

An Integrated Hydrogen Production-CO2 Capture Process from Fossil Fuel

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ABSTRACT

The new technology concept integrates two significant complementary hydrogen production and CO₂-sequestration approaches that have been developed at Oak Ridge National Laboratory (ORNL) and Clark Atlanta University. The process can convert biomass into hydrogen and char. Hydrogen can be efficiently used for stationary power and mobile applications, or it can be synthesized into Ammonia which can be used for CO₂-sequestration, 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 back to fields.

This project includes bench scale experiments and pilot scale tests. The Combustion and Emission Lab at Clark Atlanta University has conducted the bench scale experiments. The facility used for pilot scale tests was built in Athens, GA.

The overall yield from this process is 7wt% hydrogen and 32wt% charcoal/activated carbon of feedstock (peanut shell). The value of co-product activated carbon is about \$1.1/GJ and this coproduct reduced the selling price of hydrogen. And the selling price of hydrogen is estimated to be \$6.95/GJ.

The green house experimental results show that the samples added carbon-fertilizers have effectively growth increase of three different types of plants and improvement ability of keeping fertilizer in soil to avoid the fertilizer leaching with water.

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INTRODUCTION AND OBJECTIVES

The increasing anthropogenic CO₂ emissions and possible global warning 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 (GCCI) 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.

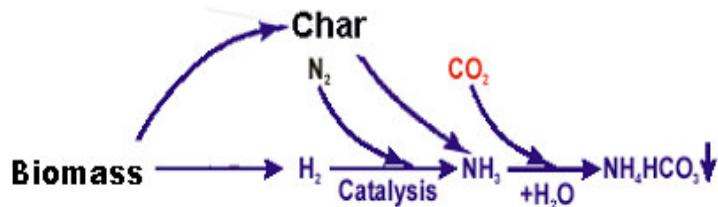


Figure 1 Schematic View of the process from Biomass to Fertilizer

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 produce hydrogen and 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 NH₄HCO₃-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 CO₂ as NH₄HCO₃ in the char. The balance of the hydrogen may be purified and sold at market prices or used as a feedstock. In this research, the effect of char time-releasing fertilizer on plants is evaluated. The economic analysis is performed.

This project has been conducted bench scale experiments and pilot scale tests. The Combustion and Emission Lab at Clark Atlanta University has conducted the bench scale experiments. The facility used for pilot scale tests was built in Athens, GA.

EXPERIMENTAL SECTION

Part A Hydrogen and char production

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 was burned at the exit.

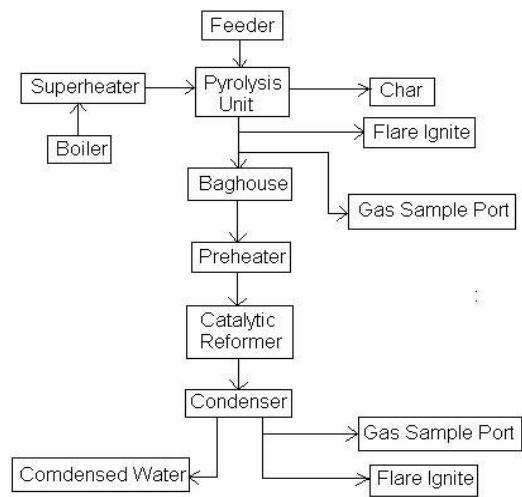


Figure 2 Schematic flow diagram of the biomass pyrolysis-reformer process.

The Photo of pilot scale hydrogen production plant from biomass via integrated pyrolysis and fluidized catalytic reforming is shown in figure 3.



Figure 3 Photo of pilot scale hydrogen production plant from biomass

The major components of the pilot scale plant comprise feeder, superheater, pyrolysis unit (Auger, figure 4), baghouse (filter), pre-heater, reformer, cooler, and condenser. The feeder takes the feedstock (pelletized peanut shell) at a rate of 25-35 kg/hour. The superheater supplies water steam to the pyrolysis unit with a rate of 15-25 kg/hour. The temperature and pressure inside the pyrolysis unit should be maintained at around 500°C and 10 psi, respectively. In the pyrolysis unit, the biomass is pyrolyzed into charcoal and pyrolysis gas. The baghouse acts as a filter, blocking the solid particles and allowing the pyrolysis gas through into the next process. The pre-heater heats up the pyrolysis gas from 500°C to 680°C to make the gas ready for reforming process without significant temperature fluctuation.



