokinetic sampling and analysis of the PF. Concerns regarding the accuracy of results yielded from isokinetic PF sampling have prompted the initiation of this study.

Purpose

This study has identified various standards, procedure and practices associated with PF sampling which have been evaluated in a full scale study at one of Eskom's Power Stations. Based on the results obtained a level of accuracy for the sampling methods has been established. The purpose of the study was to recommend best practice for PF measurements in Power Utilities.

Theoretical framework

Directed interviews were carried out at five Eskom Power Stations and with Subject Matter Experts from Eskom. The scope of the project and the establishment of the following hypothesis; "Current standards and practices for PF measurement used in Eskom are not accurate enough to control the PF distribution to the required accuracy for improving combustion efficiency and LNB implementation" were then developed

Testing this hypothesis involved site tests at one of Eskom's Power Stations, validation of results and CFD modelling.

An automated rotating 4 nozzle sampler and a single nozzle manual sampler were identified as the current equipment utilised by Eskom for PF sampling. The manual sampler was utilised in one of three ways at different sites. Samples could be extracted by carrying out a single axis traverse, a 3 axis traverse or in conjunction with a target plate. These four methods of sample extraction were investigated during the site tests.

A site that utilises gravimetric coal feeders was selected for the site tests to facilitate accurate comparisons of the PF mass flows. A total of 924 PF samples were extracted. These samples were further analysed in a Laboratory to determine the moisture content and size fractions.

Additional work was carried out to compare results yielded from sampling in vertical pipes to that obtained when sampling in horizontal pipes. The effect of adjusting setting such as velocity and g-factor on the automated sampler were also investigated. The coal flow rates were also compared to models utilised by Research, Testing and Developments in Eskom.

Flow pattern development was also studied during the site tests by carrying out incremental sampling. This made it possible to establish the velocity, mass flow and particle size distribution at each point. The information obtained was utilised to visualise the flow development through a cross section of PF pipe.

When utilising a target plate the sampling nozzle is forced to operate at different angles to reach the sampling point locations within the PF pipe. A CFD model was utilised to simulate angles that a sampling nozzle would be subjected to and to predicts the effect on the sample being extracted.

Results and conclusions

Preliminary results of the CFD modelling results showed a reduction of 22% in the number of particles collected in an angled nozzle compared to a nozzle oriented in the axial direction of flow. The preliminary results of the site testing highlighted that the target plate sampling method overestimated the coal flow, the 3 axis method and the automated rotary sampler yielded very similar consistent and accurate results and the 1 axis sampling unreliable results and proved to be erratic.

Implications for Eskom and the power industry in Southern Africa

The accuracy of the various PF sampling techniques has been investigated and quantified in this project. Based on the results obtained the standard for PF sampling should be revised to include a correction factor for the application of target plate sampling. The practice of single axis traversing for sampling should be discontinued.

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Applications of Online Coal Analysers in South Africa

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Conveyor belt sampling and analysis of coal is rarely an effective means of process control as laboratory results tend to become historical records of what has already passed through the plant and may be totally unrelated to what is about to be processed. Real time, on-line analysers provide results every two minutes, overcoming the need to take routine samples for process control. Further, the analysis of the whole stream continuously eliminates the major source of error – sampling error.

Consistency in the feed quality to any process improves the performance of that process and in the coal industry those small improvements can add up to significant dollar benefits very quickly. Plant yields may be improved. The ability to measure the quality of a shipment during loading by analysing the whole flow continuously allows operators to provide not only an average quality that is closer to the specified target but also reduce the variability on a minute by minute basis. In many coal operations direct shipping quality material can by-pass a treatment plant, to reduce treatment costs. Measuring the coal quality and blend to a specification during stacking has also proven beneficial. Analysers give operators the ability to measure the quality of a shipment (train, ship, etc) during loading, and so provide an on-spec shipment.

On-line analysers have made a major impact in the South African coal industry in the last 30 years. Example of their application will be discussed and cost benefits calculated.

Whilst technologies are mature for on-line ash analysis, there have recently been significant developments of these technologies. An explosion proof natural gamma ray ash analyser is now on the market. In a typical application, one mine in South Africa used this technology for immediate feed-back to the miners re the coal quality.

Dual Energy Transmission (DUET) is the most commonly used on-line ash measurement technique worldwide. Although not widely used in Africa due to variations in the ash chemistry of the region's coal, a preparation plant in South Africa is using an analyser, based on DUET technology, to monitor the product coal in order to optimize station performance. New developments in the DUET ash measurement technology permit coal depths up to 400 mm in some cases to be measured.

On conveyor belt elemental analysers are now available to analyse the entire stream, avoiding not only the operating and capital costs of sampling, but also the sensitivity of older technologies to variation in ash mineralogy. Power stations use these analysers to monitor coal deliveries. As well as measuring ash, this technology measures the ash oxides, calorific value, sulphur, volatile matter and many other parameters useful for efficient process control.

These technologies can all be combined with the microwave moisture monitor, so that a complete analysis of the coal is available in real time. Moisture content is a key measurement, can affect material handling, dust control and can comprise a significant component of the cost of transport and treatment.

Benefits derived from these technologies have provided significant improvements plant efficiencies in all these applications across South Africa. The ability to monitor coal quality and its variability has been utilised to optimise processing operations and reduce plant running costs.

SESSION 19
Clean Coal and Gas to Fuels: Catalytic Study - 1

Fischer-Tropsch Synthesis in the Presence of Solvent Using Novel Carbon-Oxide Composite Supported Cobalt and Iron Catalysts

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Fischer-Tropsch synthesis (FTS) using synthesis gas produced by the gasification of coal attracts much attention because resources of coal are still large compared with petroleum or biomass. Nowadays publications related to the FTS are more than hundred and not only academic community but also industrial world have noticed the importance of this technology because of the drastic increase in the price of crude oil and the increasing demand for the clean alternative fuels.1) In this method called gas to liquid (GTL), one of the key technologies is the development of catalysts. So far various heterogeneous transition metal catalysts such as Fe, Co, Ni and Ru have been developed for this reaction. It is well-known that among them, Co based catalysts are advantageous for the practical application due to the high activity and selectivity to long chain linear hydrocarbons, high resistance toward deactivation, and lower price than Ru. Generally Co and Fe catalysts are deposited on the supports with high surface area (e.g., SiO_2, Al_2O_3, TiO_2 and ZrO_2) in order to increase the number of active Co, Fe metal species and silica-supported cobalt is one of the promising catalysts. Further, due to the high resistance to attrition and the ability to stabilize small clusters, alumina is one of the attractive support materials for Co or Fe based FT catalysts. Although usual transition metal-supported catalysts are made by the impregnation method, using sol-gel method catalysts has become one of promising methods.

On the way of researches to prepare catalysts using the sol-gel method, we are interested in the preparation of transition metal-supported catalysts including carbon sources because some of these we prepared were found to be active for steam reforming and hydrothermal gasification of ethanol and aqueous phenol. Further, we are also interested in the FTS in the presence of a solvent because there are few reports utilizing such types of the reactor in the FTS. In this study, we prepared Co and Fe catalysts supported on carbon-SiO_2, Al_2O_3 and ZrO_2 composites using polyethylene glycol as a carbon source. Their reactivity for the FTS in the presence of decalin solvent was investigated.

Silica, alumina and zirconia were used as oxide supports. Polyethylene glycol (PEG) was added as a carbon source. Starting materials for silica, alumina and zirconia were tetraethyl orthosilicate (TEOS), aluminum tri-sec- butoxide, zirconium butoxide, respectively. Iron nitrate nonahydrate was used as an iron source. These catalysts were prepared using the sol-gel method. The typical preparation procedure is as follows: To ethanol solution of TEOS was added aqueous solution of cobalt nitrate at 0ºC over 1 h, and the mixture was stirred for 10 h. After that, the mixture was dried at 90˚C for 3 h to obtain a clay-like paste. The solid obtained was calcined under nitrogen atmosphere at 500˚C for 3 h. Measurements of XRD and nitrogen adsorption were performed to analyze the crystal structure and pore structure in a catalyst. The F-T reaction was performed under the conditions, gas flow 40ml/min, syngas composition H_2 66%, CO 33%, Ar 1%, and reaction temperature 250-340 ºC. The liquid solvent decalin was introduced with 10 cc/h. The collected liquid and gas were analyzed using gas chromatograph (GC-2010 FID, GC-2014 TCD).

When catalyst precursors were calcined at 500ºC under the N_2 atmosphere, conversions of carbon monoxide at 300˚C in the FT synthesis using $16Fe63C21SiO_2$, $16Fe63C21TiO_2$, $16Fe63C21Al_2O_3$ and $16Fe63C21ZrO_2$ catalysts were 0.3%, 0.3%, 3.3% and 10%, respectively. When $16Fe63C21ZrO_2$ was calcined at 700ºC the conversion increased to 55%, the highest CO conversion among the catalysts examined. The result would be related to the pore size distribution of $16Fe63C21ZrO_2$. Conversions of carbon monoxide at 300˚C in the FT synthesis using $16Co63C21SiO_2$, $16Co63C21Al_2O_3$ and $16Co63C21ZrO_2$ catalysts were 6.2%, 0.4 % and 17%, respectively. In both cases of iron and cobalt catalysts, ZrO_2 supported materials showed the stable activities in the presence of solvent probably because the adsorption of solvent was inhibited by the smaller surface area and the interaction with metal species was small.

Carbon from Pine Cones as a Support for High Temperature Fischer-Tropsch Synthesis

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There is a growing demand for light olefins (C_2-C_4), a chemical feedstock for the production a wide range of materials from plastics to synthetic textiles The Fischer-Tropsch to Olefin (FTO) process is an alternative route for producing light olefin production to the energy intensive cracking process, in particular for non-petroleum feedstock such as coal, natural gas and biomass. The carbon containing feedstock is first converted into synthesis gas, which can be converted further in the Fischer-Tropsch process. The production of light olefins is favoured if chain growth is limited, i.e. by the high temperature process, whilst still controlling the methane selectivity. The latter is typically achieved by utilizing iron-based Fischer-Tropsch catalysts, which show a more moderate dependency of the methane selectivity on temperature compared to other metals active for the Fischer-Tropsch synthesis, such as cobalt and ruthenium. The common high temperature iron-based Fischer-Tropsch catalyst is a fused iron catalyst with a relative low surface area. Supported iron catalyst may offer an advantage here allowing a high catalytically active surface area, and increased mechanical stability (due to a reduction in chemical attrition by carbon formation) and thus minimizing catalyst replacement and down time.

The aim of this investigation is to determine the viability of utilising iron-based catalysts supported on activated carbon produced from pine cone biomass in a high temperature (350 °C) FTO system. The viability of a biomass-based catalyst support was tested by analysing the activity, selectivity to lower olefins (C_2 – C_4) and the relative deactivation of the catalysts samples.

Activated carbon was prepared from pine cones: the pine cones were washed and crushed to a size of 0.1-0.12 mm. The material was impregnated with an aqueous solution of iron nitrate and dried at 110ºC until constant weight. The resulting material was exposed to microwave treatment at different power ratings for different times. The elemental composition of the catalysts was determined using XRF (Bruker S4 Explorer XRF). The crystalline phases in the catalysts were characterized using XRD (Bruker D8 Advance Diffractometer utilizing Co-Kα radiation - $\lambda = 1.78897$Å). The catalysts were tested in a laboratory scale Fischer-Tropsch rig operating at 350 °C and 20 barg using a H_2:CO ratio of 1:1 and a space velocity of 300 $ml_n/(min\cdot g)$. The product gases were analysed using an online GC-TCD and offline GC-FID.

The catalyst materials ex pine cones contain 23.7 wt.-% iron and a whole range of minor elements (< 0.05 wt.-%). The iron catalysts supported on activated carbon were highly amorphous with hardly any distinct reflections present due to an iron phase (a broad reflection at ca. $2\theta = 40.2º$ was observed which may be attributed to the presence of α-Fe, and a rather broad band at ca. $2\theta = 47º$ which tentatively can be ascribed to maghemite or magnetite). After the Fischer-Tropsch synthesis, diffraction peaks attributable to different iron carbides and magnetite can be discerned in the XRD pattern.

The activity of the catalysts made with activated carbon ex pine cones were found to exhibit comparable and in many cases more desirable activity and selectivities (CH_4, CO_2, light olefins) in relation to the bulk iron sample (prepared via precipitation).The activity per unit mass of iron of the catalyst activated for 20 minutes using 800W was higher than that of the bulk iron catalyst; the activity decreased with increasing energy input during the catalyst preparation. Fe/AC catalysts were found to remain stable throughout the run, whilst the bulk iron catalyst sintered. The catalyst yields a C2-C4 olefin yield of ca. 40% with acceptable CH_4-selectivty (<10C-%) and CO_2-selectivity (25-35C-%).

Bifunctional Hydrocracking: Is the Well-Established 'Classical' Fluid Phase Diffusion Mechanism a Delusion?

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In the 1950s a mechanistic model for the bifunctional catalytic hydroisomerisation/hydrocracking of hydrocarbons was developed, at the centre of which the idea was that the individual hydrocarbon molecules may 'hop' back and forth between the metal and acid sites present on the catalysts. At first, so the model, dehydration of the substrate, say an n-paraffin, would have occurred on a metal site. The resulting n-olefin would have desorbed and diffused through the fluid phase to an acid site where it would have been isomerised or cracked. Subsequently, the resulting iso-olefin or olefinic fragment would have desorbed again and diffused back to another metal site where it would have become saturated and left the reactor as a paraffin. The model went that far that even a mathematical criterion was created that defined the maximum distance allowed between the metal and the acid sites for diffusion not to become rate limiting (the Weisz intimacy criterion). To this day, this 'classical' reaction mechanism is still the most popular one.

However, since the late 1980s hydroisomerisation/hydrocracking experiments have been carried out, results of which the 'classical' mechanism could not explain. The respective set-ups comprised, for instance, fixed bed reactors with two separate layers of metal and acid catalysts packed on top of each other; reactors with the metal function shielded by membranes (that prevented hydrocarbons from passing through); or catalysts with the metal function shielded by hydrocarbon-tight encapsulation. From all of these set-ups, regular paraffinic hydroisomerisation/hydrocracking products were obtained. The 'classical' mechanism failed to explain this phenomenon. As a result, a mechanism was suggested by which hydrogen is activated on the metal sites, 'spills over' (migrates by surface diffusion) to the acid sites and makes the entire paraffin-activation-isomerisation-cracking-saturation sequence occur on the acid sites.

Since the 'classical' mechanism fails to describe several of the phenomena seen in bifunctional hydroisomerisation/hydrocracking, the question arises whether or not this mechanism is real at all. The presentation shows and discusses results obtained from specifically designed hydrocracking experiments, whose outcome can only be interpreted in such a way that under hydrocracking conditions no olefins desorb from the acid sites (as required if the olefins had to hop to the metal sites). This proofs the first one of the central postulations in the classical mechanism wrong. Results also show that under the respective conditions hydrocarbons do not have to be olefinic in order to be adsorbed, activated and converted on the acid sites, but readily do so in paraffinic form. This proves the other central postulation in the classical mechanism (paraffin dehydrogenation on the metal sites and subsequent hopping to the acid sites) wrong as well. Consequences for practical purposes are that acid and metal sites should be as close as possible, even closer than suggested by the Weisz intimacy criterion, and that support material should be as spill-over friendly as possible, i.e., stabilise the spilling-over activated hydrogen to a point that losses by desorption en route are little, while surface diffusion rate is still high.

Catalyst Deactivation during Hydroprocessing of Coal-Derived Liquids at Pilot Plant Scale

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As crude oil is being exhausted and the demand of fuel rises, much more attention has been paid on the development of alternative resources such as bio-oil, coal derived liquid and shale oil. In China, coal plays a vital role in the chemical industry and abundant coal tar can be produced from coal carbonization and gasification every year. Coal tar can be upgraded to produce the clean transportation oils via hydrogenation. Owing to the complexity coal tar with more contaminants and more aromatics, the development of improved the activities and stability of hydroprocessing catalysts is necessary. Catalyst deactivation plays an important role in hydroprocessing design and operation and is related to the feed composition. A better understanding of deactivation could extend catalyst life and thus have enormous economic benefits. In this paper, the change of structural and chemical properties of the catalysts were characterized during hydroprocessing by coupling with hydrotreating (HT) and hydrocracking (HC), by BET, SEM-EDS, NMR, TEM, XPS, etc. In combination with the asphaltenes structure, the mechanisms responsible for the catalyst deactivation were also studied.

We used a whole-fraction tar derived from pyrolysis of Shenmu coal as the feedstock. Sulfur, nitrogen, asphaltene, iron, and calcium contents of this feedstock were 0.18, 0.68, 22.58 wt%, 117 and 103 ppm, respectively. The hydroprocessing pilot plant test was performed at severe reaction conditions, and found the hydrotreating activity such as HDM, HDS and HDN declined with TOS, while the hydrocracking activity was very low, which is reflected by the low residue conversion and product distribution. BET results showed that the total loss in surface are for HT and HC catalysts is about 48% and 73%, respectively. About 18% metals were deposited on HT catalyst while almost no metals are deposited on HC catalyst, resulting in the partial or full blockage of pores. The deactivated pores can partially be regenerated by burning the coke but metal accumulated pore will not be regenerated, indicating that metals are more effective on the pores. SEM-EDX showed that Fe and Ca are mostly deposited on the edges of extrudates and the formation of Fe sulfide was also confirmed by EDX and ICP on the surface of catalyst. In addition, the nitrogen-containing compounds on HC catalyst could inhibit the acidity of support and act as coke precursors as a result of the partial decrease of activity [3]. This deactivation is reversible and the most of activity could be recovered by catalyst regeneration. Furthermore, the amount of the nitrogen-containing compounds can be tuned to a low level to resistant nitrogen. In summary, at the early stage of reaction, coke is predominantly deposited on the external surface of the catalyst, and gradually penetrates into the interior cavity during reaction. When the metals deposition is very low, metals sulfides may cover the interior active sites rather than pore plugging, which is irreversible and couldn't be regenerated.

SESSION 20
Sustainability and Environment - 1

Hazardous Particles from Coal Fires from Santa Catarina, South Brazil

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Coal mining in Santa Catarina, South Brazil, impacted the environment by means of a large number of coal waste piles emplaced over the old mine sites and the adjacent areas of the Criciúma, Urussanga, and Siderópolis. Poor disposal of coal cleaning rejects represents significant environmental concerns due to their potential influence on soils and river sediments, as well as on the surface and groundwater in the surroundings of these zones. In this research advanced analytical techniques were performed to provide an improved understanding of the complex processes related with sulphide-rich coal waste oxidation, spontaneous combustion, sequences of mineral formation, and the transport mechanisms of hazardous elements by neoformed soluble nanominerals and ultrafine particles. The results showed the presence of massive amorphous Si–Al–Fe–Ti–Zr (oxy-) hydroxides and Fe-hydr/oxides with goethite and hematite with various degrees of crystallinity, containing hazardous elements, such as Cr, Hf, Hg, Mo, Ni, Se, Pb, Th, U, Zr, and others. Several of the neoformed nanominerals found in the burned coal rejects are the same as those commonly associated with coal mine drainage, in which oxidation of sulphides plays an important role to environment and human health. This is the first Brazilian coal spontaneous combustion research.

An Investigation on Incorporation of a Local Thermal Power Station Boiler Ash as a Raw Material in Clinker Manufacture

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Coal is the major fuel used for electricity generation in Zimbabwe and a huge contributor of solid waste like boiler ash which presents major disposal challenges. Due to high contents of silica, aluminium oxide and iron oxide, boiler ash may find use in the cement industry. Research was carried out on the possibility of incorporating boiler ash from a local thermal power station as a third raw material in clinker manufacture. The boiler ash was characterised using XRF, bomb calorimeter and proximate analysis. It was observed that the boiler ash contained an average amount of 24% silica, 21% aluminium oxide, and 15% iron oxide which are important materials in clinker manufacture. The boiler ash was also observed to contain high carbon of 28% and had a calorific value of 8.21 kJ/kg. The Mix Solution Region 96 program was used to assess the effects of varying percentages of boiler ash incorporated with other raw materials (limestone and clay). It was observed that the boiler ash can be incorporated replacing up to 14% clay without affecting the clinker quality. For the plant trial 1% boiler ash was used to replace clay instead of 14% due to high carbon content. Carbon forms carbon monoxide in the flue gases during the process which might lead to electric sparks in the electrostatic precipitator. The resulting clinker was of good quality with C_3S (tricalcium silicate) above 53% and high burnability factors. There was an increase in carbon monoxide produced during the plant trial. Using boiler ash also contributed to lowering coal consumption by 10% in the furnace.

