

Western Research Institute

2007 Publication

Boateng, A.A., G.M. Banowetz, J.J. Steiner, T.F. Barton, D.G. Taylor, K.B. Hicks, H. El-Nashaar, V.K. Sethi, 2007, "Gasification of Kentucky Bluegrass (*Poa pratensis* L.) Straw in a Farm-Scale Reactor," *Biomass & Bioenergy*, Vol. 31, Issue 2-3, 153-161.

Abstract: A novel gasification reactor was designed for conversion of grass straw to synthesis gas. Our design was to improve synthetic gas yield and thermal stability at a scale suitable for on-farm use at a cost similar to that of a combine harvester. The reactor that was constructed and tested in this study follows the newly emerging design technique whereby the endothermic pyrolysis or gasification and exothermic char combustion co-exist in the same reactor. It operates in a dual mode where straw gasification occurs in the annulus of an outer tube and an inner (draft) tube. Our trials established that the dual-mode operation could be performed without material flow problems. Sustained tests demonstrated reactor stability at gasification temperatures up to 650°C and successful gasification of Kentucky bluegrass straw utilizing combustion heat from the inner tube. Calculated equivalence ratios of combustion in the inner tube ranged from 0.3 to 0.78 indicating fuel lean combustion of residual char without slagging. Carbon conversion ranged between 34.5 and 44.8%. Energy recovery, estimated as the ratio of the heat of combustion of the gas to that of the dry-ash-free feedstock, ranged from 14.7% to 30.92%. The estimated heating value for the synthesis gas ranged from 1.27 to 2.85 MJm⁻³. Although these conversion parameters are low, a proof of the design concept was established. They can be improved with little modification by increasing the residence time in the draft tube and complete isolation of the gaseous products of combustion and the gasification. More tests are required to evaluate the economic feasibility of the farm-scale unit.

Jin, S., P.H., Fallgren, A.A. Bilgin and P.W. Barnes, 2007. "In Situ Bioremediation of Benzene, Ethylbenzene, and Xylenes in Groundwater under Iron-Amended, Sulfate-Reducing Conditions," *Proc. In Situ and On-Site Bioremediation—the Ninth International In Situ and On-Site Bioremediation Symposium*, Baltimore, Maryland; May 7–10, 2007. ISBN 978-1-57477-161-9, Battelle Press, Columbus, OH.

Abstract: Groundwater contaminated by aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), is a major environmental problem due to the recalcitrance, and potential toxic effects of BTEX (including liver, kidney, and nervous system damage and cancer). BTEX can be biodegraded under aerobic condition; however, oxygen depletion due to microbial respiration usually drives the geochemical environment to the reduced, anaerobic conditions. Studies within the past two decades have demonstrated that BTEX can be biodegraded under anaerobic conditions by organisms such as denitrifying and sulfate-reducing bacteria (SRB). Elevated concentrations of sulfide in the groundwater (~63 mg S/L in water and 500 mg H₂S/L dissipating from the well head) at the field site near South Lovedale, OK, were inhibiting sulfate reducing bacteria (SRB) that are known to degrade contaminants including benzene, toluene, ethylbenzene, and m+p-xylenes (BTEX), which, except for toluene,

were also present in elevated concentrations in this groundwater. Microcosms were established in the laboratory using groundwater and sediment collected from the field site and amended with various nutrient, substrate, and inhibitor treatments. All microcosms were initially amended with FeCl₂ to induce FeS precipitation and, thereby, reduce sulfide concentrations. Complete removal of benzene, ethylbenzene, and xylenes was observed within 39 days in treatments with various combinations of nutrient and substrate amendments including no amendments (other than FeCl₂). This indicates that the elevated concentration of sulfide is the only limiting factor to benzene, ethylbenzene, and xylenes biodegradation at this site under anaerobic conditions, and that treating the groundwater with FeCl₂ may be the only necessary remedy to facilitate and enhance benzene, ethylbenzene, and xylenes degradation by the indigenous SRB population. This study demonstrated BTEX biodegradation under sulfate-reducing conditions using water and sediments from the actual contaminated field site without adding artificial enrichment media. Although several studies have demonstrated BTEX biodegradation by SRB using the water and sediments from a contaminated site, these studies do not address the production of sulfide and its toxic/inhibitory effects on SRB. Furthermore, very few studies have used ferrous iron to immobilize sulfide and thereby reactivate BTEX biodegradation by SRB. The results from this study experiment were successfully extrapolated to pilot-scale remediation of the field site.

