U.S. Department of Energy • Office of Fossil Energy
National Energy Technology Laboratory



# Successes

An Integrated Hydrogen Production— Carbon Dioxide Capture Process from Fossil Fuels

### **ADVANCED RESEARCH**

To support coal and power systems development, NETL's Advanced Research Program conducts a range of pre-competitive research focused on breakthroughs in materials and processes, coal utilization science, sensors and controls, computational energy science, and bioprocessing—opening new avenues to gains in power plant efficiency, reliability, and environmental quality. NETL also sponsors cooperative educational initiatives in University Coal Research, Historically Black Colleges and Universities, and Other Minority Institutions.

#### **A**CCOMPLISHMENTS

- √ Innovative process
- √ Bio-waste reduction
- √ CO₂ capture/use
- √ H, co-production



# **Description**

To lessen the nation's dependence on imported fossil fuels and decrease emissions of carbon dioxide (CO<sub>2</sub>) and other greenhouse gases (GHG) associated with fuel consumption, the United States is laying the foundation for a new energy production platform. That platform will not depend on traditional combustion systems but will use clean hydrogen as an energy carrier to power fuel cells and other systems. When used to power vehicles or generate electricity, fuel cells emit virtually no air and water pollution or GHGs. While serious technical challenges must be addressed to achieve the transition to a hydrogen-based economy, hydrogen production from domestic fossil fuels such as coal is one promising avenue for ensuring plentiful, environmentally sound hydrogen supplies. Coal-based hydrogen production relies on gasification facilities that can be designed to produce pure hydrogen alone or in combination with other useful chemical products and electricity. The existing coal infrastructure provides a reliable supply network for coal-based power and transportation fuel applications.

To contribute to this effort, the U.S. Department of Energy's Office of Fossil Energy (DOE-FE) has awarded a research grant to Clark Atlanta University (CAU) to investigate an integrated process for the production of hydrogen and fertilizer from coal and/or biomass. CAU's partner for pilot-scale testing is Scientific Carbons, Inc. (SCI), Blakely, Georgia, a manufacturer of activated carbon from renewable resources for industrial and municipal applications.

The grant is administered by the Advanced Research (AR) program of the National Energy Technology Laboratory (NETL) under the Historically Black Colleges and Universities and Other Minority Institutions (HBCU/OMI) program. HBCU/OMI encourages minority participation in fundamental research to develop technologies that promote the efficient and environmentally safe use of coal, oil, and natural gas resources. At the same time, the program helps increase the diversity of the nation's skilled scientific and technical workforce. NETL is engaged in a wide array of research efforts into hydrogen and fuel cells in alignment with President Bush's Global Climate Change Initiative and Hydrogen Fuel Initiative announced in 2002 and 2003, respectively.

# **Goals and Technology Approach**

The overall project objective is to determine the feasibility of using char from a coal/biomass pyrolysis-reforming process along with CO<sub>2</sub> smokestack emissions to produce clean hydrogen and a sequestered carbon fertilizer. The concept underlying the new

# **PROJECT DURATION**

**Start Date** 09/15/03

**End Date** 03/15/07

#### Cost

**Total Project Value** \$198,000

DOE/Non-DOE Share \$198,000 / \$0

## INDUSTRIAL PARTNER

Danny Day President Scientific Carbons, Inc. 253 North Bay Street P.O. Box 573 Blakely, GA 39823-2329 229-723-6757, 800-723-4939 (toll free) research integrates two significant and complementary approaches to hydrogen production and carbon dioxide sequestration that were developed at Oak Ridge National Laboratory (ORNL) and at CAU. The first part of the process is to convert biomass or coal into hydrogen and char. The hydrogen can be efficiently used for stationary power and mobile applications, or it can be synthesized into ammonia (NH<sub>4</sub>). The second part of the process is to allow the activated char and ammonia to react with CO<sub>2</sub> emissions to produce ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>), which is solidified within the pores of the char. This ammonium bicarbonate-impregnated char may be used as a slow-release fertilizer. Thus the overall process yields hydrogen by reforming biomass/coal through pyrolysis, and a char-NH<sub>4</sub>HCO<sub>3</sub> fertilizer from a CO<sub>2</sub> capture process. The fertilizers may be returned to the fields and used to support the growth of more biomass.

Specific objectives are to:

- 1) Determine the processing conditions that will yield char with the desirable properties for CO<sub>2</sub> capture.
- 2) Conduct bench-scale tests at CAU and pilot-scale tests at the SCI facility to evaluate and optimize conditions for the char-NH<sub>3</sub>-CO<sub>2</sub> reaction to form solidified NH<sub>4</sub>HCO<sub>3</sub> within the pores of activated char.
- 3) Conduct a greenhouse-based study at CAU to evaluate the properties of the char-NH<sub>4</sub>HCO<sub>3</sub> product as a fertilizer.