Environmental and Economic Evaluation of the Production of Organic Platform Chemicals from Different Feedstocks

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Currently, crude oil is the main feedstock of the chemical industry for the production of organic platform chemicals as ethylene and propylene, which have a global production capacity of about 145 and 90 million tons per year, respectively. However, concerns about depleting resources and the local concentration of oil reserves encourage the utilization of alternative feedstock and development of different production pathways. Especially in China, the use of domestic coal as a feedstock for the chemical industry has gained importance in recent years. In Germany – which is in the midst of an energy transition – an increasing material use of biomass and coal in chemical applications is pursued, as well as the application of carbon dioxide from fossil sources as a feedstock in combination with hydrogen from renewable energy sources. From a technological standpoint, the advancements in methanol-based olefin production technologies (MTO-technologies) allow a wide range of possible carbon feedstock by means of synthesis gas from gasification or reforming processes. While efforts are underway to assess the viability of different carbonaceous resources as alternative feedstock for the production of platform chemicals, the diverse consequences of their utilization are not yet fully evaluated under environmental and economic aspects.

In the present investigation, a case study is conducted on the ethylene and propylene production in Germany based on natural gas, lignite, crude oil, biomass and carbon dioxide. The study focuses on the MTO-based pathways, which are evaluated by means of process simulation, including synthesis gas generation and purification as well as methanol and olefin synthesis and refining. The scope of evaluation is further extended to include upstream factors such as extraction, transportation and processing of raw materials. The production pathways are evaluated in terms of economic (capital and operation costs) and environmental life cycle criteria (resource depletion, global warming potential, cumulated energy demand and others). The results are compared to the economic and environmental characteristics of the olefin production from crude oil, which are obtained from environmental databases and other literature sources.

Process Simulation and Assessment of Coke Oven Gas to Methanol Integrated with CO_2 Recycle

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COG as a byproduct of coking industry abounds in China, half of it is burned out for heat required of coke oven, the other half is usually combusted or discharged into air which is not only a waste of the hydrogen-rich valuable resource but also causing some environmental problems. Though methanol synthesis from COG is mature and a good way for COG utilization, H_2/CO ratio of nearly 5 is too high for methanol synthesis, to which H_2/CO close to 2 is optimal. Generally, to tackle this issue, carbon-rich gas making subsystems is adopted to supply carbon resource and balance the surplus H_2. From this way, it can get more H_2 conversion and methanol output, but it will undoubtedly cause system complexity and investment increase. In this work, a newly designed COG to methanol process with CO_2 recycle was proposed and simulated by Aspen Plus software. The new system maintains the same merits, and also presents the potential in terms of reduction of system complexity, curtailment of capital investment, and decrease of energy consumption compared with the traditional carbon-supplementary method. Two projects concerning whether H_2 is separated from COG or not are presented, and they are marked by project CWOSH (COG without separation H_2) and CWSH (COG with separation H_2), respectively. In the CWOSH, COG is splits into two parts, one for dry reforming and the other for combustion, and syngas from reforming reactor is directly sent for methanol synthesis. In project CWSH, H_2 is firstly separated from the COG, and then COG is divided into two streams likewise in CWOSH. However, the separated H_2 mixed with the reformed gas to produce syngas with the proper H_2/CO for methanol synthesis in CWSH. In both projects, the unreacted syngas partially recycles back to react and the other part to be mixed with COG for combustion with oxygen. The heat from combustion is supplied to coking process and reforming reaction. High content of CO_2 in flue gas is roughly separated by a cooler, and then recycled to reform with COG, also to coke oven for temperature adjustment. Optimization of the two projects involving element utilization, energy conversion, and economy benefit is given by adjusting variables, like recycle ratio, COG reforming ratio, etc. It is revealed that 3-8% energy saving, about 50% CO_2 emission reduction and 5-10% internal rate of return (IRR) increase will be obtained in both projects, versus traditional COG to methanol process. And project CWSH will get more CO_2 emission reduction and economic benefit but lower energy saving than CWOSH.

SESSION 21
Shale and Coal Bed Gas

Status of Worldwide CMM and CBM Activity Including Sub-Saharan Africa

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The downturn in the global coal industry, combined with the precipitous decline in carbon credit prices, has negatively impacted coalmine methane (CMM) and coalbed methane (CBM) development projects in several countries including the US and China. However, in a number of countries, CMM/CBM activity is on the rise as new projects come on line in India, Turkey, Australia, and others. Of particular relevance to this conference is the interest in CMM/CBM development in sub-Saharan Africa which is seeing activity in Botswana, South Africa, and Zimbabwe. The growth of CMM/CBM in these and other countries is due to a number of factors including limited conventional gas resources, high energy costs, and expanding coal production.

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

Consideration of a Possibility of Enhanced Coalbed Methane Recovery by Injecting Air Into Coal Seam

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CO_2 is usually injected into coal seam for enhancing coalbed methane recovery. CO_2 however causes coal swelling and permeability reduction of coal seam, which causes reduction of injection capability. In addition, several facilities should be constructed to separate, transport and store CO_2 for CO_2 injection. This study suggests a novel technique enhancing coalbed methane recovery injecting air into coal seam. CO_2 can be generated in-situ due to coal oxidation in this technique. Desorption of coalbed methane may be also stimulated by heat which may be generated by the coal oxidation. Air can be obtained easier than CO_2, therefore, our technique is economically feasible. We estimated the possibility of air injection by carrying out experiments of coal oxidation under low temperature conditions and conducted numerical studies to estimate the coalbed methane recovery by air injection in this study. Chinese lignite whose moisture content was 20.1% was used in this study. The powder of the coal was filled in a pressure vessel whose internal volume was 75 mL. To evaluate the oxidation of coal, gases such as Air, O_2 and N_2 were injected to the pressure vessel. The pressure vessel was put in a thermostatic chamber whose internal temperature was 40 ºC. Gas sample was extracted from the inside of the vessel every 24 to 48 hours and the gas compositions were analyzed by gas chromatograph.

Air was injected into the coal at 4.0 MPa to evaluate the possibility of the coal oxidation under low temperature such as 40 ºC. 3.0 % of CO_2 was detected in the gas sample which had been extracted from the vessel after 200 hours elapsed. CO_2 was not detected in the gas sample when pure N_2 was injected into the vessel at 4.0 MPa, therefore, the CO_2 was assumed to be generated by the low-temperature oxidation of coal. The pressure vessels were filled with three different coals whose moisture content were 20.1 %, 14.6 % and 5.38 % respectively and pure O_2 was injected into them at 1.2 MPa to evaluate the effect of moisture content of coal to the oxidation. The moisture content of the coal was adjusted by vacuuming it under 100 ºC. As a result, it was shown that CO_2 can be generated much more as the moisture content of coal was higher. This result indicates that the water-soluble materials such as organic matters and/or metals might stimulate the coal oxidation. Coals whose particle size were 8 mm and 30 μm respectively were packed in the vessels and pure O_2 was injected into both vessels at 1.6 MPa to evaluate the effect of particle size of coal. Although the delay of CO_2 detection was found in the experiment using larger size coal, the delay was not significant. This result suggests that the particle size of coal may not be effective for the coal oxidation. O_2 was injected into the coal at 0.4 MPa, 0.8 MPa and 1.6 MPa respectively to evaluate the effect of partial pressure of O_2. The reaction rate constant of coal oxidation became larger as the partial pressure of O_2 was higher. Finally, the experiments were carried out under 40 ºC, 55 ºC and 70 ºC to evaluate the effect of temperature. The coal oxidation reaction rate became larger as the temperature was higher. An Arrhenius plot was created from the results of O_2 analyses in the gas samples which were extracted in these experiments. The frequency factor and activation energy were derived from the straight line approximating the Arrhenius plot. Heat generation due to coal oxidation was also found in the experiments, therefore, the increase in temperature of coal seam can be expected by air injection. Both CO_2 and heat can be generated due to coal oxidation under low temperature such as 40 ºC and high pressure conditions.

Numerical studies of coalbed methane recovery by injecting air into coal seam were carried out using CMG STARS, which was a reservoir simulator used in petroleum field. The frequency factor and activation energy which had been derived from above experiments were input into the simulator. According to the results, the enhanced coalbed methane recovery by air injection was almost similar with that by CO_2

injection. This result suggests that the air injection into coal seam can be effective and practical for enhancing coalbed methane recovery.

The Role of the Residual Bitumen of Mature Lacustrine Shale to the Gas Storage Capacity: A Case Study of the Triassic Yanchang Shale, Ordos Basin, China

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Recent past decades, shale layer have been recognized as commercial natural gas reservoirs with enormous shale gas reserves or potential in the North America. And successful exploration and production of shale gas in the North America have encouraged many other countries, to evaluate the shale gas resources. At present, the global shale gas exploration and development mainly focus on the marine shale, such as the Barnett Shale in the United States and the Longmaxi Shale in Sichuan Basin, China.

The Upper Triassic Yanchang lacustrine shale (Chang 7 and Chang 9 Member), organic matter-rich dark argillite source rocks and abundant hydrocarbon potential, are some of the most important petroleum targets, specially the terrestrial petroleum resources in China. The Upper Triassic organic-rich Yanchang shale comprise of thermally mature Chang 7 Shale (average TOC 5.1%, Type I-II kerogen, Ro 0.83%-1.0%) and relatively mature Chang 9 Shale (average TOC 4.4%, Type I-II kerogen, Ro 0.88%-1.1%). The mineralogy of Yanchang shale is dominated by clay minerals (average 48.8% and quarts (average 31.7%)。

The purpose of this work is to characterize the geochemical features of Chang 7 and Chang 9 Member of Yanchang Shale and investigate the role of the residual bitumen in the shale gas storage capacity. More than 300 samples from 5 Wells were selected to analyse the geochemical feature. And three representative shale core samples were chosen to research the role of the residual bitumen in the shale gas storage capacity.

In order to investigate the role of the residual bitumen in the shale gas storage capacity for potential terrestrial shale gas reservoirs in the Yanchang area, Ordos Basin, a series of low pressure nitrogen adsorption/ desorption and high pressure methane sorption experiments were conducted on pretreated fresh drilling cores (including three groups of core samples: one original group, one group extracted by dichloro-methane and the other group extracted by trichloromethane) selected from Yanchang shale to demonstrate the role of the residual bitumen in the shale gas potential. Low pressure nitrogen sorption method was used to describe the effect of the residual bitumen on the pore structure of Yanchang Shale. The results show that the specific surface area and pore volume and pore surface area of shale samples after the extraction greatly increase and their growth was closely related with pores of >30 nm and <10 nm respectively. A negative correlation between the surface area and TOC was observed widespread in Yanchang shale, indicating that the residual bitumen that blocks the pores and pore-throats dramatically influences the methane sorption capacity in the mature shale. Based on nitrogen adsorption/desorption isotherms, ink-bottle-shaped micropores and mesopores likely acting as narrow necks of those pores well developed and were most likely influenced by the residual bitumen, which is favorable for adsorption accumulation but disadvantageous for the seepage of shale gas. The methane sorption isotherms measured on moisture-equilibrated shale samples suggest that the dissolution in the residual bitumen could be an important gas storage mechanism in Yanchang low mature lacustrine shale.

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Analyses of Adsorbed and Free Gas Production Using Methane Carbon Isotope Fractionation during Canister Desorption of Shale Gas

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Understanding the production of adsorbed gas and free gas proportion is of great importance to the predicting of the overall shale gas production behaviour. A model combining gas volume released from canister desorption at both reservoir and elevated temperatures and its chemical and isotopic compositions variations was used to evaluate adsorbed and free gas production from two gas shales. $\delta^{13}C$ values of methane show an exponential increase with the gas volume at reservoir temperature. At elevated temperatures (60 °C and 90 °C), a similar trend exists except for a sudden drop in the $\delta^{13}C$ values during temperature increases. A model incorporating the adsorption and diffusivity behaviour of $^{12}CH_4$ and $^{13}CH_4$ was developed to describe the adsorbed and free $^{12}CH_4$ and $^{13}CH_4$ released from the Longmaxi and Shujingtuo shale cores. Calculations show that isotopic fractionation by diffusivity has similar trend with isotopic fractionation in shale gas desorption process, while the combination of adsorption and diffusivity can best fit the isotopic fractionation in shale gas desorption process. Temperature variations make carbon isotopic fractionation more complicated. The modeled results show that initially free gas makes up the major component of the released gas, while adsorbed gas becomes dominant subsequently. Increasing temperature can drastically accelerate desorption of the adsorbed gas and thus increase gas production, which could be useful to stimulate gas production. The technique of analyzing isotopic composition of produced gas can be used with reservoir simulation for better understanding the shale gas production behaviour in over-matured gas shale especially its long term production behaviour.

Anisotropic Permeability and its Relationship with Pore/Fracture Structure of Longmaxi Shales in the Upper Yangtze Region, China

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Permeability of shale gas reservoirs is key for gas production, and is extremely low compared with conventional gas reservoirs. Shale permeability ranges from sub-nanodarcies (nd) to tens of microdarcies, making it difficult for gas to flow or be produced without stimulation. Besides, shale reservoir permeability is also strongly anisotropic between directions parallel and perpendicular to bedding, because of the presence of bedding. Precisely measuring the anisotropic permeability of shales and understanding its geological controls is important for evaluating shale reservoirs. In this study, we measured the anisotropic permeability in three directions of three cubic shale samples that are with different lithologic features from Lower Silurian Longmaxi Formation in Upper Yangtze Region, which is also the target for shale gas exploration and development in China. Besides, we used Micro-CT and SEM Maps to characterize the pore/fracture structure of the three shales to investigate its relationship with shale anisotropic permeability. Results show that permeability parallel to the bedding of the three shales varies between 98.3 and 3042.4 nd, while vertical permeability varies between 5.5 and 17.3 nd in vertical direction, using helium. Permeability in two parallel to bedding directions also shows strong anisotropy and the ratio can be as high as 2.85. The SEM Maps combined with Micro-CT 3D reconstruction show that microfractures along bedding direction are developed in the two shales that with high horizontal permeability. The fracture density in the two shales also show good relationship with permeability, which strong suggest that microfractures are critical to permeability in the parallel to bedding direction, and they also lead to the anisotropic permeability between the parallel and perpendicular to bedding directions. Microfractures are greatly in fine silty shale samples so with the highest horizontal permeability of the three samples which also suggest fine silty shale might be good shale reservoir for gas production.

SESSION 22
Coal Science - 4

Desulphurization of South African Coal Using Low Power Microwave Energy

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Increasingly stringent environmental regulations force us to look at alternative or additional methods to in- and post-combustion treatment for sulphur removal. An emerging technique in the minerals processing industry for sulphur removal is microwave treatment. This study undertook to determine the effectiveness of microwave irradiation on South African bituminous coals using various alkali solutions. Optimization of the treatment process was carried out on both low and high sulphur coals at varying power levels and retention times. Particle size and alkali concentration change effects, in addition to the above were studied. Changes in structure and combustion characteristics after desulphurization using a strong caustic solution were investigated.

The optimum sulphur removal time and microwave power for the high sulphur (±3.3 per cent) coal, 600 µm size fraction, were difficult to detect due to uneven distribution of S within the coal structure and thus the samples may have been biased. Coal particles of size 212 µm and 74 µm showed optimum sulphur removal after an exposure time of 10 minutes at a power of 650 W. Structural characteristics evaluated using XRD and Raman spectroscopy showed the coal to be largely unaltered. A slight decrease in calorific value and volatile matter was noted.

The low sulphur coal yielded a 43 % sulphur decrease with pyrite occurring predominantly in the organic phase and in small quantities. Structural characteristics were unaffected whilst combustion characteristics decreased to some extent. The comparative sulphur removal values for the high and low sulphur coals indicate that the mode of occurrence of pyrite in the coal matrix does not appear to affect desulphurization in this instance.

Treatment with strong KOH solutions as well as mixtures of NaCl and NaOH yielded improved desulphurization values than that of the NaOH solution alone (40 % to 52 %). Conventional leaching with NaOH was found to show enhanced sulphur removal when compared with coals treated using microwave energy. Further investigation into alkali penetration depth with time and temperature is needed before a conclusion can be drawn.

Application of Coal Petrography in Understanding the Variation of Coal Composition in the Coalfields of Botswana

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Several companies previously carried out reconnaissance investigations at an attempt to explore the coal of Botswana. However, no petrographic information was published. The main objective of this study is to assess coal compositions in the coalfields of Botswana, through the use of detailed coal petrography. The study currently includes the following coalfields; Lechana (5 borehole samples), South Orapa (5 borehole samples), Morupule (7 borehole samples), Takotakwane (8 borehole samples) and Tuli (8 borehole samples).

This project includes both petrographic (vitrinite reflectance, maceral group analysis, and microlithotype) and chemical analyses (proximate, sulphur and CV analyses). The vitrinite reflectance is used to determine the rank of coal, and the maceral group analysis to determine the type of coal, with the microlithotype analysis for the determination of coal and mineral associations. The petrographic analysis was carried out using a Zeiss Axio Imager m2m reflected light microscope fitted with Hilgers Diskus Fossil software for reflectance and maceral analyses, at a magnification of x500 under oil immersion. The microscope consists of an automated scanning system for images, equipped with auto-image focusing. The technique requires installation of the Fossil Student software for off-line maceral group analysis and mean random reflectance.

The methodology followed to identify and quantify maceral type includes: point counting (maceral counted is that lying directly under the cross-hair) of possibly 27 selected macerals, with 500 readings taken for each block sample. The study revealed that the Botswana coal samples consist predominately of the inertinite maceral group, and less amount of vitrinite maceral group, with traces of liptinite. In most cases, inertodetrinite was reported as the dominant inertinite submaceral. Among the submacerals of the vitrinite group, collodetrinite is the most apparent component. Minerals were categorised into three groups: silicates, carbonates and sulphides. Silicate minerals were reported as the most abundant minerals in the coal samples from Botswana. The proximate analysis indicate variable ash content.

The results obtained by vitrinite reflectance analysis indicated that the Lechana, Morupule, Orapa and Tuli coalfields consist of bituminous coal. The Takotakwane coalfield is the only coalfield that is characterised by coal of sub-bituminous rank. The South Orapa coalfield consists of 3 samples indicating coal of bituminous rank, and 2 samples that were affected by heat (yielding high vitrinite reflectance readings) indicating coal of low-volatile bituminous rank.

SESSION 23
Gasification Technologies: General - 2

Char Gasification Kinetics in Mixtures of CO_2 and H_2O: Understanding the Roles of Actives Sites and Catalysis

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Over the last decade there has been considerable interest in studies of char gasification reactivity in mixtures of CO2 and H2O. This interest has been fueled by the appearance of (apparently) contradicting perspectives: one suggesting that these two reactions occur independently and that their kinetics should be considered in isolation; and the other suggesting that they actually compete for active surface and the subsequent reaction kinetics should be treated accordingly. Some more recent work by the authors has shown that these two perspectives are probably consistent with our understanding of the mechanisms of the reactions, and that they are not contradictory in any way. This was shown to be the case using bituminous coal chars and related directly to the availability of reactive surface.

This paper continues this work to include low rank coal chars, where catalysis of gasification reactions is significant (thereby reducing the role of surface reaction processes). It is shown that for chars where catalytic reaction effects are expected to be large there is a significant impact on the manner in which the two reactants react with the char. While there is still evidence of competition for active sites, there is also the strong influence of non-competitive catalytic processes, which in this case strongly influences the observed results. This further demonstrates that the diversity of results in the literature may well be consistent with our understanding of the fundamentals of char gasification, provided an adequate description of the relevant processes is part of the analysis.

Green Coal Development for Application in Fixed-Bed Catalytic Gasification

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A novel “Green Coal” product formulation has recently been developed and the utilisation concept satisfactorily tested at the North-West University coal research laboratories. This innovation relates to: (1) the development of a process for the production of a carbonaceous feedstock material from waste-containing carbon sources (fine discard medium rank C bituminous coal from the Highveld coalfield and bio-char residue from liquefaction) together with an alkaline metal catalyst/sorbent, and, (2) to the use of the carbonaceous feedstock material in a fixed-bed catalytic gasification process, whereby hazardous emissions of greenhouse gases and sulphur are significantly minimized and reaction rates are greatly enhanced in a single step. Hydrothermal liquefaction was used to produce bio oil and biomass char from sweet sorghum bagasse at operating temperatures ranging between 280 - 300 °C, and the resultant char was mixed in various ratios (0, 0.25, 0.50, 0.75, and 1) with fine discard coal (<212um) and $CaCO_3$ (1-5wt%). The mixtures were pressed into pellets (12mm x 12mm) using an LRX press at a pressure of 4 bar and gasified using CO_2 at atmospheric pressure and temperatures ranging between 800 - 1000 °C. Kinetic parameters were obtained from the experimental data and showed that the pre-exponential factor of the Arrhenius equation of the bio-char was an order of magnitude higher than that of raw coal, with the blend containing 3 wt% $CaCO_3$ having the fastest reaction rate. In order to study the temperature and catalyst effect on the retention of elemental sulphur during combustion of the various pellets, a combustion setup consisting of a furnace, glass bayonet-type reactor, Liebig cooler, liquid traps and an SO_2 gas analyzer were used, with experimentation occurring at 500 - 800 °C. As expected, low sulphur retention was observed for the raw coal and bio-char blends, but increased significantly to values between 56 – 86% sulphur retention; decreasing with increasing temperature, in the presence of the added metal catalyst/sorbent runs. A simulated example using Fact-Sage ^{TM} predicted that >50% of the pyritic sulphur entering the fixed bed gasifier is removed from the gaseous phase as insoluble $CaSO_4$ when operated in a catalytic gasification mode at a temperature of 800 °C, in good agreement with the experimental findings.