Jin, S. and P.H. Fallgren, 2007, "Site-Specific Limitations of Using Urea as a Nitrogen Source in Biodegradation of Petroleum Wastes in Soil," *Soil and Sediment Contamination*, 16:5, 497 – 505.

Abstract: Nutrient addition is important to achieving the carbon/nitrogen balance and successful biodegradation of petroleum contaminants. Urea has been considered as a preferred nitrogen source in enhancing biodegradation because of its high nitrogen content and commercial availability. This study investigated urea in the biodegradation of petroleum-contaminated soils collected from an arid and sandy area in Egypt. Ammonium nitrate served as the nitrogen amendment control in this study.

Biodegradation of petroleum-contaminated soils from Wyoming was monitored as a comparison. Addition of urea failed to improve the enhancement of biodegradation of petroleum-impacted soil from the Egyptian site; in addition, urea demonstrates an adverse effect on the biodegradation rates. Results indicate that urea or its intermediates may inhibit the microorganisms involved in petroleum degradation. Data from this study suggest that the application of urea in the enhancement of biodegradation of petroleum compounds should consider site specificity, and may not be applicable in geological areas or soils structures similar to those in this study.

Jin, S., P.H. Fallgren, J.M. Morris, Q. Chen, 2007, "Removal of Bacteria and Viruses from Waters Using Layered Double Hydroxide Nanocomposites," *Science and Technology of Advanced Materials* 8, 67–70.

Abstract: We have identified synthetic layered double hydroxides (LDH) nanocomposites as an effective group of material for removing bacteria and viruses from water. In this study, LDH nanocomposites were synthesized and tested for removing biological contaminants. LDH was used to remove MS2 and fX174 (indicator viruses), and *Escherichia coli* (an indicator bacterium) from synthetic groundwater and to remove

mixed communities of heterotrophic bacteria from raw river water. Our results indicate that LDH composed of magnesium–aluminium or zinc–aluminium has a viral and bacterial adsorption efficiency $\geq 99\%$ at viral concentrations between 5.9×10^6 and 9.1×10^6 plaque forming units (pfu)/L and bacterial concentrations between 1.6×10^{10} and 2.6×10^{10} colony forming units (cfu)/L when exposed to LDH in a slurry suspension system. Adsorption densities of viruses and bacteria to LDH in suspension ranged from 1.4×10^{10} to 2.1×10^{10} pfu/kgLDH and 3.2×10^{13} – 5.2×10^{13} cfu/kg LDH, respectively. We also tested the efficiency of LDH in removing heterotrophic bacteria from raw river water. While removal efficiencies were still high (87–99%), the adsorption capacities of the two kinds of LDH were 4–5 orders of magnitude lower than when exposed to synthetic groundwater, depending on if the LDH was in suspension or a packed column, respectively.

Jin, S., P.H. Fallgren, A.A. Bilgin, J.M. Morris, P.W. Barnes, 2007, “Bioremediation of Benzene, Ethylbenzene, and Xylenes in Groundwater under Iron-Amended, Sulfate-Reducing Conditions,” *Environmental Toxicology and Chemistry*, Vol. 26, No. 2, pp. 249–253.

Abstract: Elevated concentrations of sulfide in groundwater (~ 63 mg S_2 /L in water and 500 mg dissolved H_2S /L dissipating from the wellhead) at a field site near South Lovedale (OK, USA) were inhibiting the activity of sulfate-reducing bacteria (SRB) that are known to degrade contaminants, including benzene, toluene, ethylbenzene, and xylenes. Elevated concentrations of these contaminants, except for toluene, also were present in this groundwater. Microcosms were established in the laboratory using groundwater and sediment collected from the field site and amended with various nutrient, substrate, and inhibitor treatments. All microcosms initially were amended with $FeCl_2$ to induce FeS precipitation and, thereby, to reduce aqueous sulfide concentrations. Complete removal of benzene, ethylbenzene, and *m-p*-xylenes (BEX; *o*-xylene not detected) was observed within 39 d in treatments with various combinations of nutrient and substrate amendments, including treatments with no amendments (other than $FeCl_2$). This indicates that the elevated concentration of sulfide is the only limiting factor to BEX biodegradation at this site under anaerobic conditions and that treating the groundwater with $FeCl_2$ may be a simple remedy to both facilitate and enhance BEX degradation by the indigenous SRB population.

