

An Integrated Hydrogen Production-CO₂ Capture Process from Fossil Fuel

Semiannual Progress Report

Reporting Period Start Date: March 15, 2005
Report Period End Date: September 15, 2005

Principal Authors: Z. Wang (PI) and K. B. Bota
Clark Atlanta University, Atlanta, GA 30314
Email: zwang@cau.edu Phone: 404-880-6934

D. Day
Scientific Carbons Inc, Blakely, GA

Date Report Was Issued: Dec 2005

DOE Award Number: DE-FG26-03NT41914

Submitted by: Clark Atlanta University, Atlanta, GA 30314
Eprida Scientific Carbons Inc., Atlanta, GA

DISCLAIMER

DISCLAIMER OF LIABILITY: This report was prepared as accounts of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER OF ENDORSEMENT: Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of document authors herein do not necessarily state or reflect those of the U.S. Government or any state government or any agency thereof.

ABSTRACT

The major project objective is to determine the feasibility of using the char from coal and/or biomass pyrolysis, ammonia and CO₂ emissions at smokestacks to produce clean hydrogen and a sequestered carbon fertilizer. During this work period, literature review has been completed. The project plan, design and test schedules were made on the basis of discussion with partner in experimental issues. Installation of pilot scale units was finished and major units tests were fully performed. Modification of the pyrolyzer, reformer and gas absorption tank have been done. Integration testing is performing recently. Lab scale tests have been performed. Field tests of char/fertilizer have been conducted. The experimental results are discussed in this paper.

TABLE OF CONTENTS

INTRODUCTION AND OBJECTIVES.....	3
EXPERIMENTAL SECTION.....	4
RESULTS AND DISCUSSION.....	7
Hydrogen and Char production	
Fertilizer production	
Evaluation of char effect on plants	
FUTURE PLANS.....	11
SUMMARY AND CONCLUSIONS.....	11
REFERENCES.....	12

INTRODUCTION AND OBJECTIVES

The increasing anthropogenic CO₂ emissions and possible global warming have challenged the United States and other countries to find new and better ways to meet the world's increasing need for energy while, at the same time, reducing greenhouse gas emissions. The improved technology for integrated hydrogen production/CO₂ capture that we plan to develop through this R&D effort could significantly support President Bush's Global Climate Change Initiative (GCCCI) that commits America to an aggressive strategy to reduce greenhouse gas intensity by 18 percent over the next 10 years. Our new technology concept integrates two significant and complementary hydrogen production and CO₂-sequestration approaches that have now been developed at Oak Ridge National Laboratory (ORNL) and Clark Atlanta University.

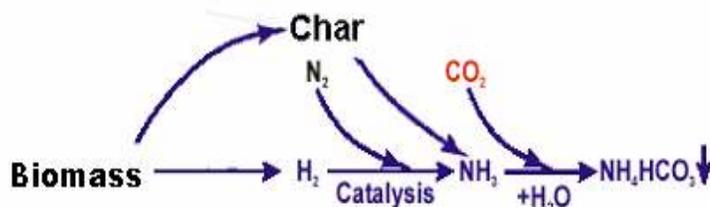


Figure 1 Schematic View of the process from Biomass to Fertilizer

Figure 1 illustrates the schematic view of the process of converting biomass into hydrogen and char. Hydrogen can be efficiently used for stationary power and mobile applications, or it can be synthesized into Ammonia, while char can be used for making time-release fertilizers (NH₄HCO₃) by absorption of CO₂ and other acid gases from exhaust flows. Fertilizers are then used for the growth of biomass

The objective of the proposed study is to determine the feasibility of using the char from a coal and/or biomass pyrolysis-reforming process and CO₂ emissions at a smokestack

to form a solid NH_4HCO_3 -char product that may subsequently be used as a fertilizer. Part of the hydrogen from the pyrolysis-reforming process may be converted to ammonia that is used to solidify the CO_2 as NH_4HCO_3 in the char. The balance of the hydrogen may be purified and sold at market prices or used as a feedstock.