Experimental Investigation on Char Gasification Kinetics at Elevated Pressures

Sascha Russig, Victor Gonzalez, Mark Zink, Steffen Krzack, Stefan Guhl, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

It is well known that the experimental boundary conditions present at the investigation of reaction kinetics are crucial for the received kinetic data. In the lab and bench scale range of test equipment mass and heat transfer conditions can vary widely between test facilities. This results in different effective gasifying agent concentrations at the char surface. Especially the concentration of reaction products is not to be neglected in the evaluation due to their inhibiting effect. The acquisition of representative kinetic parameters is therefore essential for computer aided modeling of gasification processes and improving gasifier designs. A novel test facility, named KIVAN, for the investigation of heterogeneous gasification reactions under high pressures is presented. Facility properties and the possibilities of experimental test procedures are explained in detail. An innovative temperature measurement system enables the determination of the process temperature along the reaction zone in real-time. 12 evenly distributed gas sampling ports allow for sampling of the gas composition along the reaction zone. Gasification experiments were carried out under CO_2 atmosphere with in rhenisch lignite char at a minimum pressures of 20 bar. The obtained concentration profiles are evaluated utilizing classical kinetic approaches as well as a computer aided modeling approach.

The aim of this research is to extend the current knowledge of gasification kinetics, especially the Boudouard reaction, taking into account the variation of temperature and concentration as the reaction progresses.

Ash Agglomeration in the Modified Internal Circulating COORVED Coal Gasifier

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Based on the previous design of the COORVED reactor for coal gasification the technical and operational limits of the former system can be shown. First the flow pattern within the simple tube reactor exhibits the expected behaviour a heavy recirculation in the jetting fluidized bed, later on limits occurred in the gas and particle residence time and therefore in the achievable over all carbon conversion of the process in the given geometry.

In the present design the lower part of the reactor has changed completely to reduce the necessary gas flow, required to fluidize the powdery feedstock with its specific superficial gas velocity. Thus the inner diameter of the two bottom segments has been reduced. Supporting the necessity of increased residence time, the main reaction zone around the primary gasification agent nozzle in the middle part of the reactor was widened in diameter to double size.

Even with the new reactor design the limits caused by the chosen start-up fuel, a hearth furnace coke, have been reached soon. Due to the missing content of volatiles in the fuel it is challenging to heat up the lower reactor part in the process and the temperature management is based more on random than controlled ignition. Owing to the low reactivity of the high temperature coke, the high temperature of the central oxygen jet is not easily reduced by endothermic gasification reactions until the gas flow reaches the refractory lining, which increases the risk of slagging.

As a result of the given limits a further change to another fuel needed to be done. Lusatian lignite was chosen as the new feedstock, with which the ash agglomeration occurred almost immediately in the COORVED process in an O_2/CO_2-run. The further work shows different parameters influencing the agglomerating process in the new reactor geometry and the required proof of the patented INCI coal gasification principle has been produced.

SESSION 24
Clean Coal and Gas to Fuels: New Technologies

Supercritical CO_2 Cycles for Power Production

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The Allam Cycle is a high-pressure, highly recuperative, oxygen-fired, supercritical CO2 cycle that makes carbon capture part of the core power generation process. This cycle utilizes supercritical CO2 as a high-pressure working fluid through a very compact high-pressure turbine. Cycle efficiencies are capable of reaching up to 47% on a higher-heating-value basis for a lignite feedstock while producing a near-sequestration-ready CO2 stream requiring some O2 reduction and dehydration (Forrest, B. et al. *Oxy-Lignite Syngas Fueled Semi-Closed Brayton Cycle Process Evaluation – Evaluation of Cycle Performance, Cost and Development Plan*; Final Public Report, Jan 2014, 100 p.). According to a recent study, the coal gasification/supercritical CO2 cycle can offer a 25% to 50% increase in net cycle efficiency when compared to an integrated gasification combined cycle with 90% CCS (carbon capture and storage) (Phillips, J. et al. *Can Future Coal Power Plants Meet CO2 Emission Standards Without Carbon Capture & Storage?* Electric Power Research Institute, Oct 2015, 16 p.).

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

This paper reviews the Allam Cycle principles and also the challenges and opportunities of producing power with the Allam Cycle using North Dakota lignite. Points of emphasis include corrosion analysis, efficient removal of impurities from syngas, gasifier integration, and design considerations of a high-pressure oxy-fired syngas combustor. The lignite design needs further development to assess the challenges of operating key equipment in a syngas environment and to identify the best gasifier and combustor design to support the supercritical CO2 power cycle on North Dakota lignite. The EERC and 8 Rivers are utilizing prior research experience to develop a short list of gasifier technologies to be considered for selection and will ultimately choose the best technology based on the ability to successfully gasify North Dakota lignite and integrate the gasifier into the Allam Cycle with highest system efficiency and lowest cost. This presentation reviews the challenges and opportunities of gasifying North Dakota lignite, including high-sodium content and high reactivity, and develops the groundwork for the gasifier selection process. Additionally, initial results of system modeling and integration, evaluation of process components, and economic considerations will be provided along with a technology development pathway road map for lignite-fueled applications.

Integration of Gasification and Fuel Cells: Interaction between the Anode and Contaminants in the Syngas

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Integration of gasification with fuel cells can lead to higher efficiencies in relatively small scale power generation systems. Among fuel cell technologies, solid oxide fuel cells (SOFC) present a good match with gasifiers in terms of operating temperatures and resistance to contaminants present in the gas. However, questions remained regarding the level of contamination that the cell anode can tolerate and therefore the level of gas cleaning necessary.

Studies conducted on the interaction between tars and the SOFC anodes showed that carbon formation can quickly lead to deactivation of the anode. This work has identified the more volatile tar fractions as those most adversely affecting the anode. However, operating conditions that minimize carbon formation can be chosen such as high current densities and presence of steam. Interestingly, certain amount of sulfur was found to be beneficial to cell operation as it competes with the carbon formation process.

Liquefaction of South African Bituminous Coal Using Phenol as a Solvent

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Direct liquefaction of a South African, vitrinite-rich bituminous coal (Waterberg) was carried out under mild conditions on a laboratory scale using a SS316 stainless steel autoclave. The results found from this study show that the coal is moderately liquefied with the use of a solvent (phenol) in a ratio of 1:10 (coal: solvent). The study found that the conversion and extraction yield of oil are 49.5 and 26.3% d.a.f. respectively at 360 °C. With increasing temperature (300-360 °C), the conversion and yield of product increases, whilst the yield of intermediates (pre-asphaltene + asphaltene, PAA) increases from 300-340 °C and then decreases from 340-360 °C. This suggests that at 340 °C that PAA is thermally cleaved and hydrogenated into gas and oil. The gas products from coal liquefaction are mainly CO_2 followed by C_1-C_4 constituents. The low yields of hydrocarbon gas (less than 0.35 wt. %) formed suggests that coal liquefaction using phenol as solvent favours the production of liquids more than that of gases. Extracted fractions obtained at different temperatures were examined by Fourier transform infra-red spectroscopy (ATR-FTIR), gas chromatography mass spectrometry (GC-MS), liquid state ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) and simulated distillation by gas chromatography (SimDis GC). The results of these analyses were consistent, and revealed a progressive increase of poly-aromatic hydrocarbons (PAH's) and low amounts of aliphatic species in the coal-derived products with increasing temperature under mild conditions without the use of a catalyst.

Effect of Direct Addition of Alcohols to an Oligomerisation Reaction System

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The conversion of alcohols to olefins for energy is receiving considerable attention worldwide since the discovery of methanol to gasoline and distillates (MTGD) process by Mobil Oil, now known as EXXON-MOBIL. Thus far, only a few research papers on the conversion of higher alcohols to gasoline and distillates exist. A well-known research study was the conversion of bio-ethanol to gasoline (ETG) process conducted in 1980s. The alcohols are converted to gasoline and distillates through oligomerisation of light olefins formed during the dehydration. The intent of this research work is to explore the operating strategies for the direct addition of alcohols to an oligomerisation reactor model for the primary and secondary linear alcohols based feed such as ethanol, propanol, butanol, pentanol and hexanol. These alcohols form part of by-products generated from high temperature Fischer-Tropsch (HTFT) synthesis in which some of light olefins are also generated. The current oligomerisation reactor model is able to accept any of the following feed species, hydrogen, C2-C40 linear, mono-branched, di-branched and tri-branched olefins and paraffins. Only the olefins are reactive. The model can be run in gas phase, liquid phase or multiphase mode and in each case isothermally, adiabatically or with wall heat loss. In order to carry out this task, the reaction mechanisms and kinetic constants of alcohol dehydration over HZSM-5 catalyst need to be determined and further associated with phase and physical properties. The latter will be determined through the best fit rate expression and regression of the rate constants from the data measured at 220-280 0C. The experimentally determined olefin formation kinetic expressions and rate constants of ethanol and other alcohols will be added to a multiphase adiabatic oligomerisation reactor model typically operating at 250 0C and 50 bar. The model results will be further validated against micro-scale, pilot scale and plant scale due to unavailability of operational data in the literature.

The alcohols higher than ethanol have a different dehydration mechanism compared to ethanol when co-fed to the light olefins. This is due to ethanol potential to dehydrate through the hydrocarbon pool mechanism, thus generating C2-C4 or higher olefins. The ethanol dehydration through hydrocarbon pool mechanism can be described by the reaction scheme shown below.

$$C_2H_5OH_{(g)} \rightarrow C_2H_{4(g)} + \; H_2O_{(g)} \qquad (1)$$

$$2C_2H_5OH_{(g)} \leftrightarrow \; C_2H_5OC_2H_{5(g)} + \; H_2O_{(g)} \qquad (2)$$

$$C_2H_5OC_2H_{5(g)} + [C_2H_4]_{n(g)} \rightarrow \left(\frac{n+1}{n}\right)[C_2H_4]_{n(g)} + C_2H_5OH_{(g)} \quad (3)$$

$$C_2H_5OH_{(g)} + [C_2H_4]_{n(g)} \rightarrow \left(\frac{n+1}{n}\right)[C_2H_4]_{n(g)} + H_2O_{(g)} \quad (4)$$

$$C_2H_5OC_2H_{5(g)} \rightarrow \left(\frac{2}{n}\right)[C_2H_4]_{n(g)} + H_2O_{(g)} \quad (5)$$

where n is the average carbon number as a function of conversion to hydrocarbons (HC)

This hydrocarbon pool reaction may occur at temperatures under or slightly greater than the oligomerisation reactor temperature rather than extremely high temperatures i.e. 350 0C, when dehydrating ethanol without co-feeding it to the light olefins. During the hydrocarbon pool, the light olefins act as a pool when co-fed with ethanol thus lowering the reaction temperature.

It is known that the alcohols dehydrate to form water, and the respective ether and olefin(s) at temperatures reasonably within the adiabatic oligomerisation reactor. Once the alcohols are co-fed to the light olefins the nature of the reaction changes due to the fact that the dehydration of alcohols higher than methanol is endothermic whilst the oligomerisation of these light olefins is highly exothermic. Consequently, feeding strategies may need to be explored to study the effect of endothermic reactions on the oligomerisation reaction temperature. This strongly depends on the relationship between catalytic reactor's bed temperature and axial distance due to the exothermic nature of oligomerisation reaction. The effect of alcohol(s) feed composition on the oligomerisation reaction temperatures will be studied. In addition, study the effect of process variables such as partial pressure, space velocity and recycle ratio on the product distribution.

SESSION 25
Sustainability and Environment - 2

Environmental Pollution and Nano-Mineralogical Characterization of Coal, Overburden and Sediment from Assam (India) Coal Mining Acid Drainage

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Coal mining is one of the major industries that contribute development of economy of a country but it also deteriorates the environment. As a primary source of energy, coal has become essential to meet the energy demand of a country. In northeastern region of India, it is excavated by both open cast and underground mining methods and has the large environmental effects, especially water resources like streams and rivers, by discharging huge amounts of mine water. The Assam coals have high sulfur content, which is present in both in organic and inorganic forms. The Coal mine drainage (CMD) is produced due to high sulfur content in coal and degrades the water quality of the coal mine region in terms of lowering the pH of the surrounding water resources and increasing the level of Total Dissolved Solids (TDS), hardness etc. high hardness of mine water reduces its utility in domestic purposes. The chemical parameters including moistures, volatile matter, ash content, total sulfur, C, H and N contents have been analyzed for coal, overburden, soil and sediment collected from Ledo and Tirap collieries under North Eastern coalfield, Margherita. From the analysis, it has been found that the total sulfur content of coal samples is noticeably high compared to overburden and soil samples. The volatile matter of coal samples is sufficiently high against the high ash content of soil and overburden samples. The high Electrical Conductivity (EC) and TDS values have been observed and lowering of pH indicates the dissolution of minerals present in coals as well as other mine rejects. The chemical and mineralogical composition was studied using High Resolution-Transmission Electron microscopy (HR-TEM), Energy Dispersive Spectroscopy (EDS), Selected-Area Diffraction (SAED), Field Emission-Scanning Electron Microscopy (FE-SEM)/EDS, X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman and Ion-Chromatographic analysis. The present study aims to illustrate the effect of acid mine water of open cast mining in Ledo and Tirap coal mines (Assam) to the nearby areas. The presented dates of the minerals and ultra/nano-particles, puts in evidence their ability to control the mobility of hazardous elements, suggesting possible presentations in environmental technology, including restoration of delicate Indian coal mines.

Bench-Scale Testing of Stabilized Flue Gas Desulfurization Materials to Treat Acid Mine Drainage

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Small-scale laboratory tests carried out at The Ohio State University have shown the promise of neutralizing acid mine drainage (AMD) using stabilized flue gas desulfurization (FGD) material. These tests indicate that one pound of this sulfite-rich FGD material can treat and neutralize up to 20 gallons of AMD.

Prior to full-scale field implementation of the technology, a bench-scale laboratory study was carried out to better understand the flow of acid mine drainage and associated water quality as the AMD seeps through the FGD fill. The bench-scale mine highwall reclamation testing module, which has dimensions of 3 feet by 4 feet by 12 feet, was used to investigate the effectiveness of using stabilized FGD material for coal mine reclamation and AMD neutralization (see Figure 1). A number of potential placement designs of stabilized FGD material against a mine highwall for AMD treatment were tested in the module, which simulates the conditions similar to AMD penetrating stabilized FGD material during and after mine highwall reclamation under real-life scenarios. The module has pre-installed testing ports for water pressure measurement and leachate collection, which allows the detections of AMD flow within the mass of the fill as well as the change of AMD water quality along the flow. Results obtained from the laboratory- and bench-scale investigations were used in the design of a full-scale demonstration project, in which an AMD-producing unreclaimed coal mine highwall complex located at Cheshire, OH will be reclaimed.

Results obtained from the bench-scale studies will be discussed and demonstrate the potential impacts associated with coal mine reclamation using FGD by-products. The overall goal of these studies is to assess the potential of using high-volume CCBs in a manner that is economically viable and beneficial to the environment, the public's health and safety, and the generating industry.

Figure 1: Bench-Scale Assessment of AMD Infiltration in Simulated Highwall Reclaimed with Stabilized FGD Material

Orbitrap Analysis of Fullerene on Surface Soils and River Sediments from Santa Catarina (Brazil) Coal Area

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In the present work, a new analytical approach is proposed for the analysis of seven fullerenes (C60, C70, Nmethylfulleropyrrolidine, [6,6]-phenyl C61 butyric acid methyl ester, [6,6]-thienyl C61 butyric acid methyl ester, C_{60} pyrrolidine tris-acid ethyl ester and [6,6]-phenyl C_{71} butyric acid methyl ester fullerenes) in soils and sediments. This procedure combines an ultrasound-assisted solvent extraction (UAE) with toluene followed by liquid chromatography (LC), using a pyrenylpropyl group bonded silica based column, coupled to a high-resolution mass spectrometer (HRMS) using atmospheric pressure photoionisation (APPI) in negative ion mode. The analytical performance for fullerene separation of the pyrenylpropyl group bonded silica column was compared to the C_{18} column. For the ultra-trace analysis of fullerenes in complex environmental samples, the use of the APPI source and the use of the electrospray ionisation (ESI) source were compared. Using this approach for the analysis of fullerenes in complex matrices, a series of advantages, in terms of sensitivity and specificity, have been demonstrated. The method limits of detection (MLOD) and the method limits of quantification (MLOQ) in soils and sediments ranged from 0.022 to 0.39 pg/g and from 0.072 to 1.3 pg/g, respectively. Recoveries were between 68 and 106%. The analytical method was applied in order to assess the occurrence of selected fullerenes in 45 soils of Sul Catarinense (Santa Catalina State, Brazil) and 15 sediments from the Tubarão River, presenting different pressures of contamination: a coal-combustion power plant, car exhaust, coal mining industry and wastewater effluents. C_{60} and C_{70} fullerenes have been detected at concentrations ranging from the MLOD to 0.150 ng/g. None of the functionalized fullerenes were detected in any of the samples. Combustion processes, in particular car exhaust, were identified as the main source of fullerenes. However, the potential degradation of residual concentrations of engineered fullerenes to more stable forms, such as C_{60} and C_{70}, should also be considered.

Fireside Corrosion Monitoring, Control and Prevention in a 600 MWe Pulverized Fuel Boiler

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Introduction

Fireside corrosion is the corrosion of tubes due to chemical attack occurring on the furnace or fireside of heat exchanging surfaces in a fossil fuel-fired furnace [1]. This attack mechanism is one of the problems affecting the efficiency and availability of Eskom (Electricity Supply Commission) coal fired steam generators, commonly known as boilers.

Fireside corrosion reduces the service life of fireside wall tubes and in severe cases, has resulted in unplanned electrical power grid separations and unplanned outage time extensions. In Eskom the replacement of water-wall tubes below allowable minimum operating wall thickness, during outages, has since been used as the mitigating measure to deal with this phenomenon. The latter mitigating measure has proved to be effective, however, due to the increasing material wastage of water-wall tubes; the practise of tube replacement has become extensive and very costly.

Purpose

This research is aimed at establishing combustion/firing parameters that are conducive to oxidizing conditions by means of extracting and analysing specific post combustion gas concentrations under both oxidising and reducing conditions while monitoring the brake-point of H_2S (hydrogen sulphide) formation.

Theoretical framework

Boilers are fired with excess air in order to achieve complete combustion. Under ideal combustion conditions, oxidizing conditions are established in the flue gas corresponding to the excess air levels [2]. Oxidising conditions yield an environment that is necessary for favourable boiler combustion conditions, while reducing conditions promote the formation of H_2S which causes sulphidation corrosion on boiler walls [3].

Therefore, it is essential to monitor the gas concentrations of O_2, CO and H_2S in the flue gas stream at fireside corrosion susceptible locations. Flue gas monitoring is fundamental to determining suitable combustion conditions and controlling the formation of H_2S so as to prevent fireside corrosion in PF boilers.

Results and conclusions

The full scale combustion tests entailed extracting and analysing flue gas samples at maximum boiler load capacity achievable. The furnace exit O_2 concentration was reduced in attempt to simulate reducing atmospheres in the furnace. It was observed that at a furnace exit O_2 concentration of 2.5%, which is a value lower than the minimum 3% recommended value by the Eskom Fossil Fuel Fired Regulation (FFFR) for the specific boiler, oxidising conditions were still maintained.

Further tests were conducted at the Eskom Pilot Scale Combustion Test Facility (PSCTF) utilising coal from the Eskom power station where full scale tests were conducted. Results from the latter tests were used to determine the break-point of H_2S formation and validate what is stated in literature with regards to H_2S formation.

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SESSION 26
Gasification Technologies: UCG - 2

Can UCG Give Coal a New Lease on Life in 21st Century?

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Coal gasification has long been considered a pathway to making cleaner chemicals and energy from coal – a fossil fuel that many in 21st century believe is no longer compatible with sustainable and environmentally responsible development. Aged all but 200 years, conventional coal gasification technologies face problems with the safety, health hazards and environmental stigma of coal mining; handling of ash and other effluents; plant availability and prohibitively high cost. Underground Coal Gasification (UCG) technology safely produces gaseous and liquid hydrocarbons without coal mining, leaves ash deep in the ground and at its best is much less expensive. Low base cost means that, unlike conventional gasification, UCG can afford CO_2 sequestration while remaining competitive. Why has not it seen so far a wide global industrial deployment? Is there a chance that broad application of UCG will make wide use of coal environmentally acceptable? What is required of UCG to achieve recognition of investors, regulators and general public?

We answer the above questions by reviewing modern achievements of UCG development and pointing out the aspects that require further work to overcome apparent deficiencies. In doing so, we focus on technical viability of UCG technology and the factors that can make it commercial: scale, conversion efficiency, extraction rates, product quality and consistency. Environmental performance of UCG is presented using examples of recent UCG trials.

The Ergo Exergy's ***ε***UCG™ technology is an example of such a commercial technology, which is based on over forty years of operating experience in the Ukraine, Russia and Uzbekistan. Its performance is considered using examples of its application in the UCG projects in Australia, South Africa, New Zealand, the USA and Canada.