Jin, S., J.I. Drever, and P.J.S. Colberg, 2007, “Effects of Copper on Sulfate Reduction in Bacterial Consortia Enriched from Metal-Contaminated and Uncontaminated Sediments,” *Environmental Toxicology and Chemistry*, Vol. 26, No. 2, pp. 225–230.

Abstract: The effects of copper amendments on bacterial sulfate reduction in enrichment cultures obtained from two types of freshwater sediment were examined. Sulfate-reducing bacterial (SRB) consortia were enriched from pond sediment with no known history of metal contamination (uncontaminated) and from reservoir sediment with a well-documented history of metal contamination (metal-contaminated). The rates and extent of sulfate reduction in each sediment type in the absence of added copper were indistinguishable. With amendments of 0.8 mg/L copper, no inhibitory effects on sulfate reduction were observed in either consortium type. At 8.0 mg/L copper, activity in uncontaminated SRB consortia was significantly inhibited, as evidenced by a delay in

and decreased rate of sulfate reduction; sulfidogenesis in metal-contaminated consortia was apparently unaffected. When the dissolved copper concentration was 30.0 mg/L, sulfidogenic activity in pond sediment consortia was completely inhibited. The rate of sulfate reduction temporarily decreased in the metal-contaminated enrichments but recovered after a short time. In active microcosms, copper was precipitated as CuS. The results of this study suggest that SRB from metal-contaminated environments have a markedly higher metal tolerance than those enriched from uncontaminated environments. The most significant inference from this work is that metal sulfide formation alone does not explain observed differences in metal tolerance between SRB consortia enriched from uncontaminated sediments and those that are derived from metal-contaminated sediments. Keywords: Sulfate-reducing bacteria copper metal toxicity metal removal metal sulfides.

Jin, S., and J.M. Morris, 2007, "Link of Power Generation and Waste Remediation in Sediments and Sludge Using Microbial Fuel Cell", *Proc. The 3rd International Green Energy Conference*, June 16-22, 2007, Västerås, Sweden.

Abstract: A microbial fuel cell (MFC) is a device that harvests electrons from anaerobic degradation of organic substrates, such as sludge and sediments, and generates electricity. In an MFC, organic compounds (e.g., wastes) serve as the fuel (substrate) and bacteria play the role of extracting electricity from the substrate. Compared to conventional hydrogen fuel cell, in which energy input is required to produce hydrogen fuel, the MFC technique significantly increases the efficiency of energy yield by skipping the step of energy-consuming hydrogen production. Aerobic metabolism, in which oxygen serves as the terminal electron acceptor, is the most thermodynamically favorable pathway to degrade organic wastes. However, oxygen is usually depleted in organic-rich sediments and sludge due to strong microbial respiration, and other electron acceptors (e.g., nitrate, sulfate) have to be used by microorganisms to break down the organic compounds. An MFC provides anaerobic bacteria with a solid-state terminal electron acceptor (anode) that transfers electrons originated from biodegradation of these organic compounds (on or near the anode) to the cathode, where electrons are consumed by oxygen (from ambient air on or near ground surface) and protons to form the end product H₂O. In this case, the MFC process practically achieves an aerobic degradation rate of organic compounds in an anaerobic environment. Therefore, this technique can be used to significantly enhance the efficiency of waste mitigation. Results from our work and others demonstrate that it is possible to harvest electricity from the degradation of organic wastes in sediments and sludge, meanwhile enhancing the remediation of these wastes. Our work has also identified cost-effective electrode materials that can maximize power generation of an MFC and making it an economically feasible device to implement in the field. Though individual MFC can only generate limited electricity, by using an innovative modular design, MFC units can be bundled and the electricity generated from individual MFC can combine into a substantial power output. This design is particularly beneficial to provide alternative energy to rural communities, remote areas and developing regions where organic wastes are generated and stored at large quantity and power supply is limited. This concept can also be applied in municipal wastewater plants and other areas with problems of organic wastes.

Jin, S. and J.M. Morris, 2007, "Effective Removal of Biogenic Contaminants from Waters Using Layered Double Hydroxide Material," *Proc. WaterMicro 2007 14th International Symposium on Health-Related Water Microbiology*, Tokyo, Japan, September 9-15, 2007.