This project plans to conduct bench scale experiments and pilot scale tests. The Combustion and Emission Lab at Clark Atlanta University has prepared to conduct the bench scale experiments. The facility used for pilot scale tests has built in Athens, GA.

In This period, the effect of char without NH_4HCO_3 on plants are evaluated. The evaluation of the fertilizer, NH_4HCO_3 Char product, will be conducted later

EXPERIMENTAL FACILITIES

Our integrated process consists of two stages: 1) pyrolysis of biomass to generate pyrolysis gas/char, and 2) catalytic steam reforming of pyrolysis gas. Figure 2 shows the schematic flow diagram of the developed process. The flow procedure of the process is as follows: Feeder accepts biomass; the pyrolysis unit pyrolyzes the biomass into pyrolysis gas and char at around 500°C ; char is leaked out at this stage, while pyrolysis gas flows into baghouse to filter out solid components accompanied with pyrolysis gas; before the gas is introduced into catalytic reformer, the pyrolysis gas is heated up to 680°C ; in the reformer at 850°C , most of pyrolysis gas is finally converted into hydrogen, carbon dioxide and water; after condensed and cooled down the water vapor, the mixtures of hydrogen and carbon dioxide, along with the nitrogen and other gases at normal temperature are produced. Hydrogen can be purified from the mixed gases. In our experiments, hydrogen is burned at the exit.

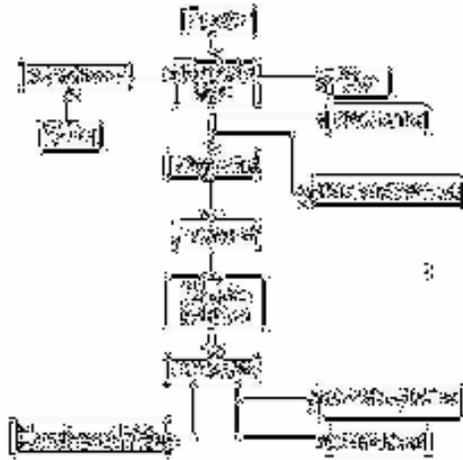


Figure 2 Schematic Flow Diagram of Char and Hydrogen Production

A photo of the pyrolysis unit of the pilot scale plant is shown in Figure 3. Char is led out from bottom of this unit.



Figure 3 Pyrolysis Unit with Biomass feedstack system

The next step after char produced is to make fertilizer. Figure 4 is the Schematic diagram of the bench scale experiments for $\text{NH}_3\text{-CO}_2$ solidification. Before the NH_3 and CO_2 Introduce into the reactor, the char (activated carbon) needs to be mixed with water at various ratio and filled into the reactor. Then, the reactants (NH_3 and CO_2) flow into the reactor to

form a solid NH_4HCO_3 -char product that may subsequently be used as a fertilizer. The flow rates of each gases are controlled by MKS flow controllers. The remaining Ammonia is absorbed in water bath Carbon Dioxide can be detected by Agilent Micro GC.

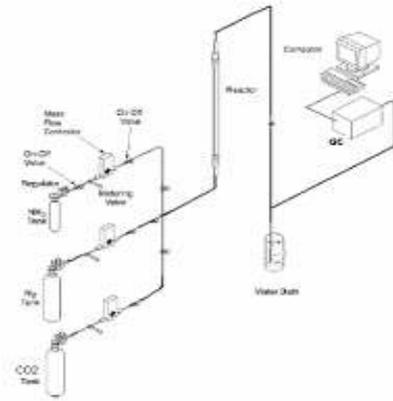


Figure 4 Schematic of Bench Scale Test of NH_3 - CO_2 solidification

Figure 5 shows the fertilizer reactor for the bench scale experiments. The 1/3 reactor is filled with wet char (20g). After reaction, 3-7 gram of NH_4HCO_3 can be formed.