The work has involved bench-scale experiments and analytical development work in materials characterization. CAU's Combustion and Emission Laboratory has conducted the bench-scale experiments. SCI is performing the pilot-scale testing at a small fluidized bed reactor (FBR) built in Athens, Georgia at the University of Georgia Bioconversion facility, as shown in Figure 1. The FBR produces hydrogen and char from biomass in a 50-kg/hr cross-flow pyrolysis-steam reforming system. This reactor is being utilized for the coal and/or biomass pyrolysis-reforming studies.



Figure 1. Pilot plant pyrolysis unit with biomass feedstack system

Extensive characterization of the pyrolysis char was undertaken to determine the conditions that yield the most desirable char properties with respect to composition and physical properties such as size, surface area, and pore size distribution. The CO<sub>2</sub> capture experiment combined char from the pyrolysis-reforming step with ammonia, water vapor, and a simulated equivalent discharge from coal-fired power plant exhaust, while using the FBR to produce a high percentage ammonium bicarbonate nitrogen fertilizer within the char structure. The char-NH<sub>4</sub>HCO<sub>3</sub> product will subsequently be characterized and evaluated in a greenhouse as a potential fertilizer.

Thus, the methodology and overall scheme have involved the pyrolysis of coal and/or biomass to generate char, catalytic steam reforming of the pyrolysis vapors to hydrogen and carbon dioxide, the conversion of part of the hydrogen from the reformer into ammonia, and the final step of combining the char, ammonia, water vapor, and exhaust gases in a fluidized bed to create the carbon-based fertilizer.

The conversion of hydrogen into ammonia has not been studied, as it is a well-established technology. Instead, a simulated flue gas stream containing ammonia and carbon dioxide is being used. An ongoing project at SCI, with the goal of producing hydrogen from the pyrolysis-reforming process for urban transportation, offers the present project the opportunity to evaluate the char while simultaneously producing hydrogen. This study, therefore, is designed to test and characterize the produced materials, conduct experiments on the char-NH<sub>3</sub>-CO<sub>2</sub> solidification reaction, test the char-NH<sub>4</sub>HCO<sub>3</sub> product as a potential fertilizer, and undertake the economic and technical evaluation of the integrated process.

# **Accomplishments and Future Work**

Work to date has resulted in the following accomplishments:

- Developed an integrated process for hydrogen production, char production, and CO<sub>2</sub> capture;
- Built and tested a pilot-scale test facility to demonstrate the developed process;
- Successfully ran the test facility in 24-hour continuous operation, and produced 49 percent hydrogen that was nitrogen-free;
- Successfully produced 32 percent char as a co-product, through the integrated process;
- Conducted a bench-scale study for optimization of the char-NH<sub>4</sub>HCO<sub>3</sub> production process, and evaluation of fertilizer characteristics;
- · Developed models for process scale-up; and
- Evaluated the effect of char used as fertilizer without NH<sub>4</sub>HCO<sub>3</sub> on corn and another vegetable (see Figure 2).

Tasks remaining to be performed include the following:

- Perform a 1,000-hour pilot-scale test run;
- Test the scaled-up CO, capture reactor; and
- Perform greenhouse studies to evaluate time-release fertilizer usage with NH<sub>4</sub>HCO<sub>3</sub> and verify nitrogen uptake rate.

Following project completion, additional technical information will be released based on final results from remaining project activities.



No char applied (plants about 2 feet high)



Char fertilizer made from traditional slow burning process with heap of shells in a barrel and limited oxygen (plants about 3 feet high)



Char fertilizer made using integrated hydrogen production process (plants about 4 feet high)

Figure 2. Simple trial comparison of corn plants with char produced from peanut shells used as fertilizer

# **Benefits**

The ability to convert char from coal and biomass into hydrogen and a slow-release fertilizer will facilitate the use of hydrogen as a clean source of energy, and simultaneously provide a way to sequester carbon dioxide. These capabilities will help lay the foundation for a new strategic energy production platform that decreases both the nation's dependence on imported fossil fuels, and emissions of greenhouse gases associated with fossil fuel consumption.

"The overall project objective is to determine the feasibility of using char from a coal/biomass pyrolysis-reforming process along with  $CO_2$  smokestack emissions to produce clean hydrogen and a sequestered carbon fertilizer."

# STATES AND LOCALITIES IMPACTED

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