Figure 4 Pyrolysis Unit with Biomass feedstack system

The reformer is a vessel loaded catalyst at its bottom. At the beginning of the operation, pressure nitrogen should fill into the system before the reformer fluidizes the catalyst and keeps a proper pressure inside the reformer. The reforming temperature is about 850°C and the pressure inside the reformer should be around 7psi. When the pyrolysis gas

flows through the catalyst and form the fluidized bed, the pyrolysis gas is reformed into hydrogen and carbon dioxide. The gas flowing out of the reformer is cooled down to room temperature and the steam is condensed into water by the cooler and the condenser.



Figure 5 Fluidized Reformer and Pre-heater Unit

Besides the above components, an OPTO 22 SNAP system is equipped to control the operations of the valves and switches, and to monitor the temperature, pressure, and flow rate of components. Two sampling lines are inserted at the ports after the baghouse and after the cooler to analyze the gas compositions of the pyrolysis gas and the exit gases from reformer. An Agilent Micro Gas Chromography system (micro-GC) is used to analyze the gases. The display model of hydrogen and char production plant is shown in figure 6.

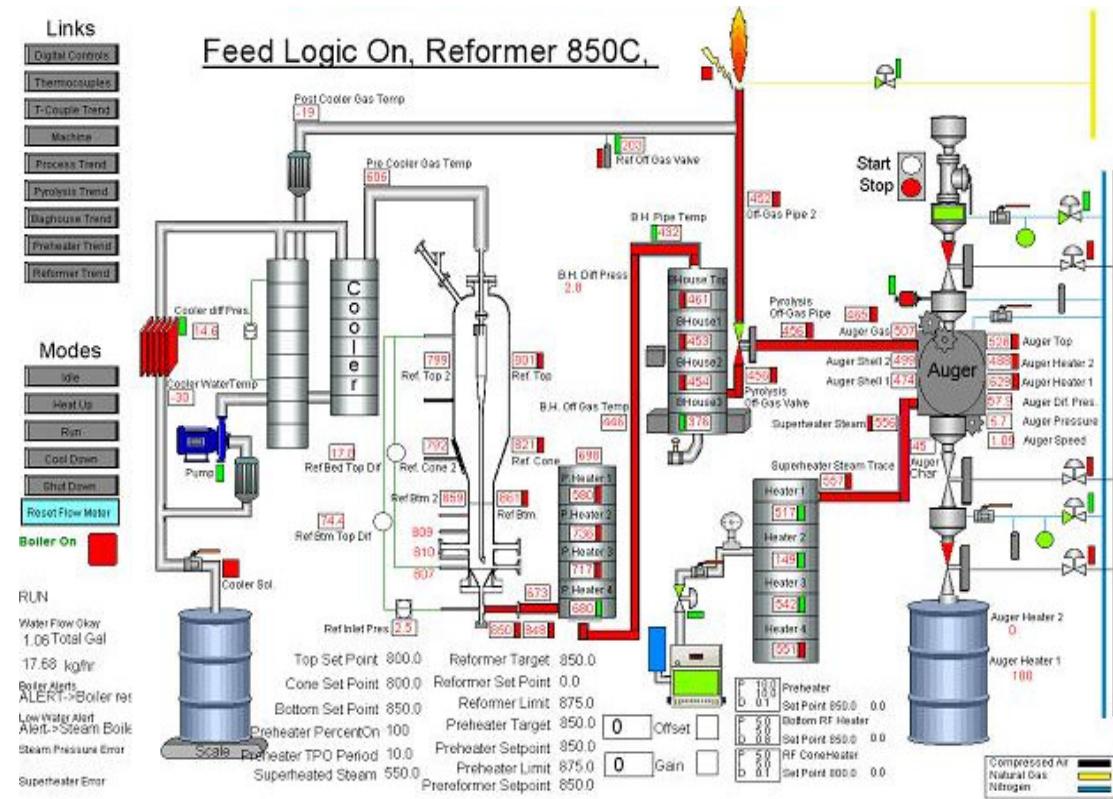


Figure 6 Display model of hydrogen and char production plant

After a period of operation, the catalyst needs to be reduced. We can introduce hydrogen to reduce the catalyst. Figure 7 is a sample process to reduce catalyst. The reduce process takes about 3 hours.