The ***ε***UCG™ produced syngas at a substantially lower cost than conventional gasification. Performance and economic comparisons are presented for producing SNG, gasoline, diesel fuel, ammonia, urea, methanol, and electricity - from ***ε***UCG™ syngas and the syngas of conventional gasification.

Life Cycle Sustainability Assessment of Integrated UCG-CCS Systems, Comparison with Clean Coal Alternatives

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Underground Coal Gasification (UCG) and utilising the produced gas for heating, power generation or as chemical feedstock may have many benefits, such as the avoidance of mining, applicability to uneconomic seams, avoiding the disposal of solid wastes and the use of lower cost/more efficient gas turbine power plant or fuel cell power generation. On the other hand, UCG has the potential to release environmental emissions from the UCG reactor to the underground strata and groundwater, such as the escape of product gas, leaching of pyrolysis products from the char zone produced by incidental pyrolysis of the reactor walls, and leaching of inorganic contaminants from the mineral ash produced. UCG may also require more water processing load than conventional underground coal mining.

Imperial College is leading an EU 7th Framework Programme funded international project on "Combined Underground Coal Gasification and CO_2 Capture and Storage" which has been developing life cycle inventory (LCI) models for the UCG processes and alternative syngas utilisation options with and without CO_2 Capture and Storage (CCS) at unit process level. The LCI models developed trace/quantify all important environmental emissions from UCG and across syngas utilisation options to their final release to the air, water and soil environmental compartments. The model considers coal seam quality, panel design parameters, and UCG process operational parameters (such as oxygen to steam ratio, temperature, and pressure). The alternative syngas utilisation option LCI models developed at unit process level include: syngas turbine combustion power generation with pre-combustion capture; full acid gas removal and post-combustion chemical adsorption CO_2 capture; syngas with pre-combustion CO_2 capture through sour shift of CO and hydrogen turbine combustion to electricity; syngas to SNG, methanol and ammonia with/without CO_2 capture; and syngas with fuel cell power generation with/without CO_2 capture.

Imperial College has already developed life cycle inventory (LCI) models for alternative coal and conventional/unconventional natural gas production (including CO_2 ECBM and shale gas) and power generation with and without CO_2 capture, pipeline transportation, injection, and saline aquifer storage, as well as coal mining. All LCI models developed are at unit process level and successfully trace all the emissions to individual unit processes. This paper will present the LCI models developed during the current UCG project and compare the life cycle impacts of UCG with/without CCS with conventional coal mining and coal fired power plant options (including plants with post-combustion CO_2 capture, oxyfuel combustion CO_2 capture and pre-combustion CO_2 capture) with/without CCS. The environmental impact comparisons will also include CO_2 ECBM with CO_2 storage and CO_2 enhanced oil recovery (CO_2 EOR) with CO_2 storage to allow for comparisons with alternative complete chains.

Ex-Situ Simulation of High Pressure Underground Gasification of Hard Coal and Lignite

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Underground coal gasification (UCG) is a technique that converts coal directly underground into valuable gaseous products. It has recently attracted a considerable attention as an alternative to the traditional mining methods, especially in coal seams where traditional coal extraction technologies are economically, technically or environmentally not feasible. One of the most important factors affecting the chemistry of gasification, and therefore the composition of the product gas from UCG is the operating pressure. Higher operating pressures promote methanation reactions, which lead to the increase in gas calorific value:

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta H = -\ 87{,}5\ \text{MJ/kmol}$$

$$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)} \qquad \Delta H = -\ 206.2\ \text{MJ/kmol}$$

The operating pressure is determined by the seam depth. The hydrostatic pressure increases with depth at about 1 bar/10 m, however operating slightly below the hydrostatic pressure is the main preventive measure to effectively control the migration of contaminants during UCG operation.

Two experimental simulations of high pressure UCG (5 bar) with large bulk samples of hard coal and lignite were conducted in an 3.5 m ex-situ laboratory installation in the Clean Coal Technology Centre of Central Mining Institute, Poland. The average moisture contents of the coals were 4.9 wt% (hard coal) and 27.6 wt% (lignite) and their calorific values were 29.4 MJ/kg and 15.5 MJ/kg, respectively. Changes in the gas composition, gas production rates and distribution of the in-seam temperature profiles were controlled over the course of the two multi-day, oxygen and CO_2 blown gasification experiments.

This paper presents the general findings of the experimental study conducted with the main aim to evaluate the role of the elevated gasification pressure on the UCG process, depending on the coal rank. The study was carried out under a 7FP funded research project entitled: *Technology Options for Coupled Underground Coal Gasification and CO_2 Capture and Storage* (TOPS).

Experimental and Computational Studies on Underground Gasification of Turkish Lignite

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Underground coal gasification (UCG) is more advantageous than conventional coal combustion processes, as the first requires lower investment/ handling costs and operates environmentally friendly. Lignite is of utmost importance for the Turkish economy as Turkey has ~15 billion tons of lignite reserves. In this work, we have performed ex-situ reactor experiments to explore the gasification ability of Turkish lignite and to simulate and characterize the UCG process. Preliminary coal gasification tests were carried out with oxygen and steam for Malkara Pirinççesme (Turkey) lignite, which is characterized by high ash contents and low moisture. During the gasification experiments, temperature distribution inside the coal seams was monitored and the syngas outflow rate was measured. Additionally, syngas compositions were analysed using an MRU Varioplus Syngas analyser and an Agilent 7890B gas chromatograph. Results represent that the Turkish lignite sources are suitable for gasification. Experiments were divided into several phase: 1) oxygen phase 2) air-oxygen mixture phase, 3) steam-oxygen mixture phase, 4) air-oxygen-steam mixture phase, The syngas produced in the oxygen gasification stage was characterized by high calorific values of 6-9 MJ/Nm3, carbon monoxide contents of 23-33 vol.%, and hydrogen contents of 20-30 vol.%. Also, computational models of the experimental set-up was built and simulations were performed in ANSYS Fluent to elucidate the optimal parameters required for the high calorific syngas production; such as gasification agent rates, shape of the gasification channel, etc.

SESSION 27
Coal Science - 5

Trace Elements Associated with the Upper Coal Zones of the Springbok Flats Basin, South Africa

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The coal zones of the Springbok Flats Basin, Limpopo Province, South Africa, occur in the upper and lower parts of the Vryheid Formation. They are characterised by intercalations of mudstones, carbonaceous mudstones, and bright coals. The upper coal zones can be subdivided into 3 seams: upper, middle, and lower coal seams, which are separated by mudstones and carbonaceous mudstones. The three seams are well developed in the central sector of the Basin and are characterised by 37 – 62 % coal and 38 – 64% mudstones (carbonaceous and non-carbonaceous). The coals are vitrinite rich (79.7% to 94.1%, mineral matter free basis), dominated by collotelinite, pseudovitrinite, corpogelinite, colledetrinite, telinite, gelinite and vitrodetrinite. Mean random vitrinite reflectance of the coals range between 0.61 and 0.75%, indicating coal rank of medium-rank high volatile bituminous C. The coal seams in the central sector of the Springbok Flats Basin show average moisture content between 1.68 to 2.12%, ash contents of 20.97 to 30.8%, volatile matter average values between 17.72 to 33.07 % (air dried basis) and fixed carbon average values between 40.08 and 50.4%. Average sulphur content of the upper coal seams in the central sector is 2.56% (air dried basis).The average gross calorific value of the coal seams range from 20.39 to 24.36 MJ/Kg (dry basis). The upper coal zones in the central sector of the Springbok Flats Basin are unique in terms of trace elements when compared to the coal zones of other South African coalfields (i.e Witbank, Highveld and Waterberg coalfields) and average global coal Clarke values. The coals are characterised by high amounts of potentially hazardous trace elements such as Zn, V, U, Ni, Mo, Mn, Cu and Co (average values of 46.48 ppm, 80.64 ppm. 106.04 ppm, 39.86 ppm, 26.50 ppm, 1448 ppm, 32.20 ppm and 27.62 ppm respectively). These trace elements are considered to be of environmental interest due to their diverse effects on plants, animals and humans. Proton-Induced X-Ray Emission (PIXE) and proton backscattering spectrometry (BS) in conjunction with Nuclear Microprobe showed that Zn is associated with sphalerite; V and U are finely disseminated in the coal matrix; Mo, Cu and Co are associated with euhedral, subhedral pyrite in the coal samples. Mn is associated with carbonate minerals (i.e. siderite) in coal. The upper coal zones of the Springbok Flats Basin have potential to be mined for electricity generation provided they can be beneficiated (reduction of toxic and hazardous trace elements) and uranium can be extracted (as a by-product).

Organic and Inorganic Characterisation of Different Coals by Single Particle Analysis

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Single particle analysis, using techniques that provide structural, elemental and morphological information on particles of interest, has shown promising results when applied to coal. The main advantage of this non-destructive approach is that the inorganic and organic composition, and its potential influence on the behaviour of coal applied in different processes, can be probed at the same time. Characterisation of coal routinely aims to provide bulk information on its potential performance and usually comprises ultimate and proximate analysis. Of late, more sophisticated techniques such as petrography, QEMSEM and ICP-OES/MS would probe some additional properties (maceral composition, mineral composition, elemental profiles). There is however, a need to investigate the individual particle character to better understand the coal chemistry. This paper describes relationships between the organic structures in terms of disorder between 3 different South African coals and a discard coal (classified as medium rank C bituminous coals that are inertinite-rich), using micro Raman Spectroscopy on single particles. Using the well-described G (graphitic) and D_{1-4} (disorder) bands classification, the organic composition of the 4 samples are describe. The general parameters and predictors for disorder (I_{D1}/I_G, FWHM D_1 and G) and their relationship to rank seemed to indicate no major differences between the coals. However, a relationship between the three main macerals in the coal and their sp^3-sp^2 character could be established. Following Morga (2011), a prediction, based on the ratios of the areas of the deconvoluted Raman bands (A_{D3+D4}/A_{all}), of the reactivity of the coals were made. The ratios compared well with those of Morga (2011) for inertinite rich coals containing reactive and inert semi-fusinite. Single particle analysis was further conducted on the raw coals to characterise the inorganic component of the raw coals. A combination of micro Raman spectroscopy and computer controlled SEM-EDS / Electronprobe Microanalysis with X-Ray Detection (EPMA) was used for this purpose. This allowed elemental association of individual coal particles and therefore clusterisation of mineral classes. In total, 11 mineral classes were identified of which the silicate minerals were the most dominant group. Other mineral groups identified included quartz, Fe-rich particles, carbonates, gypsum, Ti-rich particles, dolomite, sulphates, sulphate silicates, and halites.The structural composition of these mineral classes identified were elucidated using micro Raman spectroscopy, with which different polymorphs of minerals could be discerned in addition to the classification based on elemental association. The coals differed in their respective inorganic content and composition. The coal samples with the lowest inertinite content had the most varied mineral composition and the lowest clay content. It was established that clay minerals were associated with organic matter, indicating a syngenetic origin of the clay minerals. None of the particles investigated (particle sizes on average <2 µm) was purely carbonaceous, leading to a conclusion that all organic matter is closely related to inorganic components.

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Coal Cleaning Rejects and Sulphide Oxidation by Fenton's Reaction

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Fenton's reaction is proposed as an accelerated weathering test for sulphides associated with Brazilian Coal Cleaning Rejects (CCRs), that are exposed to oxygen and water during the mining of coal. TEM and SEM/EDX were used to evaluate the nature, occurrence and distribution of minerals in remaining coals and other lithological units, before and after applying the test. Oxidation of CMRs was examined by analysing soluble sulphur (sulphate) and dissolved metals by ICP-MS or ICP-OES. As dissolved sulphate increases, dissolved Zn, Cd, Cu and Co concentrations increase, leading to undetectable amounts in the remaining solid phases; dissolved Ni and Mn also increase with the mobilized sulphur, but the remainder in the solids is the most important fraction; Fe and Pb are not mobilized due to precipitation as jarosite or hematite in the case of Fe or as sulphate in the case of Pb. Agreement between the observed results and the predictions by geochemical modelling is discussed.

Petroleum Coke-Based Activated Carbon Modified by Binary Metal Oxides for Elemental Mercury Removal in Flue Gas

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Mercury is considered as one of the most toxic heavy metals because of its persistence and bioaccumulation around the world. The release of mercury and some toxic trace metals/metalloids into the environment have an adverse effect to human health and throughout the ecosystem. Among all the anthropogenic mercury emission sources, coal combustion is the major one. In the face of increasingly serious problems of mercury pollution, it has been an urgent issue to protect environment by reducing mercury emission from coal fired power plants. Activated carbon injection is one of the mercury removal approaches which can remove mercury effectively from flue gas using conventional particulate matter controller. However, application of activated carbon sorbents is limited by huge cost, lack of products for low rank fuels. Therefore, it is important to developing alternative cost-effective sorbents or chemical treatments to promote mercury removal capacity of carbonaceous sorbents. Petroleum coke is a low-priced carbon which can be obtained as a vast sum of byproduct from petroleum refinement. With high carbon content, low volatile and ash content, it is a good precursor for preparing high surface AC. Pyrolyzed high-sulfur petroleum exhibited a mercury removal efficiency of around 50–60% at temperatures around 160-170 ^{o}C. However, the pyrolysis temperature had to reach to 1100 ^{o}C in N_2 atmosphere that could be a heavy burden to apparatus. In this study, mercury adsorption performance of an activated carbon which is derived from petroleum coke (PAC) and modified PAC were evaluated in simulated coal combustion flue gas atmosphere. Potassium hydroxide (KOH) was used as activating agent to obtain PAC by chemical activation. Impregnation method was applied to modify PAC by Mn-Ce binary oxides(MnCe-PAC). The adsorption experiments of vapor-phase elemental mercury were carried out in a laboratory-scale fixed-bed reactor. Specifically, the effects of loading values of metal oxides, temperature (100 - 250 ^{o}C) and individual flue gas components (O_2, SO_2, NO, HCl) on Hg^0 removal efficiency were investigated. In addition, thermal stabilities of mercury compounds were studied by using temperature-programmed desorption (TPD). MnCe-PAC showed the best performance at 100 ^{o}C, and Ce−Mn binary metal oxides could adsorb more elemental mercury than MnO_y-PAC and CeO_2-PAC. The samples were characterized by X-ray diffraction (XRD), N_2 Adsorption, Fourier Transformed Infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). The results indicated that the presence of 200 ppm SO_2 in flue gas significantly promoted the Hg^0 adsorption and oxidation over MnCe-PAC. Furthermore, the XPS spectra of Hg_{4f} and Hg-TPD results showed that the form of captured mercury was oxidation state on the samples, which illustrated that catalytic oxidation and chemisorption was the main process for Hg^0 removal over sorbent. It indicated that Mn-Ce binary metal oxides are a promising sorbent for the mercury removal from flue gas.The understanding of elemental mercury removal would help developing a cost-effective sorbent by utilizing carbon-rich high sulphur petroleum coke or shot coke with pore activities.

SESSION 28
Gasification Technologies: Modeling - 1

Effect of Alkali Species in Australian Coals on Slag Composition and Viscosity

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Inorganic species in coal play a significant role in gasification systems as they must have characteristics (such as chemical composition, ash fusion temperatures, viscosity) that allow reliable gasifier operation and not pose operational issues for downstream syngas processing plant or any opportunities for beneficial reuse. Mineral matter in Australian coals covers a wide range of coal ash compositions, many of which are suitable for use in entrained flow gasification technologies with or without addition of flux or other material to help manage its behaviour. A significant database of ash compositions and slag viscosity has been developed and used to generate models enabling prediction of slag viscosity for range of compositions in $CaO–SiO_2–Al_2O_3–FeO–MgO$ systems, representing most of the Australian bituminous coal ash compositions. The alkali oxides (Na_2O, K_2O) are not a major components in these ashes; however, some coals may have up to 4 wt.% K_2O, and Na_2O can reach more than 15 wt.% in brown coal ashes. These oxides may affect the slag viscosity as network modifiers, and also change phase equilibria in multicomponent system. This paper demonstrates the effect of Na_2O, K_2O on slag phase composition and viscosity for selected Australian coals which have a variable concentrations of alkali oxides in the ashes.

It was found that for compositions representing Australian black coals the viscosity and temperature of critical viscosity (T_{CV}) may change quite significantly, if the addition of potassium shifts the phase composition of the molten slag to regions with higher or lower liquidus temperatures or promotes precipitation of crystalline solids. Therefore, a careful analysis of possible effects is required for using coals with high potassium content, as it can drive slag composition into a T_{CV} precluded area and minimize the gasifiers operational temperature range.

For Australian brown coals, slag with variable sodium content from olivine and cordierite primary phase fields have low liquidus temperatures, and the slag viscosity at 1200-1600ºC was always lowered only by increase of sodium in liquid phase and not affected by solids. For slags from silica and spinel primary phase field, the increased sodium content lowers slag viscosity and reduce the formation of solids.

Numerical Study of the Hitecom Reactor for In-Situ Measurement of Single Char Particle Conversion

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The test reactor HITECOM (High Temperature Conversion Optical Measurement) allows to study in detail the conversion processes of isolated coal particles under operating conditions close to industrial-scale entrained-flow gasifiers. The test reactor was developed and operated at the Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg, and can be operated at pressures up to 40 bar and temperature up to 1400 °C. The reactor consists of a horizontal tube, which is flushed by a preheated gas stream at different velocities. One or more isolated particles can be fixed on a TGA (thermogravimetric analysis), which enables to measure the conversion rate at particle Reynolds numbers between 10 and 150. Optical ports are arranged around the gas tube. The temperature and gas concentration around the isolated particle(s) can be measured in-situ using thermographic camera and Raman spectroscopy. The final goal of this work is to get a more detailed understanding of the char particle conversion processes. Based on these results, advanced char conversion sub-models for the numerical simulation of entrained-flow gasifiers have to be developed.

In this work, numerical simulations of the three-dimensional flow field inside the HITECOM reactor were carried out in order to study in detail the mass and heat transfer inside and outside the gas tube, including the TGA and the optical ports. Based on the numerical results, the temperature and species distribution in the gas tube and around the reacting particles were evaluated, which allows to adjust the experimental data. In addition, the influence of thermal convection and radiation on the flow and temperature distribution was studied and will be discussed in detail, and the influence of the Reynolds number will be discussed.

CFD-Based Accelerated Gasification Technology Development

Andreas Richter, Philip Rößger, Thomas Förster, Peter Seifert, Bernd Meyer, TU Bergakademie Freiberg, GERMANY

Gasification is a key process to convert carbonaceous materials into basic chemicals. Especially the importance of entrained-flow gasification is increasing, since this technology provides the highest throughput capacities compared to fluidized-bed and fixed-bed gasification processes. Because political and economic frameworks, and therefore the utilized feedstock are changing continuously and more rapidly, an accelerated development of new technology or an optimization of existing technology are needed. CFD provides the opportunity to evolve new technology without the classical, long and cost intensive way from lab-scale to demo- and pilot-scale plants. Basis for an accelerated development are reliable CFD models that are validated against large-scale experiments with conditions close to the industrial process to guarantee the accuracy of the numerical results. In this work, development strategies for new entrained-flow gasifiers are presented. We start from non-catalytic reforming of natural gas and adapt some of the concepts for coal gasification. The CFD model was validated against in-house measurements based on the semi-industrial test plant HP POX at pressures up to 70 bar. This test plant provides a comprehensive set of experimental data, e.g. the gas temperature along the reactor, gas composition and temperature at the outlet, and flame characteristics such as flame shape and length based on an optical probe system.

Syngas-Based Annex Concepts and CO_2-Based Power-To-X Concepts Within Pulverized Coal Combustion Power Plants

Christian Wolfersdorf, Clemens Forman, Bernd Meyer, IEC, TU Bergakademie Freiberg, GERMANY

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

Different concepts are introduced to improve the flexibility of an existing base-load pulverized coal combustion power plant (PCPP). The first option is a coal gasification unit of lower thermal capacity (“Annex”). This unit comprises fluidized-bed steam drying of lignite, coal gasification, water electrolysis (optional), gas treatment and subsequent CO-based synthesis of a storable fuel or chemical product. The second option extends the PCPP by an amine-based flue gas scrubbing for the provision of CO_2 and a “Power-to-X” unit with water electrolysis, intermediate hydrogen storage and subsequent CO_2-based synthesis. The synthesis product (e. g. SNG, methanol) can be used externally or for peak load power generation. Both concepts are characterized by a high degree of integration between synthesis unit and power plant. The power plant covers the auxiliary power consumption and steam demand of the synthesis unit and integrates excess steam and waste streams such as waste water, waste gases or carbonaceous residues. Each concept is analyzed for the cases of low and high electricity prices at strong and weak renewable energy penetration. During low electricity prices, the power plant is running at minimal load and the main electricity consumers, especially the electrolyzer stacks, are operating at nominal load. In case of high electricity prices the power plant is operating at nominal load and the electrolysis unit is out of operation, while hydrogen is supplied from storage. The “Annex” unit and the “Power-to-X” unit are a power sink in times of low electricity prices and reduce the overall net power output of the total plant without lifetime-consuming start-up and shutdown processes of the PCPP.