Abstract: Layered double hydroxide (LDH) was used to remove bacteria and endocrine disrupting compounds (EDCs) from natural water sources. Efficiency of bacterial adsorption was $\geq 99\%$ at bacteria concentrations between 1.6×10^{10} and 2.6×10^{10} colony forming units (cfu)/L. Loading capacity of bacteria on LDH reached 5.0×10^{13} cfu/kg. Removal of the estrogen 17β -estradiol (E2) was studied in LDH-packed columns and slurry exposure techniques. Natural concentrations of 12 ng E2/L decreased to non-detect levels (MDL 1.6 ng/L) in column studies and spiked concentrations of 317 ng E2/L decreased to non-detect levels in slurry studies.

Jin, S., P.H. Fallgren and J. Bensch. 2007, "Ozone Oxidation of MTBE and Resultant Formation of Cr(VI) in Groundwater," *Proc. The 5th International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater*, Niagara Falls, NY, USA, Sept 24-27, 2007.

Abstract: Ozone injection is an increasingly popular method to remediate a variety of compounds in soil and groundwater. Improved ozone production technologies and injection methods allow greater ozone to be applied to the subsurface at less cost. Ozone, however, also has the potential to oxidize soluble metals, including non-toxic trivalent chromium (Cr(III)) to the toxic hexavalent chromium (Cr(VI)). Ozone production under pressure and pulsed-pressurized injection were used during a field pilot study that generated significant concentrations of Cr(VI) while reducing MTBE concentrations from 10,000 micrograms/liter (ug/L) to non-detect in one month. A research study was conducted to evaluate the formation of Cr(VI) and the reduction of MTBE concentrations under varying dosages of ozone. This study investigated ozone oxidation of MTBE by applying a range of zone dosages to groundwater/soil slurry samples under laboratory conditions. A total oxidizing demand method was used to determine the design dosage of ozone for the field samples. Concentration changes in MTBE and chromium were monitored at specific ozone dosages less than and greater than the design dose. The results indicate that MTBE is preferentially oxidized by ozone at the stoichiometric dosage prior to oxidation of Cr(III) to Cr(VI). The study also demonstrated that the total oxidizing demand method may be a useful tool to identify an optimal dosage that will effectively destroy MTBE while minimizing the oxidation of chromium.

Miknis, F.P. and K.P. Thomas, "NMR Analysis of Polyphosphoric Acid-Modified Bitumens," *Road Materials and Pavement Design*, in press.

Abstract: Phosphorous-31 NMR spectroscopy has been used to study the behavior of polyphosphoric acid (PPA) in bitumen. Phosphorous NMR spectra were acquired on a PPA-modified bitumen immediately after blending, and on samples that were stored at 135°C for different periods of time. The initial NMR spectra showed resonances characteristic of phosphorous atoms in orthophosphoric acid, and in middle and end groups of phosphate chains. However, over time the number of phosphorous atoms in the middle and end groups decreased, indicating a preference of polyphosphoric acid to revert back to the orthophosphoric acid in the presence of bitumen. The NMR data did

not suggest the formation of organic phosphate esters as a result of PPA modification. Phosphorous NMR spectra were also acquired on bitumen samples modified with Elvaloy[®] in which polyphosphoric acid was used as a catalyst. The data showed that over time only one type of phosphorous atom remained in the bitumen. The NMR data suggest that the PPA did not react with Elvaloy[®] to form esters.

Morris, J.M., S. Jin, J. Wang, C. Zhu, and M.A. Urynowicz, 2007, "Lead Dioxide as an Alternative Catalyst to Platinum in Microbial Fuel Cells," *Electrochemistry Communications*. 9: 1730-1734.

Abstract. Lead dioxide (PbO₂) was compared to platinum (Pt) as a cathode catalyst in a double-cell microbial fuel cell (MFC) utilizing glucose as a substrate in the anode chamber. Four types of cathodes were tested in this study including two PbO₂ cathodes fabricated using a titanium base with butanol or Nafion[®] binders and PbO₂ paste, one Pt/carbon cathode fabricated using a titanium base with a carbon-Pt paste, and a commercially available Pt/carbon cathode made from carbon paper with Pt on one side. The power density and polarization curves were compared for each cathode and cost estimates were calculated. Results indicate the PbO₂ cathodes produced between 2 to 4× more power than the Pt cathodes. Furthermore, the PbO₂ cathodes produced between 2 and 17× more power per initial fabrication or purchase cost than the Pt cathodes. This study suggests that cathode designs that incorporate PbO₂ instead of Pt could possibly improve the feasibility of scaling up MFC designs for real world applications by improving power generation and lowering production cost.