Figure 5 Photo of Bench Scale Test

RESULTS AND DISCUSSION

The Char and Hydrogen production experiments have been done. Figure 6 illustrates the dry N₂-free basis gas composition during a 24-hours operation. It is the final output gas that excludes nitrogen and water. During the 24-hours continuous operation of experiment, 48% (at dry N₂-free basis) of hydrogen is obtained from the integration system. Other major components are 35% carbon dioxide, 9% methane and 8% carbon monoxide. Using peanut shells as feedstock, the overall yield from this system is up to 6wt% hydrogen and 32wt% charcoal/activated carbon.

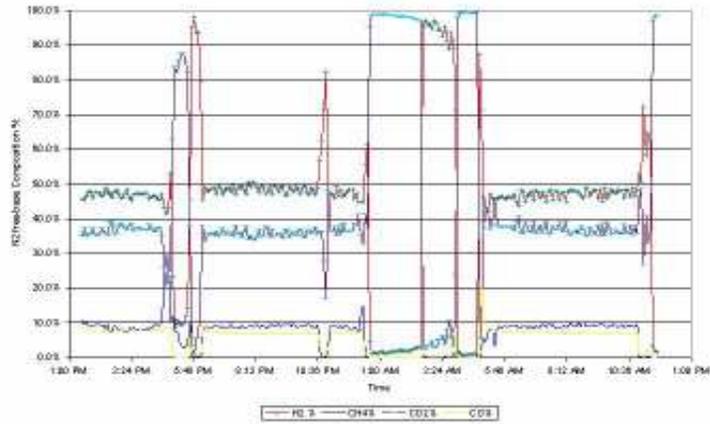


Figure 6 Dry N₂-free basis gas compositions via Time

The pyrolysis unit has produced char samples, which planned to use as the sequestration material. Figure 7 is the photo of sample char material.



Figure 7 Char material produced by the Pyrolyzer

Figure 8 is the result of investigation of the leaching examination of different chars, which are produced with different exit temperatures, from 400°C-900°C. This figure shows that the 400°C char has the potential of long term slow release of nutrients, hinting good candidate for a time-release fertilizer.

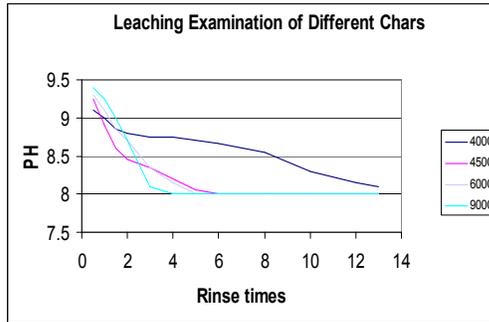


Figure 8 leaching examination of different chars.

Since the char around exit temperature 400°C is good to keep fertilizer time-release. We tested the fertilizer absorption of the char around this temperature (380°C- 420°C). Figure 9 shows that the 380°C-420°C chars have similar absorbability and 400°C char is little better.

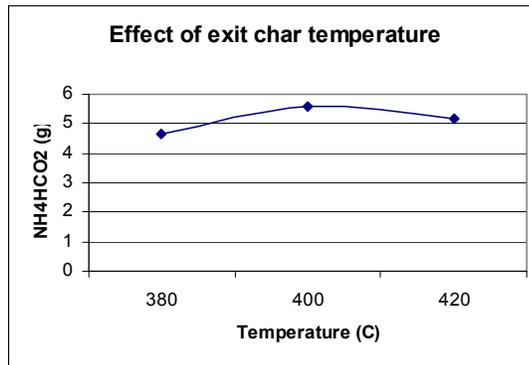


Figure 9 Effect of exit char temperature

The effect of char without NH₄HCO₃ on plants are evaluated in this period. The evaluation of the fertilizer, NH₄HCO₃ Char product, will be conducted later.

Figure 10 and figure 11 are the simple trials to explore the effect of three different chars on the plants. The two chars that applied in these experiments as fertilizer were

produces from peanut shell through two different processes. One char was made from our integrated hydrogen production process, another was from the traditional slow burning heap in a barrel, with limited oxygen. One group of plants that did not apply any char was used to compare with other two groups.