The techno-economic study compares the concepts regarding efficiency, CO_2 emissions, specific investment costs and production costs for methanol generation. The study was performed for a power plant with a thermal input of 2,300 MW at nominal load. The “Annex” concept is based on a 500 MW gasifier. For coal-based synthesis concepts, CO_2 removal is usually necessary because of gas composition requirements for subsequent synthesis processes. Hence, the removed and concentrated CO_2 stream can be stored at comparatively low effort. The utilization of CO_2 by “Power-to-X” concepts leads to a reduction of CO_2 emissions for the PCPP. Both concepts are investigated with equal sizes of an alkaline water electrolysis unit to quantify the potential for chemical electricity storage and flexibility improvements of the linked power plant.

The capital expenditure of the “Annex” unit is more than 20 % lower than for an equally sized stand-alone gasification plant with subsequent synthesis because of taking advantage of the shared infrastructure of the existing power plant site. The integration between synthesis unit and power plant offers synergies for the reduction of operating costs as well. Despite the growing share of power generation by renewable energy sources there will be a demand for base load power plants. The introduced concepts can contribute to flexibility and economics of existing coal-fired power plants. Simultaneously, the CO_2 emissions can be reduced by incorporation into chemical synthesis.

SESSION 29
Clean Coal and Gas to Fuels: Catalytic Study - 2

Spontaneously Activatable Iron-Based Catalysts in Fischer-Tropsch Synthesis: From Lab-Scale Study to Pilot-Scale Demonstration

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Fischer-Tropsch synthesis (FTS) has received much attention as an attractive route to convert syngas (H_2+CO) into premium liquid fuels or high value-added chemicals. Iron-based catalysts are highly promising for FTS due to their low cost as well as high activity. Thus far, hematite-based (α-Fe_2O_3) Fe/Cu/K/SiO_2 catalysts, prepared by a precipitation technique, have been conventionally used as industrial iron-based catalysts for FTS, in particular for low-temperature FTS (≤ 280 ºC). The conventional hematite-based catalysts are known to exhibit poor catalytic performance unless they are pre-activated using CO or low-pressure syngas (≤ 0.3 MPa). Ferrihydrite is a nanocrystalline iron-oxyhydroxide with the general formula of $FeOOH \cdot nH_2O$ ($0 < n < 1$), which has great potential as a catalyst or a catalyst precursor for iron-catalyzed catalytic reactions such as FTS. But, no detailed investigation into the ferrihydrite as a FTS catalyst has yet been performed. In this study, we report a novel characteristic of ferrihydrite-based Fe/Cu/K/SiO_2 catalysts: spontaneous activation of ferrihydrite-based catalysts in the FTS condition (syngas pressure = 1.5 MPa). In a lab-scale test using a plug flow reactor, the ferrihydrite-based catalysts were readily transformed into Hägg carbide (χ-$Fe_{2.5}C$), an active phase for FTS, during the initial period of FTS. As a result, the ferrihydrite-based catalysts showed high catalytic performance even though no activation pre-treatment was carried out. The catalytic performance of spontaneously activated ferrihydrite-based catalysts was comparable to that of pre-activated catalysts. In contrast, the conventional hematite-based catalysts showed poor catalytic performance unless they are subjected to an appropriate activation pre-treatment. Furthermore, we successfully demonstrated that the spontaneous activation of ferrihydrite-based catalysts in the FTS condition holds true for a pilot-scale test (5-15 bbl/d) in a slurry bubble column reactor.

Single Pass Fischer-Tropsch Synthesis over Iron-Based Catalysts

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Materials, such as natural gas, oil residue, coal, or biomass, can be converted into easily transportable liquid products using the Fischer-Tropsch process. This process is typically optimized for the production of liquid fuels only. Carbonaceous feedstock is reformed/gasified using pure oxygen to avoid the introduction of the inert nitrogen into the process and thus enabling the recycle of unconverted synthesis gas. The required air separation unit can make up ca. 15-25% of the overall capital cost of the Fischer-Tropsch plant. Omission of this unit in the process, i.e. generating synthesis gas with air, results in a synthesis gas with ca. 50% nitrogen, whose effect on the reaction kinetics can be partially countered by increasing the reaction pressure. However, the product gas cannot be recycled and the unconverted synthesis gas (together with the gaseous products formed) must be used to generate power in the so-called co-generation option. For optimization purposes, the effect of conversion on activity and selectivity needs to be known. Here, we report on the effect of activity and selectivity of two iron-based catalysts for the co-generation option.

Co-precipitated iron-based catalysts (Fe/Cu/K/SiO_2 and Fe/Al_2O_3 /K) catalysts were used. The catalysts were tested in a slurry reactor operating at a pressure of 20 bar with a synthesis gas containing H_2:CO:Ar = 2:1:1. The iron-based Fischer-Tropsch catalysts were activated in-situ at 270ºC for 16 hrs and tested at 250ºC. The activity and selectivity of the catalysts were tested at different space velocities. The extent of deactivation was examined after a run time of 280 hrs by returning to the original space velocity.

The space velocity was changed over a period of ca. 16-18 days, after which the original space velocity was tested again to monitor the extent of permanent deactivation. It was noted that the silica-containing catalyst was more active at high space velocity, but when the conversion of CO exceeded 85% the alumina-containing catalyst was more active. Furthermore, it was noted that the extent of deactivation was higher with the alumina-containing catalyst than with the silica containing catalyst. This may be attributed to the higher driving force for the formation of iron aluminate under the influence of product water in comparison to the formation of iron silica (the formation of both these compounds may lead to permanent deactivation). An often quoted disadvantage of using iron-based catalysts is the formation of CO_2 in the Fischer-Tropsch process, which deters from the formation of liquid fuels. It should however be realised that in a co-generation concept some CO_2-generation in the Fischer-Tropsch process can be accepted (and can be even desirable if carbon capture is anticipated). The CO_2-selectivity increases with increasing CO-conversion up to ca. 60%, at which point the CO_2-selectivity remains constant at ca. 25 C-% for the silica containing catalyst and 30 C-% for the alumina containing catalyst. The obtained methane selectivity is low (even at 90% conversion with ca. 5-6C-%), but increases with increasing conversion. At low CO-conversion, the methane selectivity obtained over the silica containing catalyst was lower (ca. 2-3%) compared to the alumina-containing catalyst (ca. 4 C-%). The selectivity for the various classes of organic products can for both catalysts be interpreted in terms of reduced partial pressure of CO and reducing the extent of inhibition resulting in a reduction in the chain growth probability, a decrease in the olefin content, and an increase in the extent of double bond isomerisation. The obtained data can form a basis for a rationale decision on the extent of reaction required in the Fischer-Tropsch reactor, when operating in a single reactor.

Low-Temperature Methanation of Syngas in Slurry Reactor over NiO@SiO_2 Core-Shell Catalyst

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A series of NiO@SiO_2 core-shell catalysts were prepared using modified Stöber-method. Their catalytic performances in methanation of syngas were investigated in slurry reactor at 320 ºC. The catalysts before and after reaction were characterized by XRD, TEM, XPS, N_2-physisorption, etc. It was found that the NiO@SiO_2 core-shell samples have well-shape morphologies and relatively uniform size. The methanation test revealed that the activity of the catalysts decreased dramatically with the increase of core particle size. The catalysts with distinct size of core and shell showed remarkably rapid deactivation in the initial period of 20 h and then deactivated slowly during the following reaction, while their CH_4 selectivity maintained at about 80%. Void-shell was formed during the reaction probably because easily-migrated $Ni(CO)_x$ species were generated. Apparently, it was concluded that the increase of core particle size, decrease of BET surface area, pore volume and abatement of mesopores within 3-5 nm in the shell were responsible for the deactivation of these core-shell catalysts based on the characterization of the catalysts.

SESSION 30
Sustainability and Environment - 3

American Electric Power's Experience with Mercury and Air Toxics Standards (MATS) Compliance

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The Mercury and Air Toxics (MATS) rule went into effect in the United States, April 2015. This rule included a required for coal fired power plants to limit their mercury emission to the air ($<1.2x10^{-9}$ lb/Btu for sub-bituminous and bituminous fuels, $<4x10^{-9}$ lb/Btu for lignite). This rule also included remediation limits for emissions of PM and acid gasses. American Electric Power (AEP) operates large coal fired fleet of over 18,800 MWs. The fleet has various configurations and designs to comply with the MATS rule. The fleet also fires a range of fuels from lignite, high sulfur bituminous which have various ash chemistries and mercury content. The presentation describes AEPs approach to compliance strategy and the issues we expected. In addition we will present the performance and how compliance has changed the operation of the power plant.

AEP's MATS control method includes a wide variety of solutions from co-benefit of SCR and wet FGDs, Activated Carbon Injection (ACI) with Fabric Filter, ACI with cold side Electrostatic Precipitator (ESP), and ACI, SCR, and Dry FGD. At a few locations halogen addition to the fuels was added to promote mercury oxidation. Each of these configurations has unique challenges and adjustments to how the plants operated prior to MATS compliance.

Future of Coal Utilization in the US and China

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The US and China are the two largest coal producing and consuming countries in the world. Both countries face challenges in protecting the environment while at the same time maintaining sustainable development based on the use of coal as a major national energy source. In the US, the Environmental Protection Agency's (EPA) Mercury and Air Toxics Standards (MATS) and the Cross-State Air Pollution Rule (CSAPR) regulations led in part to closing more than 68 coal-fired power generation plants in a US fleet of about 600 plants. Recent analysis shows that more than 280 coal-fired generating units across 32 states may also be closed in the near future or undergo fuel-switching modifications. The low price of natural gas due to an overabundance of supply is driving more industrial users to switch from coal to natural gas. Similar situations also occur in China because of the enforcement of stricter environmental regulations on coal use and the increased use of natural gas and renewable energy for electricity supplies. China's coal output fell in 2014 for the first time this century as a result of slowing economic growth and government efforts to reduce air pollution. It is expected that coal consumption to be reported for 2015 will decrease about 8% compared to 2014. China is targeting its coal consumption to be controlled below 2.72 billion metric tonnes per year by 2020. Such a drop in production compared to annual levels that were in the range of 4 billion metric tonnes per year will result in major challenges to maintain the Chinese coal industry.

The focus of this paper is to overview the current status and to present scenarios about future trends for coal industries in the US and China. The paper will assess the impacts of the new EPA regulations on the coal and power industry in the US and both assess and contrast the similar challenges to the Chinese coal sector. Focusing on future energy markets and long-term environmental concerns, the paper outlines both power generation and coal conversion (production of fuels and chemicals) combined with CO2 capture, utilization, and sequestration (CCUS) to protect the sustainability of coal-related industries in the US and China. The US and Chinese governments have established collaborative programs such as the US-China Clean Energy Research Center (CERC) to conduct joint activities that will benefit both nations. How the US and China coal industry responds to todays' problems and lessons will help prevent the future collapse of coal markets in the rest of the world.

Carbon Tax in South Africa: Sustainability Challenges

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The study aims to review the sustainability challenges pertaining to the implementation of carbon tax in South African mining industry. The primary objective of the national treasury in imposing carbon tax is to reduce greenhouse gase emissions and address the environmental dimension of sustainability. The study will demonstrate that, although government's good intention in reducing greenhouse gas emissions, its subsequent impacts on different sectors of the economy including the mining industry is still uncertain. Amongst the policy' expectations are firstly pricing mechanisms on the environmental and economic damages caused by excessive emissions of greenhouse gases. Secondly the policy will drive further investment in green technology projects thereby creating jobs and alleviating poverty in the country. Conversely, the business's view is that carbon tax will inflict destructive socio-economic implications across emitting industries including the mining industry. There is still uncertainty that carbon tax will achieve environmental objectives and succeed to put much emphasis on the prevention of further pollution to the environment in which businesses operate. The government put emphasis on the preservation of environment on one side, the industry on the other side prefers to salvage the socio-economic in lieu of environmental consideration.

The investment in renewable technologies expected to create jobs and alleviate poverty is yet to overcome challenges pertaining to the cost involved in repairing the environmental damages caused by the carbon emissions. Although carbon taxation was designed to promote environmental sustainability, however its implementation in the mining industry may not lead to economic and social sustainability. Sustainable development is an integrated theory structured in three dimensions namely the economic, social and environmental aspects. A policy instrument which is effective in one dimension but detrimental to the other dimensions may be an ineffective choice when considering sustainable development as a whole. If the carbon taxation instrument is to be considered effective it has to be sustainable from an environmental, economic and social perspectives of South Africa. In this study, an overview of sustainable development and carbon tax challenges is presented from literature data gathered through books, journals, scientific papers, academic conferences and other relevant publication channels. The literature review will be applied as an approach to develop the topic in an integrated way such that new perspectives and ways of addressing sustainable development and carbon tax challenges would be generated. A three-pronged approach encompassing environmental, economic and social review will be used in discussing and validating the sustainability challenges of carbon tax on South African mining industry.

The Application of Coal Quality Database Over Time and Space Across the Mpumalanga Coalfields

M. P. Kekana, N. J. Wagner, University of Johannesburg, SOUTH AFRICA

The Mpumalanga coalfields represent the most mined and studied coalfields in South Africa. This research project focuses on the use of historical coal quality data to study different trends in coal quality over time throughout the Mpumalanga coalfields. The No.2 coal seam in the Witbank and Ermelo coalfields and the No.4 seam in the Highveld coalfield were used. Statistical models were applied to the data in order to produce integrated geological models. This use of statistical methods were useful in verifying and determining the usefulness of historical coal quality data in modern research projects.

Multiple histograms, scattergrams and variograms were plotted to verify relationships between different coal quality parameters. These geostatistical methods were applied to chemical characteristics, specifically calorific value, volatile matter, ash content and total sulphur. Calorific values and ash scattergrams showed an inverse relationship where an increase in ash corresponded to a decrease in calorific values. Micromine and surfer were used for contouring of the data points. A spherical model semi-variogram showed that over short distances the data points become more and more predictable as it was expected with the No. 2 coal seam. Sulphur content in mined coal over time can help in future selective mining. A centralised database has many advantages and could be useful in future mining activities.

SESSION 31
Gasification Technologies: General - 4

Kinetic Studies for CO_2 Gasification of HOK Cokes Using Thermogravimetric Analyzers at High Pressures

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Many parameters can influence the gasification kinetics such as the gasification temperature, pressure, coal composition and particle size. Several approaches determination of reaction kinetics out of experimental data have been previously discussed. In this study, the gasification of different cokes in carbon dioxide atmospheres was investigated under different pressures and temperature by using a thermogravimetric analyzer (TGA). The influence of the gas velocity on the particle at higher pressure is also considered.

The reaction step was held under isothermal conditions and only Boudouard reaction was considered in the evaluation. Temperatures from 800°C till 1000°C were applied under different carbon dioxide concentration. The results of the different parameters were compared and discussed.

Study on the Effect of Particle Size on Gasification Characteristics of Different Ranked Chars under High Temperature

Xin Gong, XiaoPeng Zou, Haifeng Lu, Qinghua Guo, East China University of Science and Technology, CHINA

The effects of gasification temperature and particle size on reaction rate are different according to the difference in the coal rank of char. Six chars with various coal ranks from Chinese entrained-flow gasifiers were selected as the materials in this paper to investigate the effects of temperature and particle size on the CO_2 gasification of char using a thermo gravimetric analyzer (TGA).The gasification rates of chars at different carbon conversions were compared. In particular, much attention was paid to the high carbon converted stages. The study shows that the effect of particle size on gasification should be associated with both coal rank and gasification temperature. For high ranked char such as anthracite, when the gasification temperature increases from 1000℃ to 1400℃, the time needed to reach a 90% carbon conversion ratio for a 300μm char will be from 2 times to 5 times of that for a 40μm char. On the contrary, for the low ranked char such as lignite or bituminous, there is little effect of particle size on gasification rate due to the developed pore structure of char. However, the effect of particle size on gasification rate will become more significant with increasing carbon conversion ratio. When the carbon conversion ratio exceeds 50%, the particle size will show obvious effect even for lignite or bituminous.

Experimental Study of Particle Evolution Characteristics at Different Region in an Opposed Multi-Burner Gasifier

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On the basis of the bench-scale opposed multi-burner (OMB) gasifier and the advanced visualization techniques, the particle evolution characteristics along the axial direction of a gasifier has been studied. Particle images in different focusing planes from burner plane to the refractory dome are obtained by the optical sectioning tomography method. The morphology, particle size distribution, types and mutual transformation principles of particles in different focusing planes were statistically analyzed after image processing. The results show that the burner plane contains all the particle types, most of them are high/low temperature particle without wake (HTP/LTP) and low temperature particle with high temperature wake (LTP-HTW). Particle shapes in the burner plane are mainly round-like. The most intense particle pyrolysis occurs at 100 mm above the burner plane. In this region, the number of low temperature particle with low temperature wake (LTP-LTW) increased significantly, the particle shapes become more irregular and the median particle diameter are slightly increased with respect to those in the burner plane. Char gasification reactions accompanied with particle fragmentation mainly occurs in the space between 200 mm above the burner plane to the top of refractory dome. Most of the particles transform to low temperature particle without wake (LTP) in these areas and have a high probability to break up at 400 mm above the burner plane, resulting in the decrease of the median particle diameter. In addition, the proportion of round-like and irregular particles are both increased.

Corrosion Testing of Steel for Production and Injection Well Applications in a UCG Process

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Underground coal gasification (UCG) is a process used to produce gas from coal *in situ* by injecting air, oxygen or steam, into coal seams and extracting the product gas via surface wells. The coal is ignited and the gasification agent is fed into the coal seam through the injection well, producing syngas and then extracted through a production well. The injection and production well are in-between connected by the gasifier or cavity. Various chemical reactions, temperatures, pressures and gas compositions exist at different locations within an UCG gasifier, and in the injection and production wells. The injection and production wells are exposed for years, or entire life time of an UCG operation, to a mixture of gas atmospheres, in the presence of varying temperature gradients. This creates a highly corrosive environment that erode the well lining, resulting in cracks, forming metal oxide shavings and in extreme conditions to a total plant shut-down and significant cost implications. Corrosion of process equipment costs considerable time and money each year, which means selection of the correct material is central to overall process safety, economy and efficiency.

The overall objective in this study was to expose a number of steel / alloy types to experimentally simulated UCG environments and conditions in order to determine the most suitable steel type for the injection and production well. A secondary goal was to fit the experimental data to a corrosion rate model to determine the actual corrosion over the life of the UCG plant.

The gaseous and temperature specific environments selected exposed a general corrosion attack on the samples. The metal loss and corrosion rate were tested with weight loss analysis by periodically removing the samples from the corrosive environments, cleaning and weighing them before placing them back for the rest of the experiment's duration. SEM imaging was used to confirm the type of corrosion observed and determine the oxidation products present on the surface of the corrosion coupons.

In general, all runs displayed comparatively steady corrosion rates, clear differences between the different steel and alloy types with a high correlation coefficient when fitted to the corrosion model of Du Plessis (2014) and Frayne (1999). The best correlation fitting ($R^2 > 0.95$) was observed with the CO and syngas runs and with the oxygen-and-steam runs resulting in a correlation coefficient of $R^2 > 0.85$. SEM imaging confirms general corrosion characteristics through a homogenous coating of iron oxides over the entire exposed surface of each examined sample. The results obtained in this study highlighted a clear difference and indication to narrow down options for the selection of the final steel / alloy type and to determine which steel type to be used in which part of the UCG process.

SESSION 32
Coal Science - 6

Property of Extract Prepared by Hydrothermal Extraction of Brown Coal

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Brown coals contain large amount of water (~60%) in general, and they show high spontaneous combustibility when dried. Therefore, it is essential to upgrade as well as to dewater for storage and transportation of brown coal. We have already presented a hydrothermal extraction method that not only removes water from brown coal but also upgrades the coal and extracts low molecular mass compounds simultaneously. In this work, the hydrothermal extraction behaviors of three brown coals were investigated, and the molecular compositions of the extracts were analyzed in detail by high-resolution mass measurements. An Australian brown coal, Loy Yang, was extracted by pressurized hot water at 300°C and 10 MPa, 350°C and 20 MPa, and 380°C and 24 MPa for reaction times of < 120 min to examine the effects of the parameters on the yields and elemental compositions of extracts, including solid extract ('deposit') and water-soluble extract ('soluble'). As a result, 350°C, 20 MPa, and 90 min may be the most practical conditions because the extract yield was as large as 35% coal and the deposit contained the most volatile matter, 66% of the sample. Using two Chinese brown coals, Inner Mongolia and Yunnan, it was confirmed that hydrothermal extraction under the same conditions was applicable even for brown coals having higher ash and sulfur contents. The high-resolution mass measurements with Kendrick mass analyses identified the chemical compositions and the abundance of common molecular species in all the deposits prepared from the three brown coals, classified as C_nH_m, C_nH_mO, $C_nH_mO_2$, $C_nH_mO_3$, $C_nH_mO_4$, and C_nH_mN. Consequently, 35-50% of the deposits consisted of the same molecular species. The results indicated the presence of abundant compounds with similar molecular compositions in all of the extracts, regardless of the parent coal. The determined compound distributions may be helpful in developing a conversion process for brown coals using a hydrothermal method.