Morris, J.M. and S. Jin, 2007, "Feasibility of Using Microbial Fuel Cell Technology in Bioremediation of Hydrocarbons in Groundwater," *Journal of Environmental Science and Health-Part A*, In press.

Abstract. A single-cell microbial fuel cell (MFC) design was used to study anaerobic microbes that utilize petroleum contaminants as a sole substrate to produce power during remediation. Additionally, we tested various proton bridge designs to physically separate the anode and cathode chambers of a two-cell MFC by ~9 m (~30 ft.). This separation enables the potential use of MFC technology for in-situ bioremediation of petroleum hydrocarbons in the groundwater, in which oxygen is usually depleted and oxygen availability only exists at or near the surface. Sustained power generation (as high as 120 mW/m² cathode) was recorded for ~6 d in a single-cell MFC utilizing a mixture of refinery waste (containing various concentrations of hydrocarbon contaminants) and cell growth media. MFC cell potential (1KΩ external resistance) decreased by ~55% over the length of 9-m proton bridge with a 6.9% decrease in potential per m of bridge.

Netzel, D.A., and J.F. Rovani, 2007, "Direct Separation and Quantitative Determination of (*n*-, Iso-)Alkanes in Neat Asphalt Using Urea Adduction and High-Temperature Gas Chromatography (HTGC)," *Energy & Fuels*, 21 (1), 333 -338.

Abstract: Urea adduction and high-temperature gas chromatography were used to separate and quantify the amount of normal plus iso-alkanes (*n*-, iso-)alkanes in 13 neat asphalts. Treating neat asphalt directly with urea eliminated the separation steps necessary for extracting the saturate fraction containing the alkanes from the asphalt. The

amounts of *n*-alkanes including 2-methyl and 3-methyl isomers for the 13 asphalts ranged from 0 to 1.84 wt %. Saturate fractions from three asphalts were obtained by adsorption-desorption chromatography. The amounts of (*n*-, iso-)alkanes and the highly branched plus cyclic alkanes were determined also for these fractions using urea adduction and were found to be in good agreement with the direct determination of (*n*-, iso-)alkanes in the neat asphalts. The amount of (*n*-, iso-)alkanes was found to correlate with the crystalline wax content measured by differential scanning calorimetry, but the method does not account for all of the crystalline wax content. In addition, the amount of (*n*-, iso-)alkanes does not account for the large *n*-alkane methylene signals observed in the hydrogen-1 and carbon-13 nuclear magnetic resonance spectra for the asphalts. No correlation was found between the amount of (*n*-, iso-)alkanes in asphalt and the fracture temperature. However, an apparent correlation does exist between the highly branched plus cyclic alkanes in asphalt and the fracture temperature.

Schabron, J.F., 2007, "Evaluation of Mercury Calibration Devices for Continuous Emissions Monitoring," WRI report to the Electric Power Research Institute under EPRI Contract EP-P19442/C9595.

Abstract: Approximately 1,000 coal fired power plant stacks will need installation of mercury continuous emissions monitors (CEMs) during 2007. The power industry desires to begin a full year of monitoring before the formal monitoring and reporting requirement begins on January 1, 2009. It is important for the industry to have available reliable, turnkey equipment from CEM vendors. Western Research Institute (WRI) is working closely with the Electric Power Research Institute (EPRI), the National Institute of Standards and Technology (NIST), and the Environmental Protection Agency (EPA) to facilitate the development of the experimental criteria for a NIST traceability protocol for dynamic elemental mercury vapor generators. The generators are used to calibrate mercury CEMs at power plant sites. The Clean Air Mercury Rule (CAMR) which was published in the Federal Register on May 18, 2005, requires that calibration be performed with NIST-traceable standards. It also requires that the calibration standard value be accurate within 2%. The traceability protocol will be based on the actual analysis of the output of each calibration unit at several concentration levels ranging from about 2-40 $\mu\text{g}/\text{m}^3$, and this analysis will be directly traceable to analyses by NIST using isotope dilution inductively coupled plasma / mass spectrometry (ID ICP/MS) through a chain of analyses linking the calibration unit in the power plant to the NIST ID ICP/MS.