(a) No char applied



(b) Char made from slow burning process



(c) Char made from integrated hydrogen production process

Figure 10 Comparison of con plants with different chars applied as fertilizer

Corn plans were used as samples in figure 10. Figure 10 (a), (b) and (c) are photos of the corn plants, which applied no char, char with traditional slow burning process and our integrated process, respectively. All the seed were put down at the same time and three

groups of corn plants grew at the same conditions, except the char application. In the photos, the yellow sticks in the back are just over four feet, so that the no char group (fig.10 (a)) is approximately 2 feet, the char group (fig.10 (b)) made with a slow burning in the barrels at low temperature is approximately 3 feet and the char group (fig.10 (c)) made from integrated hydrogen production process is almost 4 feet.



(a) No char applied



(b) Char made from slow burning process



(c) Char made from integrated hydrogen production process

Figure 11 Comparison of vegetable plants with different chars applied as fertilizer

Vegetable plants were used as samples in figure 11. Figure 11 (a), (b) and (c) are photos of the vegetable plants, which applied no char, char with traditional slow burning process and our integrated process, respectively. All the seed were put down at the same time

and three vegetable plants grew at the same conditions, except the char application. In the photos, the plant with no char applied (fig.11 (a)) is approximately 12 inches, the plant with char (fig.11 (b)) made with a slow burning in the barrels at low temperature is approximately 20 inches and the plant with char (fig.11 (c)) made from integrated hydrogen production process is almost 28 inches.

FUTURE PLANS

In the past year, we have finished the char and hydrogen production experiments, produced char samples, built the setup of bench scale experiments, and initiated the characteristic analysis of char products. The future works include the following tasks.

1. Testing, Analysis and characterization of the char and gaseous products
2. Process optimization
3. $\text{NH}_3\text{-CO}_2$ solidification process
4. Further tests to evaluate fertilizer usage

CONCLUSIONS

1. The pilot scale hydrogen and char production tests have completed.
2. The bench scale equipment is prepared and ready for more lab analysis.
3. The pilot scale facilities are installed and finished char and hydrogen production tests
4. Primary investigation to char characteristics has been conducted.
5. Evaluated the effect of char without NH_4HCO_3 on corn and vegetable.

REFERENCES

1. Lee, J.W.; Li, R. "A Novel Strategy for CO₂ Sequestration and Clean Air Protection", Proceedings of Fire National Conference on Carbon Sequestration, Washington,DC, May14-17,2001.http://www.netl.doe.gov/publication/proceedings/01/carbon_seq/p12.pdf
2. Lee, J.W.; Li, R. "Method for Reducing CO₂, CO, NO_x, and SO_x Emissions", 1998 ORNL Invention Disclosure, ERID 0631; 2002 U.S. Patent No. US 6,447,437 B1.
3. Lee, J.W.; Li, R (2002). "Integration of Coal-Fire Energy Systems with CO₂ Sequestration through NH₄HCO₃ Production." Energy Convers. Manage, vol. 44, no.9, pg.1451-1464, June 2003.
4. Yelverton, F "The use of activated carbon to inactive agriculture chemical spills", North Carolina Cooperative Extension Service, March,1996.
<http://www.bae.ncsu.edu/bae/programs/extension/publicat/wqwm/ag442.html>
5. Li, E. Hagaman, C. Tsouris, and J.W. Lee (2002). "Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase," Energy & Fuels, 2003, 17(1), 69-74.
6. Miller, D.W., and W.P. Miller, Land application of wastes. P. G217-G241. In M.E. Sumner (ed.) Handbook of Soil Science. CRC Press, Boca Raton, FL.
7. Miller, D.W., and W.P. Miller, S. Dudka, and M.E. Sumner. 2000, Characterization of Industrial By-Products. Soil Sci. Soc. Am., Madison WI.
8. Oren, R; Ellsworth, D.; Johnsen, K, et.al. (2001) "Soil fertility limits carbon sequestration by forest ecosystems in a CO₂-enriched atmosphere" Nature 411, 469-472 (24 May, 2001), Letters to Nature.