Process Characteristics Investigation of Shendong Coal Co-Pyrolysis through Solid Heat Carrier

Wenying Li, Baofu Li, Xiaohong Li, Jie Feng, Taiyuan University of Technology, CHINA

Pyrolysis of low-rank coal through solid heat carrier (SHC) can increase tar yield and improve upgrading efficiency. Besides the roles of heat storage and transfer, SHC also have some catalytic activity to regulate tar quality. In co-pyrolysis of direct coal to liquid residue (DLR) and coal, tar yield increase duo to the synergistic effect. Simulating experiments of pyrolysis of Shendong coal and DLR with their co-semi-coke as SHC were carried out to study product distribution and cycling stability. Yield of tar maintained around 10.4% (wt. ad) in ten cycling experiment, which was 3.0% higher than the result from a fixed-bed reactor. After seven cycles over the range of the conditions employed, the dilution effect of the relatively large amount of semi-coke heat carrier could counteract adhesion of DLR for softening and melting during pyrolysis. A two-stage reactor was used to a study the interactions between SHC and nascent volatiles. Co-semi-coke heat carrier has a cracking effect on volatiles during the pyrolysis process, which made tar yield decrease little, higher amount of light tar components, and more gaseous products. Co-semi-coke also reacted with CO2/H2O in nascent volatiles produced, causing changes of product distribution. The interaction of volatiles and SHC led to certain changes of the specific surface and pore structure of semi-cokes. Along with ultimate analysis of the SHC, the content of H decreased slightly, while C and O had a modest increase. Low-rank coal pyrolysis with a rapid heating rate through SHC lead to extensive thermal breakdown of macromolecular fragments of coal, which outweigh the cracking effect of semi-coke heat carrier for more light tar components.

The Prediction of Pyrolysis Products in Grading Lignite Pyrolysis Process

Wenying Li, Lan Yi, Jie Feng, Yuhong Qin, Yuhong Qin, CHINA

Pyrolysis is the core unit of lower-rank coal upgrading and refining. A coal pyrolysis model which can be used to predict the product distribution is important to study the grading Lignite pyrolysis process. Based on mass balance in this paper, a pyrolysis model which combines prediction of volatile yields and component analysis of coal tar under different operating temperature is developed. The FG-DVC (Functional group-Depolymerization Vaporization Crosslinking) model is used to quantitatively predict the yields of pyrolysis char, light gases and coal tar. The Van Krevelen diagram which can provide the input parameters of the FG-DVC model by interpolation method is modified to cover more lower-rank coal. A non-linear programming (NLP) model is employed to analysis the component of coal tar, which includes phenols, aromatics, hydrocarbons, oxy-components and pitch. The proximate analysis of char and ultimate analysis of coal tar are obtained based on the mass and element conservation of coal pyrolysis unit. The comparison between model prediction and experimental data validates this model both in total volatile yield and in tar yield.

Influence of Oxygen Group and Coal Structure on the Migration of Biomass Alkalis during Coal/ Biomass Co-Pyrolysis

Wengying Li, Rong Zhu, Yuncai Song, Laisong Wang, Jie Feng, Taiyuan University of Technology, CHINA

Co-gasification of biomass and coal can not only decrease coal consumption effectively but also reduce gas pollutants especially CO_2. Alkali metal K/Na rich in biomass could transfer to the coal char in co-pyrolysis stage and then promote catalytic gasification of coal char in our previous studies. However, the biomass alkalis K/Na how to migrate and how to retain in coal char is still unclear. The raw material was placed in fixed bed reactor to be fast pyrolyzed on separate and co-pyrolyzed experiments. Gasification reactivity characteristics of char samples were investigated in a thermogravimetric analysis. By designing co-pyrolysis of acid coal with biomass and graphite with biomass under 973 K, 1073 K and 1173 K to obtain the effect of the oxygen or carbon structure of coal on the migration of biomass alkalis K/Na. Results showed that co-pyrolysis of biomass and coal was beneficial to enhance the oxygen content in acid coal char (ACC) and which was increased with the pyrolysis temperature. Additionally, the increase of the oxygen content in ACC is advantageous to the migration of alkali metals K/Na of biomass. XRD analysis indicated that the biomass K mainly existed in coal char as amorphous phase. Co-pyrolysis of graphite with biomass results reveals that biomass K/Na combined with carbon structure of graphite, the presence of biomass K/Na enable the conversion rate of graphite char increased by 20%.

Heat Release Characteristics of the Oxidation of Aliphatic Hydrocarbon Groups and its Effects on the Spontaneous Combustion of Coal

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The heat release characteristics of reactions of $-CH_3-$, $-CH_2-$ in coal were studied based on organic chemistry and quantum chemistry analysis methods. The structure model of $-CH_3-$, $-CH_2-$ was established and the reaction processes of the functional groups during spontaneous combustion were analyzed. Using quantum chemistry analysis method, Gibbs free energy change and enthalpy change of the reactions were calculated. The results indicate that aliphatic hydrocarbons can react with oxygen and there is a lot of heat of about 400 to 500 kJ/mol released from these reactions. By comparing the heat release characteristics of the reactions of the aliphatic hydrocarbon groups with the oxygen consumption, gas production and temperature rising characteristics of the coal, it is concluded that oxidation of aliphatic hydrocarbons do not occurred in the initial stage of spontaneous combustion of coal and it is the key to determine the spontaneous combustion characteristics of the coal.

SESSION 33
Gasification Technologies: General - 3

CO_2 and H_2O Gasification Under Chemically and Diffusion Controlled Conditions

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In this work the heterogeneous char-CO_2 and char-H_2O gasification reactions are investigated experimentally in a small-scale fluidized bed reactor. This methodology enables high heat up rates (~10^4 K/s), long timescale observation (up to several hours), operation over a wide range of particle sizes and accurate control of reaction conditions. Reaction rates and time dependent carbon conversion curves are established from real-time gas product analysis by FTIR-spectrometry through a detailed data analysis procedure. This procedure employs different particle surface-evolution models and accounts for sampling system signal attenuation.

Here, the gasification reactions of biogenic wood-char particles with CO_2 (Boudouard reaction) and H_2O (Watergas reaction) are investigated under atmospheric pressure. The char particles are gasified at different temperatures (1173 - 1473 K), CO_2 and H_2O partial pressures (0.2 - 0.8 bar) and particle sizes (90 - 2200 μm) in order to examine the influence of these parameters on reaction rates.

Experiments conducted are divided into two groups:

The first set of experiments is operated under conditions where intrinsic kinetics control the observed reaction rate (low temperatures, small particles). For the expression of measured intrinsic chemical kinetics an nth-order approach has been adopted. Activation energies, order of reaction and frequency factors are determined for both reactions investigated.

For the second group of experiments temperatures and particle sizes are increased. This leads to rising influences of mass transfer processes, limiting the overall reaction rate. The Thiele-analysis is used for the description of reaction rates measured under those conditions. Thereby, the effect of intra-particle gas-diffusion on carbon conversion rates is quantified by calculation of effectiveness factors.

Experimental data is further compared to results from one-dimensional, unsteady single particle simulations. In this simulation coupled partial differential equations, stemming from energy and species balances, are solved simultaneously to calculate temperature and concentration distributions with respect to time and space. Changing surface area due to pore growth and coalescence is modeled by Bhatia's random pore model; multi-component intra-particle gas-diffusion is taken into account by application of the dusty-gas-model.

New Approach in Gasifying Reactive Low Rank Coals Under Non/Partial Slagging Entrained-Bed Conditions: 20 TPD Pilot Test Results

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A non/partial slagging entrained-bed type gasifier has developed and tested at the 2 and 20 ton/day scale pilot plants. Typical subbituminous coals possess a higher content of volatile matter that exhibits a reactive property in coal conversion processes. Most commercial entrained-bed coal gasifiers based on the idea of melting all inorganic ash components in gasifying process into slag, and tried to treat all ranks of coal in the same gasifier type. Considering the reactive nature of low rank coals, actual required temperature in gasifying reaction itself for the organic components in coal would not be high as 1,400-1,600°C which is the typical operating temperature of the current entrained-bed coal gasifiers. From the point of gasifying the organic part in coal, the 1,200°C temperature should be sufficient in completing the gasification reaction when the particle size is small enough and the coal powder is well mixing with reacting agents. The gasifying temperature of 1,400-1,600°C has been applied in entrained-bed gasifiers to guarantee the melting of ash into slags. But, this high temperature causes many practical problems in utilizing the gasification technology more widely, typically due to the related high cost in gasifier materials. Current construction cost of IGCC plant showed more than two times higher than the competing USC(Ultra Supercritical) power plant at the similar plant efficiency of 40-41%.

In addition, slag that is the melting product after the entrained-bed gasification is no longer a coveted product as first anticipated. Good quality coal ash can be recycled as filler in cement industry and has a proved market in most countries. Unfortunately, slag does not prove yet as a commercial profitable product, rather it remains as an item that needs to remove in any way. Molten slag all the time possesses the dangerous property in operating the gasification system. It can plug the gasifier, can wear the refractory, and can reduce the heat recovering efficiency in syngas cooler. The ash can be processed and can be sold as a profitable product, whereas the slag can be a waste even after spending more energy in melting. Combining the facts that reactive low rank coals can be gasified lower than 1,400-1,600°C, and coal ash would not become slag at this temperature, it was thought that the coal gasifier operating in the temperature range of 1,200-1,400°C might be a feasible choice. But, ash sometimes causes a heavy metal leaching environmental problem, and the ash-treating temperature should be high enough to block the heavy metal leaching. From several partial slagging tests in the non/partial slagging entrained-bed type gasifier, it was proved that there is no leaching even at the 1,200-1,400°C range.

All in all, reactive low-rank coals can be gasified differently without relying on the high gasification temperature of 1,400-1,600°C, and without converting ash into slags. Price of low rank coals is still quite low, and has not been used widely. In this presentation, a possibility of a dedicated gasifier for low rank coals will be discussed with the underlying idea and the test results from the 2 TPD and 2 TPD pilot plants. Syngas composition from the tests using Australian and Indonesian subbituminous coals yielded CO 57-61%, H_2 28-31%, CO_2 3-5%, which is comparable with the syngas composition form the commercial full slagging coal gasifiers. Even in non-slagging mode, test results exhibited above 90% carbon conversion with a single pass of coal feed through the gasifier. Recycling of the un-reacted carbon fraction would yield more than 98~99% conversion eventually. The non-slagging mode gasification would yield a lower carbon conversion in a first pass through the gasifier, but it would guarantee the lower construction cost and much lower problem chances by fluid slags at the slag-tap and other parts of the system. Especially in a small pilot-scale coal gasifier that has an inside reactor diameter of 20 ~30 cm, operational problems like blocking the slag-tap caused by slags could be a frequent event. This proposed gasification system for low ran coals can be the choice to overcome this type of problems.

Influence of Quench Water Temperature and pH Value Variations on Selected Trace Components in Autothermal Gas Reforming Processes

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In the authothermal reforming of natural gas mode of operation of the Freiberg High Partial Pressure Oxidation (HP POX) test plant, deionized water is used to cool down the synthesis gas from the gasifier in the quench chamber. This helps to remove some traces to have the raw gas composition. These traces which include dissolved molecular H_2S, NH_3, HCN, CO_2 and their resultant ions are present in the quench water outlet and recycled streams. They are known to support corrosion effects on plant facility and acts as catalyst poisons.
The quench water system cycle was modelled and optimized in Aspen Plus^{TM}. The sensitivity analysis results from the quench system´s steady state simulation elucidate the behaviors of different traces emanating from the raw gas and quench water outlet streams which were influenced by quench water temperature variations from 130 °C to 220 °C, changes in the quench water pH values and amount of quench water outlet stream. The experimental data from the operations of the HP POX test plant were used to develop the simulation model in Aspen Plus^{TM}.
The understanding of the behavior of these trace components distribution are significant to the development of the gas cleaning processes required to have the required syngas quality to be used for Gas-to-Liquids or methanol synthesis process. The chemistry involved in the formation and dissociation of all these traces are important to the development of mechanisms that can influence them and their ions.
The required raw gas cleaning depends on the composition of synthesis gas (the main source); the quenching operations which are the focus of this study and the use of the syngas.
It is understood that the quench water outlet stream is a complex system of molecular and ionic dissolved species with different complex interactions due to temperature dependency with respect to the species Henry´s and dissociation constant.
When quench water temperature increases: quench water pH values are reduce because of increasing self-dissociation constant of water as well as the distribution of traces found in quench water outlet stream.

Influences of the Cross Angle on the Granular Jet in Annular Gas Stream with Thick Wall of Inner Channel

Chenchen Fang, Haifeng Liu, East China University of Science and Technology, CHINA

The granular jet in the annular gas stream is widely used in the industrial processes such as pulverized coal gasifiers. The entrainment phenomenon for different cross angles, which occurs for the thick-wall inner nozzle, is investigated by morphology. As the annular gas velocity increases, three entrainment modes of the granular jet, such as the undisturbed granular jet, the granular jet with entrained particles and the granular jet with full entrainment emerge in sequence. The phase diagram of the entrainment modes for different cross angles is obtained. Moreover, the cross angle of the coaxial nozzle enhances the radial component of the annular gas and decreases the axial downstream distance before the interactions between gas and particles. Hence, the length of the particle entrained decreases with the increase of the cross angle for the same annular gas velocity. Results show that particle velocities in the particles-wall collisions increase with the cross angle. The larger cross angle make more easily entrained particles assemble at the surface of the thick wall. The large cross angle of the coaxial nozzle intensifies the wear damage of the inner nozzle.

SESSION 34
Clean Coal and Gas to Fuels: Processing

Methane Quality, Processing and Hydrogen Production

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We will demonstrate for the first time, that the conversion of methane to acetylene with yields of over 99 % and selectivity greater than 200:1 with the use of "continious wave" (cw) micro wave plasmas is possible on an industrial scale. In contrast to previous works the advantage regarding yield and selectivity could be shown using a *cw* microwave plasma. The often described problems or advantages of soot formation or diamond creation could be completely solved by the use of specially designed plasma reactors.
In addition, the possibility to use the product gas as a chemical energy storage by regenerative surplus electricity (photovoltaic or wind power) will be discussed. In this context we will highlight the "power to gas" (PtG) strategy. In this context the formed hydrogen opens more possibilities of use.
In case of the activation of carbon dioxide (from fossil or renewable sources) the reaction of methane and carbon dioxide to synthesis gas (CO + H2) is mentioned here. This reaction could serve as the basis for so-called organic synthesis gas. In the fermentation process a mixture formed of CH4 and CO2 is formed. A further preparation for the organic synthesis gas and then to "liquid fuels" as biofuel; for example, in the frame of a Fischer-Tropsch synthesis appears very promising. Under the aspect of the energy revolution it is possible to synthesize "green" chemicals in excellent yields when using 100% renewable electricity and the supply of reactant gas, which was obtained from biomass.

The Development of Highly Anisotropic Coke from an Aliphatic Fischer-Tropsch Waxy Oil Residue

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The Sasol Fischer-Tropsch process produces a range of aliphatic molecules which are mainly utilised for the production of liquid fuels. The heavier ends are called Waxy Oil and can be transformed into a highly anisotropic needle-like carbon. Waxy Oil is a heavy aliphatic residue produced by the Sasol Coal to Liquid process. As the residue is produced from a gas phase reaction of carbon monoxide and hydrogen, the nitrogen and sulphur contents thereof are low (as compared to historical needle coke feedstock). Waxy Oil is contaminated with a high catalyst content which reports to the ash content of the coke and causes the formation of isotropic carbon exhibiting multi-phase graphitisation upon further thermal treatment. A further obstacle to the formation of anisotropic carbon is the reactive nature of the carbon oxygenates and aliphatic molecules. It is widely regarded that the formation of anisotropic carbon (needle-like coke) requires the maximisation of carbon aromaticity in the delayed coker feedstock. The process for the production of highly anisotropic carbon necessitated filtration; thermal treatment and distillation prior to static carbonisation. The result shows the formation of a 100% anisotropic carbon with low ash content. The mechanism for the transformation of a highly aliphatic residue includes stabilisation of the higher c-number aliphatics before conversion to four to six ring aromatics during the coking process. The anisotropic carbon also contains negligible nitrogen and sulphur contents.

The Conversion of FT Olefins: Multiphase Reactor Simulation Study

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The conversion of olefins to transportation fuels via oligomerisation has attracted considerable attention over the last 5 years, as a technology to provide clean, sulphur and metals free gasoline and diesel. More over the olefins can be derived from a variety of diverse sources; indirectly via syngas or methanol conversion where these have been obtained from natural gas, bio-gas or coal, or directly from the conversion of bio-alcohols. The oligomerisation of olefins using in particular ZSM5 catalysts, was largely pioneered by the then Mobil Oil Corporation in the 1970s. In order to optimally use this reaction system within the framework of a complex modern diverse feed stock refinery, a reasonably precise simulation of the reactor system is required. In particular, it is required to have a good approximation of the heat release, since these reactions are extremely exothermic and easily undergo temperature run-away. Many early models, where based on either few component lumps or more detailed carbon number lumped species assumed to be an ideal gas mixture. More recently, more complex reaction schemes have been proposed, but these do not describe systems beyond about 12 carbon numbers. The oligomerisation reactor is actually quite complex, not only is the reaction extremely exothermic, but depending on the operating conditions chosen and the reactor feed, the reactor can operate in vapour phase, two-phases or entirely in the liquid phase. Moreover, this phase behaviour changes during the course of the reaction – it can go from all vapour to all liquid as the reaction proceeds. Since these reactors operate around 50 atm, there are far from ideal and can produce products with carbon numbers beyond 20.

The aim of this work is to develop an adiabatic oligomerisation reactor model that will account for phase behaviour, temperature effects, provide a good approximation to the degree of branching (needed for cetane and octane) and consider carbon numbers up to 40. The figures show typical results of this model. All possible oligomerisation, cracking and isomerisation reactions between C3 and C40 between linear, mono-branched, di-branched and tri-branched olefin species are considered. Physical and chemical properties of the species are correlated and Peng-Robinson or ESD equations of state describe phase behaviour and estimate fugacity coefficients. The reaction rates, based on species fugacities, enable phase independent reaction rate calculations.

Figures A and B show typical simulation results of the reactor model for a typical reactor feed at 220°C and 40 atm. Figure A shows the gasoline and diesel fractions through the reactor. These fractions have been obtained by lumping the detailed distribution at each reactor slice, an example of which is given in figure B for the reactor exit. Of particular interest in figure A is the psi=V/F (green line), which shows that the phase split starts off at about 10% and as the reaction proceeds, at around V=0.7, the reactor phase is completely liquid, but as the temperature rises, at about V=3, the reactor again moves into the two phase region. The model smoothly moves across the phase boundaries without changing the state equations or doing a re-start. This model has been used to study optimal operating strategies for the oligomerisation reactor system.

Coal to Liquids by Oxidative Cracking in Near-Critical and Super-Critical Water

Marcos Millan, Pedro Arcelus-Arrillaga, Klaus Hellgardt, Imperial College, UNITED KINGDOM

Water at near-critical and super-critical conditions is a promising medium for the conversion to polynuclear aromatic (PNA) structures, such as those found in coal, into lighter products, therefore making it an interesting alternative to conventional coal to liquid processes. This study explored oxidative cracking in near- and super-critical water, which involves activation of the PNA by oxidation as a first step followed by cracking.

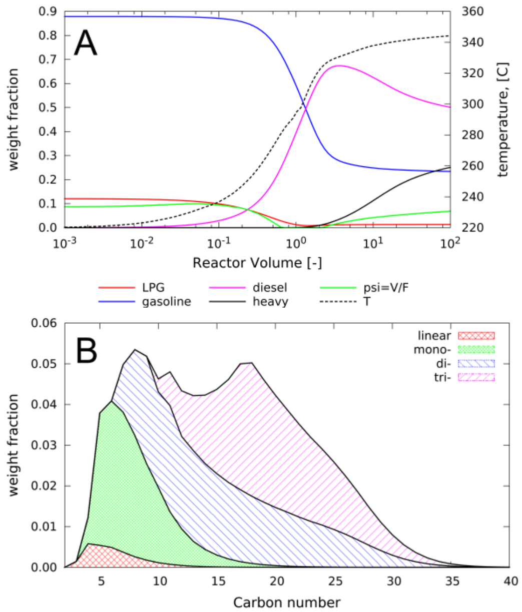
Phenanthrene was used as a model compound and it was observed that the initial activation by oxidation preferentially took place in the middle ring. This is a positive outcome as it provides a pathway to smaller molecules decreasing the conversion to gas that tends to predominate when cracking occurs in peripheral rings. Therefore, this process may improve the selectivity to liquid fractions such as benzene, toluene and xylene (BTX). The effect of temperature and reaction time on conversion and product distribution is presented in this study and the reaction pathways observed are highlighted.