Prior to this project, NIST did not provide a recommended mercury vapor pressure equation or list mercury vapor pressure in its vapor pressure database. The NIST Physical and Chemical Properties Division in Boulder, Colorado was subcontracted under this project to study the issue in detail and to recommend a mercury vapor pressure equation that the vendors of mercury vapor pressure calibration units can use to calculate the elemental mercury vapor concentration in an equilibrium chamber at a particular temperature. A NIST-recommended equation was developed and published in the peer-reviewed literature as a result of this work. This equation is used to calculate the vapor pressure of liquid elemental mercury from the triple point to the boiling point. The equation provides a vapor pressure that is consistent with the Clausius/Clapeyron thermodynamic equation. The new NIST equation is different from some other equations in use, and it provides a vapor pressure at 20 °C about 7% higher than the mercury vapor

pressure listed in the 1928 International Critical Tables. There continues to be disagreement among the vendors on the correct vapor pressure equation for use in the calibration units. Because of this, it was agreed in a special meeting held in Orlando, FL in March 16, 2006 that the NIST traceability of calibration units would be performance-based. The issue of the correct vapor pressure equation is now a side issue, and this is no longer in the critical path for establishing a NIST traceability protocol.

Schabron, J.F. and J.F. Rovani, 2007. "Asphaltene Determinator: On-Column Precipitation and Re-Dissolution of Asphaltenes," *Preprints*, Div. of Petroleum Chemistry, American Chemical Society, 55 (1) 54-57.

Abstract: A new approach to the characterization of the polar materials in petroleum has been developed. This is being evaluated with both upstream crude oils and downstream product oils from a variety of processes, such as crude oils, fuel oils, slurry oils, visbroken oils, atmospheric residua, and vacuum residua. It involves the use of an inert PTFE-packed column to conduct two automated methods based on a novel on-column asphaltene precipitation and re-dissolution technique. The separation does not involve chromatography, it is strictly solubility based. The first method measures the total weight percent of asphaltenic material. The second method breaks the asphaltenic material into three subfractions of increasing polarity, which provides a quantitative indication of the resins/polars/very polars distribution. This approach allows the detection of polar and resinous materials in minutes, even for samples that do not precipitate asphaltenes in the gravimetric method. The analysis uses standard HPLC equipment with an evaporative light scattering detector (ELSD).

Schabron, J.F. and J.F. Rovani, 2007. "On-Column Precipitation and Re-Dissolution of Asphaltenes in Petroleum Residua," *Fuel*, in press.

Abstract: A new automated separation technique was developed for measuring the distribution profiles of the most polar, or asphaltenic components of an oil, using a continuous flow system to precipitate and re-dissolve asphaltenes. Methods of analysis based on this new technique were explored. One method based on the new technique involves precipitation of a portion of residua sample in heptane on a polytetrafluoroethylene-packed (PTFE) column. The precipitated material is re-dissolved in three steps using solvents of increasing polarity: cyclohexane, toluene, and methylene chloride. The amount of asphaltenes that dissolve in cyclohexane is a useful diagnostic of the thermal history of an oil, and its proximity to coke formation. For example, about 40 % (w/w) of the heptane asphaltenes from unpyrolyzed residua dissolves in cyclohexane. As pyrolysis progresses, this number decrease to below 15% as coke and toluene insoluble pre-coke materials appear. Currently, the procedure for the isolation of heptane asphaltenes and the determination of the amount of asphaltenes soluble in cyclohexane spans three days. The automated procedure takes one hour. Another method uses a single solvent, methylene chloride, to re-dissolve the material that precipitates in heptane on the PTFE-packed column. The area of this second peak can be used to calculate a value which correlates with gravimetric asphaltene content. Currently the gravimetric procedure to determine asphaltenes takes about 24 hours. The automated procedure takes 30 minutes. Results for four series of original and pyrolyzed residua were compared with data from the gravimetric methods. Methods based on the new on-

column precipitation and re-dissolution technique provide significantly more detail about the polar constituents of oils than the gravimetric determination of asphaltenes.

