This Week at NETL

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Effects of Coal and Biomass Contaminants on Fischer-Tropsch and Water-Gas-Shift Catalysts Examined

Working in cooperation with NETL, collaborators at TDA Research Inc. (Wheat Ridge, Colo.) and the University of Kentucky Center for Applied Energy Research have completed categorizing the effects of coal and biomass contaminants on Fischer-Tropsch and water-gas-shift (WGS) catalysts. The project team first completed a thermodynamic analysis of how selected catalysts interact with 15 contaminants pertinent to syngas derived from coal and/or biomass, and then experimentally determined, at bench-scale, the effect of these contaminants on the long-term performance of the catalysts at typical industrial operating conditions. Results of the thermodynamic analysis, experiments, and catalyst characterization studies helped develop a fundamental understanding of degradation mechanisms induced by the contaminants, which could adsorb on or react with the catalysts. Analysis showed that the surface areas, pore volumes, and pore diameters of the WGS catalysts all decreased, with hydrogen sulfide and ammonia acting either singly or in combination. A trade-off analysis showed that the use of a contaminant-removal system would be economically justified in many cases to reduce the cost of premature catalyst replacement due to poisoning. Results of this work can help guide further research on catalyst improvements and/or process modifications that could reduce the capital and operating expenses associated with producing drop-in liquid transportation fuels from coal- or biomass-derived syngas mixtures.

First Carbon Capture Simulation Initiative Toolset Licensed for Use

The NETL-led Carbon Capture Simulation Initiative (CCSI) finalized its initial licensing agreements, allowing General Electric, Alstom Power, and Phillips 66 to use the CCSI Toolset to develop their own carbon capture processes. The licenses are the result of intense industry interest in gaining early access to the CCSI Toolset, which prompted the technical team to move forward its initial release by more than a year. CCSI is organized to develop state-of-the-art modeling and simulation tools to accelerate the development and widespread deployment of safe, reliable, and efficient post- and oxy-combustion carbon capture technologies. The first release consists of—

- New tools for process synthesis and optimization to help identify promising concepts more quickly.
- New physics-based models of potential capture equipment and processes that will reduce the time to design and troubleshoot new systems.
- A framework to quantify the uncertainty of model predictions.
- Enabling tools that provide new capabilities, such as creating reduced-order models from reacting multiphase flow simulations, and running thousands of process simulations concurrently for optimization and uncertainty quantification.

The CCSI technical team includes researchers from NETL, Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Pacific Northwest National Laboratory, Boston University, Carnegie Mellon University, Princeton University, West Virginia University, the University of Texas, and the University of Utah.

Novel Sorbent Captures 90 Percent of Carbon Dioxide in Simulated Flue Gas

Shakedown of a modified CO_2-capture test facility using first generation polyethylenimine (PEI) sorbent developed at NETL and prepared by Pressure Chemicals Company (Pittsburgh, Pa.) demonstrated that significant carbon capture can be achieved in a relatively simple continuous fluidized bed process. Modifications to both the reactor configuration and its operating parameters enable the newly commissioned, fully integrated, continuous flow CO_2 capture unit to generate validation data across a broad range of capture fractions. Following adsorption of CO_2 from a synthetic mix of gases representing flue gas from a pulverized coal power plant, the sorbent transfers from the fluidized bed reactor using non-mechanical valve technology into a fluidized bed regenerator, where heating to 120°C releases a concentrated stream of CO_2 gas. A phenomenological kinetic model describing the PEI sorbent is discussed in the *AIChE Journal*. Data from the CO_2 capture unit will help validate models developed by the NETL-led Carbon Capture Simulation Initiative.

Monitoring Begins for Large-Scale CO_2 Injection into Michigan's Niagaran Reef Complex

Members of the Midwest Regional Carbon Sequestration Partnership (MRCSP), led by Battelle Memorial Institute (Columbus, Ohio), initiated monitoring of CO_2 injected into six target reefs where industry partner Core Energy LLC (Traverse City, Mich.) is conducting enhanced oil recovery (EOR) operations in northern Michigan. MRCSP installed instrumented wells and pipelines to obtain geological and operational data for validating reservoir simulation models and determining how much CO_2 is retained in the formations. To date, MRCSP has monitored nearly 9,000 metric tons of CO_2 being injected into six active EOR reefs. The large-scale effort is designed to advance the understanding of injectivity, improve capacity estimates, and determine the feasibility of utilizing CO_2 and storing the greenhouse gas in geological formations. Knowledge gained will lead to a better understanding of how sequestration technologies can best be applied on a regional basis for the benefit of all MRCSP partners and stakeholders.

Novel NETL Technique Probes the Submicron Structure of Coal

NETL researchers exposed dry core samples of Pittsburgh and Sewickley bituminous coals to supercritical CO_2 at 2,200 pounds per square inch and 55 °C for 104 days to investigate any irreversible alterations induced in micro-, meso-, or macro-pores. Prior to the exposure, coal structure and porosity were imaged using a high-resolution field-emission scanning electron microscope, allowing observation of structures at nanoscale. After exposure, the imaged features were relocated, reimaged, and analyzed for structural changes. Discussion of this work in the Elsevier publication *Fuel* documents the first use of this relocation technique to study coal pore structure at high resolution. While CO_2 solvent and swelling properties did not significantly change the micro-, meso-, or macro-pores in the unconfined samples for the study conditions, further research should address confined conditions that would realistically represent those of enhanced coalbed methane recovery operations. The study found that changes on the macro-pore scale, if any, are reversible and do not permanently alter the coal structure, corroborating other reports that coal behaved like an electric material when exposed to supercritical CO_2 and returned to its fresh dimensions once the CO_2 was removed.

NETL Finds Evidence of Irreversible CO_2 Intercalation in Natural Montmorillonite

Experimenting with powdered clay samples, scientists at NETL examined mineral interaction processes relevant to CO_2 storage in geologic formations and cap rock seal integrity. Described in the Elsevier publication *International Journal of Greenhouse Gas Control*, the work shows that natural montmorillonite has significant sorption capacity for CO_2, and corroborates the hypothesis that CO_2 molecules can be irreversibly trapped in the galleries associated with the montmorillonite interlayer where, over the long term, they can chemically react with alkaline cations to form carbonates. The researchers uncovered previously unknown sorption mechanisms affecting the fate of CO_2 injected underground, as well as changes in the mechanical properties of geo-materials in contact with CO_2. The interlayer CO_2 may cause an irreversible expansion of

clay, depending on the degree of cation hydration and the dynamic application of CO_2 pressure, resulting in CO_2-H_2O mixing in the interlayer, as opposed to displacement of H_2O by CO_2 flow. Subsequent validation on montmorillonite lumps substantiated the evidence that similar processes may occur in natural clay deposits.

NETL Manager Assumes Chair of the Propulsion and Power Systems Alliance

Having served on the Propulsion and Power Systems Alliance (PPSA) Leadership Team from 2010 to 2012, and on the PPSA Materials Technology Area Team from 2007 to 2010, NETL's Mary Anne Alvin will chair the alliance from 2013 to 2014. The PPSA promotes collaboration among government agencies to better utilize existing program resources in the areas of power and propulsion. The alliance focuses on technology development, advancement, interaction, and collaboration in ten technology areas: combustors, compressors, control and health management, materials, mechanical components, modeling and simulation, noise, propulsion/airframe integration, thermal management, and turbines. Alvin received the PPSA Chairman's Award in 2009 for outstanding contributions to PPSA objectives both individually and as a team leader.

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