Optimization of Configurational Alternatives for a Gas to Liquids Process Based on Fischer-Tropsch Technology

Ashcaan Khazali, Klaus Möller, Eric van Steen, University of Cape Town, SOUTH AFRICA

The Fischer-Tropsch Synthesis (FTS) allows for the production of syncrude which may be further refined to transportation fuels in Coal, Gas or Biomass To Liquid plants (CTL, GTL, BTL respectively, collectively: XTL). These sulfur free fuels burn more cleanly than conventional fuels and in the case of BTL they may be produced renewably. At present their relative cost of production is prohibitive but new legislation, technological advances and volatile oil prices may make XTL fuels more relevant in the near future.

The base case XTL plant comprises gasification, syngas cleaning, Air Separation Unit (ASU), Autothermal Reforming (ATR), carbon dioxide removal, full conversion Low Temperature Fischer-Tropsch (LTFT) and hydrocracking of heavy wax. The ASU is a major contributor to costs therefore the effect of downsizing using oxygen-enriched or pure air is investigated. Steam Reforming (SMR), ATR and Partial Oxidation (PO) are compared individually and in combination. Combustion of syngas, biogas and off-gas are compared as means of heat supply to the ATR. The excess hydrogen from SMR is supplied to the hydrocracker while the ATR and PO require Water-Gas Shift to meet this hydrogen requirement. The gas cleaning steps will depend upon whether coal or natural gas is used and the nature of the reformer feed heating. Since production of heavy wax is prioritized the Fischer-Tropsch process represents the use of cobalt catalyst in LTFT operation. Where air is used, FTS is run to high conversion in once through mode in order to avoid the costly recycle stream containing nitrogen and light hydrocarbons. Multiple FT reactors with intermediate water/wax knock-out in series will be compared against a single reactor. The viability of nitrogen removal before FTS is investigated in the case of full conversion FTS. After separation of the FTS product, the light syncrude fraction is potentially reformed to syngas, used in a gas turbine to generate power or used for heating. The heavy FTS wax is hydrocracked to maximize distillate range material. The light products from hydrocracking are combined with the lights from FTS and the heavy oil is recycled.



The aim of this study is to find a more economical route for diesel production. With an understanding of the effects of oxygen purity on the system as a whole, ASU costs may be minimized. The interplay between the FTS alpha value and the hydrocracker operation will be investigated in order to maximize distillate range material. The sensitivity analysis sheds light on these two areas. The economic optimization and analysis is performed with the aim of minimizing diesel production cost. The results of these analyses will be presented and the best configuration will be highlighted.

Elementary reactor models are used for FTS and hydrocracking. These models respond to changes in feed and operating conditions. A one parameter, multiple phase hydrocracker model, developed in a previous study, is used to accurately model the reaction with VLE. This model has the capability to account for production of the branched isomers and lumping is only used beyond a certain level of branching/isomerization so the major compounds are well represented. The Fischer-Tropsch model, adapted from previous work, is derived for once through high conversion operation. The product distribution is modelled using Anderson-Schulz-Flory distribution with corrections. The physical property database is built using group contribution methods and includes α-olefins and n-paraffins up to C120+.

SESSION 35
Gasification Technologies: Modeling - 2

Syngas Production from Brazilian Coal Chars in the Presence of Steam

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The steam gasification of two Brazilian coal chars, classified as sub-bituminous (CMRS-02) and bituminous (CMSC-02), were investigated using a pressurized thermogravimetric analyzer (PTGA, model Dyntherm-HP-ST, Rubotherm Company) in the temperature range of 1073-1173 K and pressure range of 1-20 bar. The study area lay within the Leão-Butiá coalfield (M2 seams – sample CMRS-02) and South Santa Catarina coalfield (Barro Branco seams – sample CMSC-02), both located in the Paraná Basin. To evaluate the coals and chars, the physical and chemical properties were determined by proximate and ultimate analysis, calorific value, grindability index, free swelling index and mineralogy. For the gasification experiments, firstly, the samples were pyrolyzed in a quartz tubular reactor under nitrogen and then gasified. The operating variables used were in agreement with differential reactor and free diffusion limitations. Gasification reactions were conducted using the isothermal method and each experiment was performed in duplicate in order to test the reproducibility of the results. The gas produced during the gasification reactions was detected using a gas chromatograph (model 2014, Shimadzu) connected to the PTGA output. From the results for the carbon conversion as a function of reaction time for the reactions carried out at 1073-1173 K, it can be observed that in this temperature range the curves are strongly dependent on the specific coal properties, the Char CMRS-02 showing a higher conversion rate, which is probably related to the coal rank. The sub-bituminous coal was more reactive than the bituminous sample, which can be ascribed to the vitrinite and liptinite content, since a higher content of these macerals are known to increase the intrinsic reaction rate. In relation to the vitrinite content, it can be noted that Char CMRS-02 has a higher value (50.8%) than Char CMSC-02 (34.5%). Consequently, the sample with a higher vitrinite and liptinite contents has a higher H/C which influences the intrinsic reaction rate. The effect of the total system pressure on the intrinsic reaction rate was stronger for the bituminous sample than for the sub-bituminous one. In this study, the effect of the total system pressure on the intrinsic reaction rate was stronger for the bituminous sample than for the sub-bituminous one. The products of the gasification reactions were analyzed, it can be observed that hydrogen, carbon monoxide and carbon dioxide were produced in significant amounts and an increase in the reaction temperature clearly increased the concentration of all gases analyzed and no CH_4 was detected. The H_2/CO ratio was found to be > 2 for both chars. In this work, the temperature effect and the total system pressure were stronger for the bituminous sample than for the sub-bituminous one. The gases formed were H_2 and CO and the H_2/CO molar ratio (> 2) indicates that the syngas produced is promising for Fischer-Tropsch synthesis.

Evaluation of CO_2 Gasification Reactivity of Biomass and Coal Chars by Physicochemical Properties

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The isothermal and non-isothermal CO_2 gasification of different biomass charss and different coal rank char were conducted by thermogravimetric analyzer (TGA), and the reactivity index and peak temperature were obtained to express the gasification reactivity. In addition, the physicochemical properties of these chars, such as the alkali index, Brunauer-Emmett-Teller surface area (S_{BET}), micropore area (S_{mic}), carbon crystalline structure were examined by inductively coupled plasma spectrometer (ICP), N_2 adsorption and X-ray diffraction (XRD). The CO_2 chemisorption was also measured by TGA and the total, strong and weak chemisorbed volumes (C_{total}, C_{str} and C_{wea}) were obtained. All of these properties were used to evaluate the CO_2 gasification reactivity of these chars. The results show that the gasification reactivity of chars decreases with increasing coal rank. Comparing with the other properties, the C_{total} and C_{str} are the best parameters for predicting the gasification reactivity, and the linear correlation coefficients between C_{total} /C_{str} and gasification reactivity can reach up to 0.90 or even 0.98. It suggests that the CO_2 chemisorption can be used to evaluate the gasification reactivity of different coal rank chars. And this evaluation is valid when it is extended to biomass chars, thus the CO_2 chemisorption may be a common and useful method for gasification evaluation.

The CUMT International Research Centre for Underground Coal Gasification

Cliff Mallett, Carbon Energy Limited, AUSTRALIA

China has been one of the most active locations for UCG operation in the last 25 years with around 20 UCG trials and sites. These have focused on methods using mined tunnels in the coal seam, accessed from existing coal mine workings, but a borehole gasification demonstration was carried out in Inner Mongolia by the ENN company over the last five years. China's new five year plan places an emphasis on the development of cleaner ways to use coal and specifically identifies underground coal gasification as a major field of activity.

The China University of Mining Technology (CUMT) is China's largest mining training institution with campuses in Beijing and Xuzhou. In April 2016 the university announced the opening of a new research centre for underground coal gasification based in Xuzhou. A governing body is comprised of CUMT representatives, Chinese and international companies and scientists. An advisory committee of distinguished researchers will guide the activities of the Centre. The program will include research, development and demonstration projects in UCG, training courses for students and professionals and promotion of UCG technology. International activities include a bi-annual conference, visiting professors and scholarships, and international collaborative projects. The Centre will encourage all proponents of UCG to participate and share information, and act as a clearing house that will provide an opportunity to assess technology options and select technology most appropriate for specific applications. A global membership association will be established to communicate developments in UCG.

A first demonstration project has been selected in Pei County, adjacent to Xuzhou with participants from the CUMT, Geology Bureau of Jiangsu Provence, YiLong company and Pei County administration. The demonstration will target 1000m deep coal through borehole access. The first international collaboration project will bring together experts from industry and government around the world to develop protocols for UCG that can lead to international standards which will simplify regulation and governance of UCG projects.

SESSION 36
Gasification Technologies: General - 5

Online Detection and Retention of Trace Contaminants in Reducing Gasification Atmosphere

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Gasification of coal creates a syngas which can be used for the production of electricity or chemicals. Besides other undesired by-products, the raw syngas exiting the gasifier, contains various trace elements. Among them are mercury (as Hg^0), selenium (as H_2Se) and arsenic (as AsH_3). All of them tend to remain in the gas phase and thereby pose a threat to down-stream equipment as well as to the environment. An option to retain these contaminants are sorbent materials. A profound evaluation of their sorption performance requires reliable analytical tools with high temporal resolution and detection limits at parts per billion by volume (ppbv) levels.

This study therefore addresses the development and successful employment of an online analytical method, based on the direct introduction of a simplified flue gas (H_2, H_2O, Ar) into an ICP-MS. Applying matrix matched calibration, the individually calculated detection limits are < 1 ppbv for H_2Se, < 0.1 ppbv for AsH_3 and < 0.01 ppbv for Hg, thus being comparable to current offline methods. These low detection limits and the high temporal resolution (≈ 1 Hz) enable the use of this method as a quick and robust tool for the lab- and bench-scale performance evaluation of sorbent materials.

The capture of H_2Se by a Zn/Al_2O_3 sorbent at warm temperatures (150-350°C) was chosen as a case study. The results show that the support itself interacts with H_2Se at dry reaction conditions. However, as small amounts of steam are added to the gas stream, the sorption capacity strongly decreases, indicating competitive adsorption of H_2Se and H_2O on the support. For experiments with Zn/Al_2O_3 sorbents, sorption of H_2Se was observed up to steam contents of 10 vol% and temperatures up to 350°C with initial H_2Se concentrations below the method detection limit.

Interaction between Rice Straw and Jincheng Anthracite Single Particle During Ashing Process

Wenying Li, Zibing Zhao, QingQing Han, Chengcheng Zhu, Yuhong Qin, Jie Feng, Taiyuan University of Technology, CHINA

To elucidate the effect of diffusion and adsorption between rice straw (RS) and Jincheng anthracite (JC) particles on ash fusion characterization, a hot stage microscope was applied to observe the morphological evolution of single fuel particle from room temperature to 1400ºC under N_2 or CO_2 atmosphere, separately. The fusion performance of twenty particles were observed to represent the Jincheng coal and rice straw, respectively. Mixing JC and RS showed a lower ash fusion temperature than JC solely under CO_2 atmosphere. However, ash fusion temperature of mixture was almost same with JC solely under N_2 atmosphere. About 60% portion of JC particle melted above 1350ºC in coal solely gasification. While, 42.8% JC particles melted in 1150-1250ºC, 28.6% JC particles melted in 1250-1350ºC, and fraction melted above 1350ºC, when JC and RS co-gasified under CO_2 atmosphere. In contrast to JC particles, the melting point of 33.3% portion RS particles increased till 1000-1100ºC, and 28.5% increased above 1200ºC, in comparison with 52.4% portion of RS melting in 900-1000ºC when RS solely gasified. The mechanism of diffusion and adsorption reached through interactions between mineral.

Catalytic Gasification with Carbon Dioxide Characteristics of Alkali and Alkaline Earth Metals Catalysts in the Fixed-bed Reactor

Yifei Wang, Jilin Li, Guangsuo Yu, Fuchen Wang, East China University of Science and Technology, CHINA

Low temperature gasification is a talent technology to reduce the energy consumption and improve the heat value of gasification products. Catalytic gasification has advantage in accelerating reaction rate, and the catalytic gasification technology has gained great attention, alkali and alkaline earth metals have proved as effective catalysts for the catalytic gasification reaction. Effects of temperature, catalyst types and catalyst loadings on carbon dioxide gasification reaction were investigated on a fixed-bed reactor in this paper. Catalyst dispersion effect, BET specific surface area and crystallite constituents of Jinyou coal char with different loadings of K and Ca were also analyzed by energy-dispersive X-ray analyzer (EDX), N_2 adsorption at 77K and X-ray diffraction (XRD). Results showed that Potassium carbonate (K_2CO_3), as a catalyst, could improve gasification rate significantly, when gasification temperature was above 850℃. Cation species of the catalyst could influence its catalytic activity, and the main effects of the catalysts were the alkali and alkaline earth metal elements, the catalytic effect order was K_2CO_3>KOH＞Na_2CO_3>NaOH＞$Ca(NO_3)_2$. The reactivity of coal char increased continuously with the catalyst loadings, and showed a loading saturation level (LSL) which was 10% for K. K and Ca added to Jinyou coal could decrease its BET specific surface area, compared to the raw char. Moreover, K and Ca added to Jinyou coal could change its crystallite constituent during the process of coking and gasification, which indicated that some K and Ca reacted with minerals in the Jinyou coal char during the process of coking and gasification, resulting deactivation of some K and Ca. SiO_2 was the main mineral constituent in the raw char and its gasification residue. During the coking process, the soluble K and Ca would reacted with the minerals in Jinyou coal to produce insoluble salt of $KAlSiO_4$, $MgSiO_3$ and $Ca(OH)_2$ and $Ca_2Al_2SiO_7$, respectively. During the gasification of CO_2 process, some soluble K in the char became into insoluble salt of $K_2MgSi_3O_8$, and CaO diffraction peak appeared in its gasification residue, which indicated that some soluble K and Ca deactivated during the CO_2 gasification process.

Oxygen Co-Gasification of Coal and Rice Straw in Drop Tube Furnace

Xueli Chen, Jianye Tang, Qinghua Guo, Guangsuo Yu, East China University of Science and Technology, CHINA

Oxygen co-gasification of coal and rice straw was conducted in drop tube furnace to study the co-gasification characteristics at different gasification temperature and blending ratio of rice straw. The research results show that during separate gasification of coal and rice straw with oxygen, the syngas from rice straw gasification is mainly composed of H_2 and CO, while the syngas from coal gasification is mainly composed of H_2, CO_2 and CO. During gasification, the structure of rice straw which is regular before gasification will change. Firstly, the rice straw softens, and then curls, which results in the loose, polyporous irregular structure with rough surface. Finally, it melts and changes into a spherical shape. However, the structure of coal has no marked change. During the oxygen co-gasification experiments, when at 1200°C, CO and H_2 are inhibited and CO_2 is promoted with rice straw blending ratio of 20% and 50%. However when rice straw blending ratio is 80%, H_2 and CO_2 are inhibited. At 1400°C, H_2 is inhibited and CO_2 is promoted with rice straw blending ratio of 20%, and CO is promoted when rice straw blending ratio is 50% and 80%. According to the solid yield and gas composition, it can be found that the interaction occurs during co-gasification of coal and rice straw. The fused ash particle, which is rich of Si, Al, K and Ca et al, is formed during co-gasification of coal and rice straw.

POSTER SESSION 1
Combustion

Influence of Combustion Temperature and Oxygen Concentration in Combustion Medium on Emissions of NO_X, N_2O and SO_2

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Sewage sludge incineration is the only suitable way for disposal of large volumes of sewage sludge containing POPs and some heavy metals. Sewage sludge combustion processes reduce the volume of such waste and cause destruction of organic contaminants such as POPs, detergent residues, pharmaceuticals and various compounds with endocrine-disrupting potential. Due to higher phosphorus content, the ash from sewage sludge combustion can be potentially used for phosphorus recovery. The more volatile heavy metals and their compounds (with exception of mercury) can be concentrated in fly ash. Oxy-fuel combustion is a technology for simplifying CO_2 sequestration from the flue gas by using nearly pure oxygen instead of air for the combustion together with flue gas recirculation contribution to higher CO_2 content in inlet gas and flue gas. In order to control the oxygen concentration in inlet gas, combustion temperature, and formation of NO_x, part of the flue gas is recycled to combustion chamber. Fluidized bed technology offers also significant advantage to the combustion process due to its flexibility to burn various types of fuel with low and fluctuating heating value. Our paper brings information about investigation of the effects of combustion (fluidized bed) temperature and concentration of oxygen in inlet combustion media on the emissions of NO_x, N_2O and SO_2 in FB incineration of sewage sludge at temperatures 750–930 °C. Concentrations of oxygen in the inlet gas during experiments were 21, 25, 28 and 30 vol. %. Experiments were carried out in a bubbling fluidized bed (BFB) reactor with inner diameter of 9.36 cm and height of 130 cm above the gas distributor. To simulate oxy-fuel BFB combustion, a mixture of oxygen and carbon dioxide as a gaseous combustion medium was used. Dry sewage sludge (SS) from mesophilic stabilization (moisture content 9 mass % and ash content 44 mass % in dry matter) was used for experiments. Size of prepared particles from dry sewage sludge was between 0.5 and 2 mm. The particles were fed into the FB reactor by gas-driven slide feeder with two fuel containers (quasi-continual feeding). The SS particles were introduced to the very bottom of the FB in a cooled tube (inner diameter of 9 mm) by pneumatic transport. CO_2 was used as the gaseous medium for the pneumo-transport. The ash from SS incineration was used as primary fluidized bed material. Main components of the primary fluidized bed material were SiO_2, P_2O_5, Al_2O_3, CaO and Fe_2O_3, size of primary fluidized bed material particles ranged from 0.71 to 1.6 mm. Minimum fluidizing velocity of the primary fluidized bed material was experimentally measured and calculated to have a value of 30 cm/s at 25 °C and 101,325 kPa. The experimental results have shown that an increase in combustion temperature leads to an increase in NO_x and to a decrease in N_2O emissions in a temperature range 750–930 °C. The lowest SO_2 emissions were measured at the temperature interval from 790 to 820 °C in all experiments with different oxygen concentration in inlet gas. It was found that when the oxygen concentration in inlet gas increased, the emissions of SO_2 increased while emissions of NO_x slightly decreased. Experimental results suggest that flue gas from oxy-fuel BFB combustion of dry, stabilized sewage sludge is suitable for CO_2 sequestration (CCS process) after further purification and compression. Furthermore, the bottom ash from the fluidized bed combustion of SS can be considered as potential source for phosphorus recovery due to high phosphorus content (with about 80 % of phosphorus content from the sludge). Based on our results, emissions of nitrous oxides and SO_2 are higher at temperature 750–930 °C during oxy-fuel BFB combustion of sewage sludge when compared to combustion by O_2/N_2 at the same operating conditions. The oxy-fuel combustion or co-combustion processes are, on the other hand, generally handicapped by additional costs for production of pure or highly concentrated oxygen.

POSTER SESSION 2
Clean Coal and Gas to Fuels

Methanol Synthesis by Catalytic Hydrogenation and Photoelectrochemical Reduction of CO_2

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

Fossil fuels (coal, oil and natural gas) have allowed an outstanding era of prosperity and advancement for human development, but carbon dioxide concentration in the atmosphere has consequently risen from about 280 ppm before the industrial revolution to about 390 ppm in 2010. The increase in CO_2 emission is strongly contributing to global warming and climate changes due to the enhanced greenhouse effect. The increasing attention toward climate changes and the recent strategic policies to stabilize and reduce the amount of CO_2 emission is promoting research in the field of carbon capture, storage and more recently utilization technologies, whereby CO_2 is captured from industrial flue gas, reused if possible or permanently stored in geological formations, such as depleted oil or gas fields and saline aquifers.

In this scenario, Sotacarbo is leading the "Centre of Excellence on Clean Energy" research project, funded by the Regional Government of Sardinia, which aims to develop technologies for low emission power generation and for CO_2 capture (from fossil fuel power plants), utilization and storage. Among these technologies, CO_2 recovery by hydrogenation and photoelectrochemical reduction of carbon dioxide are experimentally studied in the Sotacarbo laboratories.

This work presents a general overview of the researches on CO_2 utilization by conversion into liquid fuels (mainly methanol), highlighting main experimental results and the potential development of the technologies.

As for CO_2 hydrogenation process, $Cu/ZnO/ZrO_2$ catalysts have been synthetized as nanopowders by a sol-gel self-combustion method. Glycine has been used as fuel and as complexing agent while metal nitrates are the source for metal or metal oxide and the oxidizer agents. To improve the structural-morphological properties, and consequently the resulting catalytic performance, active phase has been dispersed onto a high surface area silica support (mainly SBA-15, due to its high surface area, regular channels and thick pore walls). The confinement of the active phase in the SBA-15 structure enhances its ability to interact with CO_2 and H_2. Such a structure provides an ideal reactor where the mesopores act as channels for the transport of reactant. Fresh materials have been characterized by XRD (X-ray diffraction), TEM (transmission electron microscopy), FTIR (Fourier transform infrared spectroscopy), CHN/S (carbon, hydrogen, nitrogen, sulphur) analysis, TGA (thermogravimetric analysis) and N_2 physisorption in order to correlate the textural and microstructural properties with their performance as CO_2 hydrogenation catalysts. The catalysts will be finally characterized in a fully automated bench-scale unit equipped with two different fixed-bed reactors which can operate up to 10 MPa and 700 °C.