Sethi, V.K., K. Omar, P. Martin, T.F. Barton, K. Krishnamurthy, 2007, "Oxy-Combustion Versus Air-Blown Combustion of Coals," *Proc. 32nd International Technical Conference on Coal Utilization and Fuel Systems*, June 10 - 15, Clearwater, Florida.

Abstract: Oxy-combustion with flue gas recycle is a concept designed to facilitate the capture and subsequent sequestration of carbon dioxide from coal-fired power plants. The approach is applicable to both new and existing power plants. In oxy-combustion mode, oxygen is mixed with recycled flue gas to replace the normal combustion air at the burner. The volume of flue gas leaving the boiler is considerably smaller than the conventional air-fired volume, and consists primarily of carbon dioxide. This concentrated stream of carbon dioxide is then available for capture and subsequent carbon sequestration without the need for expensive and energy-consuming-separation systems.

This paper describes the relative performance of a 250,000 Btu/hr combustion test facility in air-fired and oxy-combustion modes. A series of tests was conducted in which three coals; a lignite, a sub-bituminous, and a bituminous coal, were combusted in the tangentially fired combustion test facility. All three coals were pulverized and dried to similar conditions. The coals were combusted in air, in 21/79% oxygen/carbon dioxide mixture, or in 27/73% oxygen/carbon dioxide mixture. The primary, secondary and overfire gas flow rates were fixed to keep the flue gas mass flow rate constant at approximately 236 lbs/hr. All experiments were conducted with approximately 3% excess oxygen. The heat rejection across the water-wall, superheater, and economizers were measured. Thermal distribution throughout the combustion test facility was measured with a thermocouple array. Composition of the flue gas was monitored for oxygen, nitrogen, carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen oxides, and mercury. The fly ash composition after each test was determined, with an emphasis on residual carbon.

Results showed that NO_x emissions for oxy-combustion were lower than those during the air-blown operations. The level of decrease, however, was not as large as that reported by others and appeared to be dependent on the coal type. It should be noted, however, that in these tests, no attempt was made to optimize burner staging. Carbon dioxide concentration of the flue gas, which was in the 15-18% range during air-blown testing, increased to 95-96% during oxy-combustion tests. The data also show that there may be a beneficial effect on mercury emissions. For all three coals tested, the mercury concentrations in the furnace back pass gas were lower during oxy-combustion than during air-blown operations. As expected, carbon content of the fly ashes for 27/73% oxy-combustion tests were similar to those for air-blown operations, confirming the equivalency of the thermal performance under the two firing conditions.

Urynowicz, M.A., W.C. Boyle, M.E. Bedessem, and S. Jin, 2007, "Nitrogen Removal in Recirculating Sand Filter Systems with Upflow Anaerobic Components," *Journal of Environmental Engineering*, Vol. 133, 464-470.

Abstract: Septic systems can present a risk to human health by releasing highly soluble nitrate-nitrogen into the groundwater. A research and demonstration study undertaken in

Black River Falls, Wisconsin, evaluated several promising biofilter technologies for on-site nitrogen removal. Duplicate recirculating sand filter-upflow anaerobic systems with a design hydraulic loading rate of 954 L/day (250 gal/day) were used to treat septic tank effluent from a correctional institution and produced a treated wastewater with a total nitrogen concentration of 15.2 mg/L for System 1 and 18.2 mg/L for System 2, or 72.0 and 63.0% nitrogen removal, respectively. The differences between the two systems appear to have been the result of process configuration changes made over the duration of the study. This paper evaluates the nitrogen removal performance of the recirculating sand filter-upflow anaerobic systems and the effect of operational and environmental factors, including the recirculation ratio, $BOD_5/N_0_3^-$, and temperature. Nitrogen removal was limited by the recirculation ratio with the maximum total nitrogen removal of 70.1% when the recirculation ratio=3. Improved performance was also noted for temperatures $\geq 20^\circ\text{C}$ and $BOD_5/N_0_3^- \geq 8$. Low temperatures adversely affected nitrification and low $BOD_5/N_0_3^-$ adversely affected denitrification. The relationships among nitrogen removal, recirculation ratio, $BOD_5/N_0_3^-$, and temperature are also discussed. Keywords: sand, recirculation, anaerobic treatment, denitrification, nitrification, temperature effects, filtration.