In parallel, photoelectrochemical (PEC) reduction of CO_2 could represents one of the possible alternatives to CO_2 hydrogenation: this technique may be considered "green" when solar energy and water are used to drive the process, like in natural photosynthesis. The possibility to use a photoanode-driven PEC cell in which a metal has been used as cathode, while the anode material is a nanotubular structure of TiO_2, is investigated. The photocatalytic performance of the anode has been improved by deposition of tungsten oxide.

Effect of Sparger Design and Internals Configurations on the Hydrodynamics and Overall Performance of a Slurry Bubble Column Reactor for Fischer-Tropsch Synthesis

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A three-phase, three-dimensional multi-Eulerian Computational Fluid Dynamics (CFD) model, which has been developed and experimentally validated [1, 2], was used to investigate the effect of the gas spargers and cooling internals design on the local hydrodynamics (local gas holdup, gas and liquid global and axial velocities, gas and liquid velocity vectors, and liquid backflow fraction) inside a pilot-scale Slurry Bubble Column Reactor (SBCR) for Fischer Tropsch (F-T) Synthesis.

The simulations showed that the presence of internals increased the gas holdup, the gas and liquid velocities, and the turbulence intensity inside the reactor, and strong backmixing was observed in the vicinity of the internal pipes. Moreover, the CFD simulations showed that in the presence of internals, the location of the inversion point, which is defined as the point beyond which the liquid starts flowing downward, was much closer to the wall at a dimensionless radius ≈ 0.9 in the presence of internals, whereas it was located at a dimensionless radius ≈ 0.7 in the absence of internals. The model was also used to study the effect of number of different internals (pipes) and their percentage cross-sectional coverage of the reactor, the superficial gas velocity and temperature on the local hydrodynamics in our pilot-scale SBCR. The data showed that increasing the number of pipes did not have a significant effect on the gas holdup; however the backflow fraction was about 50% higher, indicating that mixing inside the reactor increases with increasing the number of pipe. Also, the local gas holdup and backflow fraction inside the SBCR provided with different internals appeared to increase with increasing the inlet superficial gas velocity and temperature for all internals configurations used.

The CFD model was also used to investigate the effect of the type and orientation of the gas sparger on the gas holdup, Sauter mean bubble diameter, axial concentration profiles, mean axial velocity profiles and the flow structure in the SBCR. Spider-type and concentric ring spargers, with upward and downward facing nozzles, in addition to a perforated plat distributer were studied. The CFD simulations results showed that the spargers with downward facing orifices were more effective in solids dispersion when compared with the upward facing orifices spargers. This is due to the agitations provided by the gas jets from the downward facing orifices, which enhance the solid particles distribution. Moreover, upward facing orifices spargers resulted in larger Sauter bubble diameters than those of downward orifices; and that concentric ring spargers resulted in larger Sauter bubble diameter values when compared with those of the spider sparger. Additionally, the sparger type was found to significantly affect the flow structure within the column. Spider spargers exhibited smaller and faster liquid recirculation cells in the vicinity of the sparger from the startup until the steady-state. Also, larger and slower liquid recirculation cells appear to develop after around 1.2 time the reactor diameter measured from the bottom flange. Whereas, for the concentric ring and perforated plate spargers, larger and slower recirculation cells were present throughout the column beyond the distributor zone.

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Isotope Analysis for Understanding the Hydrogen Transfer Mechanism in Direct Liquefaction of Bulianta Coal

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Deuterium has been used to trace the pathways hydrogen in Bulianta coal liquefaction with or without Fe-based catalyst. The recovered solvent, asphaltene plus preasphaltene and residue were analyzed by ^{2}H-NMR or IR-MS. The ^{2}H-NMR spectroscopy of the recovered tetralin after liquefaction reaction shows that Fe-based catalyst can inhibit hydrogen transfer of tetralin in the H_α position. Results of the analysis of ^{2}H content in asphaltene plus preasphaltene by IR-MS shows that the ^{2}H content with Fe-based catalyst is higher than that without catalyst when using tetralin-$^2H_4$ as liquefaction solvent in N_2 atmosphere, indicating that Fe-based catalyst can accelerate transfer of hydrogen in tetralin to asphaltene plus preasphaltene. However, using tetralin-$^2H_4$ as liquefaction solvent in $^2H_2$ atmosphere, ^{2}H content with Fe-based catalyst is similar to that without catalyst. This indicates that the role of Fe-based catalyst is to promote the hydrocracking of asphaltene plus preasphaltene. When using tetralin-$^2H_4$ as liquefaction solvent in the absence of catalyst, ^{2}H content in $^2H_2$ atmosphere is obviously higher than that in N_2 atmosphere, however, when using tetralin-$^2H_4$ as liquefaction solvent and in the presence of Fe-based catalyst, ^{2}H content is almost the same in $^2H_2$ atmosphere and N_2 atmosphere. These results indicate that the predominant pathway of hydrogen transfer to coal is from molecular hydrogen to solvent and then from solvent to coal in the absence of a catalyst, and in the presence of Fe-based catalyst, the predominant pathway of hydrogen transfer to coal is from molecular hydrogen to coal.

Design ZSM-22 Crystal Morphology with Urea and its Catalytic Property

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Tuning the morphology of zeolites to achieve special properties remains a challenge. Zeolite growth modifiers, which are molecules absorbing on select crystal faces, have been used to tailor the morphology of zeolites. Xiao et al have used urea to alter morphology of TS-1 successfully. Recently, we have moderated the length-to-diameter aspect ratio of ZSM-22 crystals by adding urea to the synthesis mixture. The conventional ZSM-22 zeolite was synthesized following the recipe reported in the literature[4]. The composition of synthesis mixture was $Al_2O_3/13KOH/27NH_2(CH_2)_6NH_2/91SiO_2/3670H_2O$. Urea was chosen as the zeolite growth modifier. The urea was added in a molar ratio of 0.1urea/1 SiO_2. The synthesis mixtures were heated in autoclaves at 160℃ for 36h under stirring at about 42 rpm in an oven. After crystallization, the samples were filtered, washed with deionized water, and then dried overnight.

The XRD patterns of ZSM-22 and urea-ZSM-22 samples are shown in Fig.1, which are in good agreement with TON standard diffraction data without any crystal impurities. Adding urea into the starting synthesis mixture don't affect the crystallization of ZSM-22. SEM images of ZSM-22 and urea-ZSM-22 are also investigated. The conventional ZSM-22 sample shows needle-shaped crystals. Notably, when used urea in the synthesis process, the length-to-diameter aspect ratio of ZSM-22 becomes more high than the conventional ZSM-22. Urea have an important effect on ZSM-22 aspect ratio.

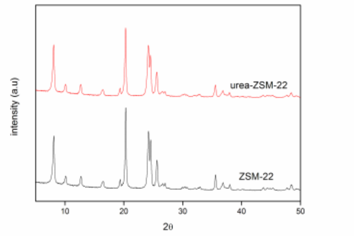

Fig.1 Powder XRD patterns of ZSM-22

In summary, urea as zeolite growth modifier plays a great role in tailoring the morphology of ZSM-22. ZSM-22 crystals with high length-to-diameter aspect ratio have been obtained successfully by adding urea in the starting synthesis mixture. The role of urea in morphology control of ZSM-22 could be that urea may adsorb on the surface of ZSM-22 crystals or change the pH during the crystallization process. Tailoring ZSM-22 crystal morphology has great influence on catalytic properties in hydroisomerization of n-alkanes.

POSTER SESSION 3
Sustainability and Environment

Geochemical Mobility of Potential Hazardous Elements of Coal Cleaning Rejects

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The geochemical characteristics of coal cleaning rejects (CCR) in Santa Catarina State, Brazil, were investigated. Around 3.5 million ton/year of coal waste are dumped in Santa Catarina State. Coal beneficiation by froth flotation results in large amounts of CCR composed of coaly and mineral matter, the latter characterised by the occurrence of sulphide minerals and a broad array of leachable elements. The total and leachable contents of more than 60 elements were analysed. Atmospheric exposure promotes sulphide oxidation that releases substantial sulphate loads as well as Ca^{2+}, K^+, Mg^{2+}, Cl^- and Al^{3+}. The metals with the most severe discharges were Zn, Cu, Mn, Co, Ni and Cd. Most trace pollutants in the CCR displayed a marked pH-dependent solubility, being immobile in near-neutral samples. The results highlight the complex interactions among mineral matter solubility, pH and the leaching of potentially hazardous elements.

Occurrence of the Hazardous Elements in Agricultural Soils Surrounding a Coal Power Plant Complex from Santa Catarina (Brazil)

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Hazard element contamination coming from coal power plants is something obvious, but when this contamination is accompanied by other contamination sources, such as, urban, coal mining and farming activities the study gets complicated. This is the case of an area comprised in the southern part of Santa Catarina state (Brazil) with the largest private power plant generator. After the elemental analysis of 41 agricultural soils collected in an extensive area around the thermoelectric (from 0 to 47 km), the high presence of As, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Sn, Tl, V and Zn was found in some specific areas around the power plant. Nevertheless, as the NWAC (Normalized-and-Weighted Average Concentration) confirmed, only soils from one site were classified as of very high concern due to the presence of potential toxic elements. This site was located within the sedimentation basin of the power plant. The spatial distribution obtained by kriging in combination with the analysis of the data by Principal Component Analysis (PCA) revealed three important hotspots in the area according to soil uses and geographic localization: the thermoelectric, its area of influence due to volatile compound deposition, and the area comprised between two urban areas. Farming practice turn out to be an important factor too for the quantity of hazard element stored in soils.

A Density Functional Theory Study on Acetic Acid Decomposition on Ni (111)

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Catalytic steam reforming of bio-oil is a potential process to convert renewable biomass feedstocks into hydrogen. However, carbon deposition on the catalyst is the major problem encountered in the steam reforming process. To shed light on the coke formation mechanism, acetic acid (CH_3COOH), the smallest organic molecule that contains C-O, C-C, C-H, O-H and C=O bonds, was selected as the model compound of the oxygenates in bio-oil. Thus, density functional theory was applied to investigate the decomposition mechanism of acetic acid on the Ni (111) surface. To gain a good knowledge of the high selectivity towards hydrogen and a comprehensive interpretation of coke formation mechanism, all of the possible decomposition pathways of acetic acid were considered, especially for the dehydrogenation pathways and C-C bond scission reactions. The stable adsorption geometry configuration and adsorption energies of different species and the important intermediates were determined. Based on our calculations, the most favorable decomposition pathway on Ni (111) surface is $CH_3COOH \rightarrow CH_3COO \rightarrow CH3CO \rightarrow CH_2CO \rightarrow CH_2 \rightarrow CH$, and the decomposition of acetyl (CH_3CO) via C-H bond cleavage to form CH_2CO is the rate-determining step with a high activation barrier of 1.33 eV. Meanwhile, the carbon deposits formation results from the accumulation of CH species, which is mostly from the dehydrogenation of CH_2. Moreover, the formation pathways of acetaldehyde and acetone intermediates were also investigated.

POSTER SESSION 4
Carbon Management

Pretreatment of Flue Gas Using Polymeric Membrane for CO_2 Capture

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The carbon dioxide, the greatest contributor to the global warming, has been mostly produced in the power generation sector so it seems like a foremost requirement for us to come up with a new power generation technology in an attempt to pro-actively respond to global warming. Therefore, it is critical to develop cost effective technologies to reduce carbon dioxide processing cost. One very promising approach to reducing carbon dioxide emissions is carbon dioxide capture. However, if the promise of this approach is to be realized, capture costs will have to be reduced through membrane technology. In this work the removal of oxygen from flue gas by combustion using polymer membrane for carbon dioxide capture have been studied. The composite membrane used in the present study the morphology was examined by scanning electron microscope to understand and correlate morphology with the performance of membrane. The effects of parameters involved in the spinning of PES hollow fiber and PDMS layer deposition, and further meso-tetraphenylporphyrin cobalt complex selective layer coating as resulting composite membranes were investigated.

The prepared composite membrane showed good facilitated oxygen transport, especially for O_2/N_2 gas pairs, it reversed the permeaselectivity and gave the selectivity 1.24. It is expected to be developed further for oxygen removal from flue gas in the pretreatment process for carbon dioxide capture. On the other hand, the activation energies of CO_2 and N_2 have positive values, which mean that they are dominated by the diffusion coefficient under the operating conditions. Generally, an increase in temperature could supply more energy, increase the mobility of the gas penetrants and enhance the mobility of the polymeric chain, leading to an increase of the penetrate diffusion coefficient. This was because the increase in CO_2 diffusivity compensated the decrease of solubility parameter under the experimental conditions. In contrast to the activation energy of N_2, that of CO_2 decreased with pressure. In the mixture gas CO_2/N_2 experimental results demonstrated that the permeance of CO_2 is higher than that of N_2, because the kinetic diameter of CO_2 is smaller than N_2. The composite membrane shows relatively good N_2/CO_2 selectivity in consideration of operating conditions with lower pressure. Compared to flat sheet membranes, hollow fiber membrane has the advantages of supporting itself, and of having a large membrane area per unit volume. Therefore, hollow fiber membranes are more acceptable for the application to industrial processes.

This membrane showed good facilitated oxygen transport from flue gas, especially for $O_2/N_2/CO_2$ gas pairs, it reversed the selectivity compared with existing data released. It is expected to be developed further for oxygen removal from flue gas in the carbon dioxide capture as well as reducing carbon dioxide capture cost due to the pretreatment of pollutant using cost-effective membrane system.

Experimental Study on CO_2 Capture From Simulated Flue Gas by Using Aqueous Ammonia with External Magnetic Field

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Coal fired power plants are large stationery sources of CO_2 which leads to the global warming. The technologies for capturing CO_2 emitted from coal-fired flue gas have been paid more attentions to alleviate the greenhouse effect. Current commercially available post combustion CO_2 capture technologies are the amine-based processes and mainly the monoethanolamine (MEA) process due to its behaving the advantages of high absorption rate and large adsorption capacity. However, the process has many drawbacks, such as high operation cost, strong corrosion, higher energy consumption for regeneration, and large consumption of auxiliary power and cooling water. Aqueous ammonia (NH_3) is considered as a promising alternative to amine-based absorbents for CO_2 absorption due to many advantages of low cost non-degradable absorbent, high capacity and affinity for CO_2, low corrosion rates, low heat of reaction with CO_2, low temperature of regeneration, stability under absorption operating conditions, and ability to regenerate CO_2 at high pressure. However, aqueous ammonia has low absorption rate which leads to a high capital cost and high vapour pressure of ammonia which results in high ammonia slip. To improve the performance of aqueous ammonia for CO_2 absorption, some additives with high CO_2 absorption rate and lower vapour pressure (such as amino acid salts) was added into the solution as a potential promoter. The published literatures also indicated that the external magnetic field (EMF) and ferromagnetic particles have significant improving effect on absorption ability for capture of SO_2 and NO_x. To our knowledge, fewer researches was reported about the effect of external magnetic field and nanoparticles on CO_2 capture based on aqueous ammonia process.

The objective of this study is to carry out CO_2 removal in an aqueous ammonia bubbling reactor with external magnetic field and nanoparticles, and to investigate the effect of aqueous ammonia concentration, inlet CO_2 concentration, flowrate of simulated flue gas, temperature, intensity and arrangement of external magnetic field (EMF), and addition of nanoparticles on CO_2 absorption. The obtained results indicated that the external magnetic field and nanoparticles (such as Fe, Fe_2O_3 and Fe_3O_4) can significantly improve the performance of CO_2 absorption. The arrangement of EMF has a certain effect on CO_2 absorption, and CO_2 removal efficiency increases with increasing of EMF intensity of 0-16 mT. CO_2 removal efficiency increases with increasing addition of nanoparticles, however, the promoting effect on CO_2 removal weakens at higher addition of nanoparticles. CO_2 removal efficiency increases by more than 7% compared with the condition absence of the EMF and nanoparticles, and the highest CO_2 removal efficiency reaches 99.40%. The ferromagnetic nanoparticles (Fe_3O_4) is better than non-ferromagnetic ones. In presence of the external magnetic field and nano-Fe_3O_4, CO_2 removal efficiency increases with the increase of the ammonia concentration, and the promoting effect on CO_2 removal is much more significant at lower range of ammonia concentration of 5%-8%. CO_2 removal efficiency gets very little decrease with the flowrate varying from 1.5 L/min to 3.5 L/min. CO_2 removal efficiency decreases with increasing the inlet CO_2 concentration. Temperature has a significant effect on CO_2 removal efficiency, and presents a tilted N curve at temperature of 20-60 °C, which behaving increasing tendency at 22-36 °C and 50-60 °C, respectively. The promoting mechanism of EMF and nano-Fe_3O_4 on CO_2 absorption may be due to the change of thermo-physical property of aqueous ammonia and enhancement of mass transfer among gas-liquid-solid. The research results provide a foundation for further research of CO_2 capture by using aqueous ammonia.

POSTER SESSION 5
Coal Science

Coal Cleaning Residues and Fe-Ultrafine Particles and Fe-Minerals Consequences

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In the present investigation, a study was undertaken to understand the origin of Fe-minerals presents in Brazilian coal mining and to understand the environmental implication and the chemical heterogeneity in the study area. Coal cleaning residue samples rich in clays, quartz, sulphides, carbonates, sulphates, etc. were sampled from Lauro Muller, Urussanga, Treviso, Siderópolis, and Criciúma cities in the Santa Catarina State and a total of 19 samples were collected and Mössbauer, XRD, SEM/EDX, and TEM analyses were conducted on the samples. The major Fe-minerals identified are represented by the major minerals chlorite, hematite, illite, and pyrite, while the minor minerals include ankerite, chalcopyrite, goethite, hematite, jarosite, maghemite, magnetite, marcasite, melanterite, natrojarosite, oligonite, pyrrhotite, rozenite, schwertmannite, siderite, and sideronatrile. Pyrite is relatively abundant in some cases, making up to around 10% of the mineral matter in several samples. The sulphates minerals such as jarosite and others, probably represent oxidation products of pyrite, developed during exposure or storage.

Zinc Occurrence in Coal Power Plant Burning Combinations of Coal and Tires

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Fly ash from the cyclone-boiler co-combustion of high-S, high volatile bituminous coal and tire-derived fuel (tdf) was studied using a variety of chemical, optical, and microbeam techniques. Fly ash, dominated by Al-Si glass with lesser amounts of coal derived carbons, Fe-spinels, and tire-derived carbons, has Zn concentrations ranging from 2200 ppm (1st ESP row) to 6900 ppm Zn (3rd ESP row). Zinc occurs in Zn-rich nanoparticles in the Al-Si glass phases and as ZnO in amorphous and crystalline nanominerals, Fe- and Zn-sulphides, Pb-Al-Fe sulphates, and Zn sulphates. Iron-rich, Al- and Ti-bearing spinels contain accessory Zn^{2+}, Cr^{3+}, Mn^{2+}, and Pb^{2+}. Fe-sulphates and phosphates nanoparticles incorporate As, Cr, V, Ni, and Zn. Fullerenes were not detected in this fly ash, potentially due to the higher temperature of combustion in the cyclone boiler. Zinc was detected by XPS, but the low binding energies mitigated against the determination of the speciation of the element.

Hard Carbon from Coal Heavy Organics as Anode Material for Li-Ion Batteries

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Lithium-ion batteries have been widely used for the portable/consumer electric markets on account of its various advantages. Hard carbon, as a novel anode material, has received considerable attention for its high capacity (740mAh/g), good rate performance, low cost and easy to large-scale production. In this study, hard carbon (HC) material is prepared from the heavy organic matter of coal direct liquefaction residue by a simple crosslinking-solidifying and carbonization two-step method. The results show that the electrode fabricated from HC-700 delivers 503 mAh/g and 200 mAh/g at current density of 100 and 5000 mA/g. Moreover, HC-700 haves a more superb capacity and stability over long-term cycling.

The Relationship between Oxygen Transfer and Pyrolysis Conditions

Wenying Li, Chaopeng Wang, Huijun Huang, Xiaohong Li, Jie Feng, Taiyuan University of Technology, CHINA

Oxygen is an important factor that contributes to the complex structure of coal, and its content and form influence coal pyrolysis properties. In the process of pyrolysis, different heating rates will make products (volatile and char) distribution and constitute different. In order to explore the relationship between oxygen transferring and heating rates (15°C /min, 60°C /min, and 300°C /min), Hulunbeir lignite was chosen to pyrolyze in the fixed bed reactor. The oxygen amount of solid product in different heating rates was measured by elemental analyzer. The results show that the oxygen gradually transfers from coal to volatile with the increase of temperature. At 600°C, at the heating rate of 15°C /min, 60°C /min, and 300°C /min, there were 9.7%, 10.2%, and 12.7% of oxygen transferred to char respectively. Rapid heating rate helps more oxygen transfer to char and tar while block the production of gas-O and water. Coal will suffer stronger power when the heating rate is faster, resulting in more free radicals forming and releasing in short time. The change of process conditions will affect elemental distribution of pyrolysis products, which means oxygen transformation is not independent, but connected with the quality and quantity of hydrogen radical in pyrolysis.