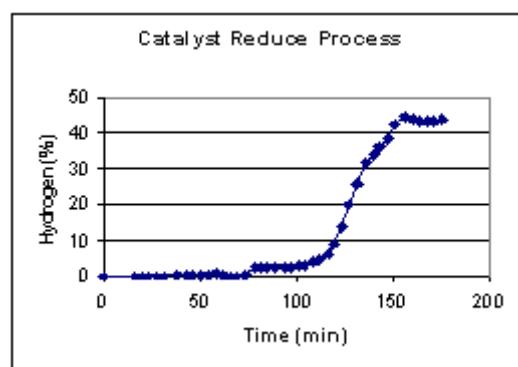


Figure 7 The catalytic process of the pilot scale fluidized catalytic reformer.

Part B CO₂ capture for fertilizer Testing

The next step after char produced is to make fertilizer. Figure 8 is the Schematic diagram of the bench scale experiments for NH₃-CO₂ solidification. Before the NH₃ and CO₂.

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 (NH₃ and CO₂) flow into the reactor to form a solid NH₄HCO₃-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.

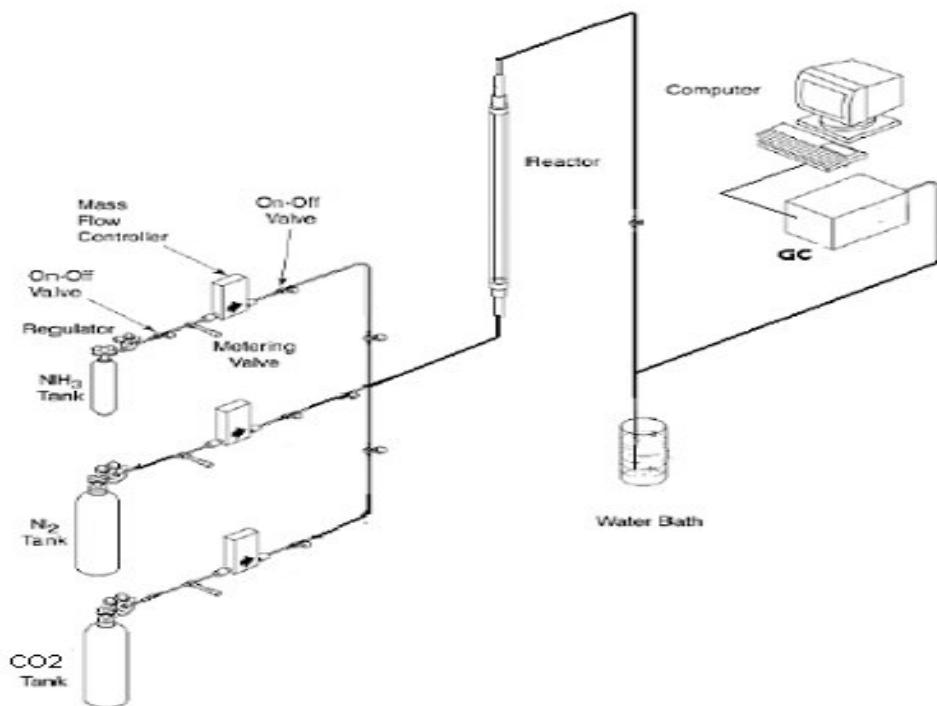


Figure 8. Schematic of Bench Scale Test of NH₃-CO₂ solidification

Figure 9 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 produced.



Figure 9 Photo of Bench Scale Test

To produce char-fertilizer at pilot scale, a char-fertilizer production reactor was built. Figure 10 is the photo of Char-fertilizer reactor.



Figure 10 Photo of the char-fertilizer reactor

RESULTS AND DISCUSSION

Part A Hydrogen production and tech-economic analysis

The pelletized peanut shell is used in our experiments as biomass feedstock. Its major compositions are listed in the table 1.

Table 1 Typical analysis of peanut shell feedstock

Compounds	Components (%)
Lignin	34.8
Glucan	21.1
Extractives	14.2
Protein	11.1
Xylan	7.9
Ash	3.4
Arabinan	0.7
Galactan	0.2
Mannan	0.1
Others (e.g., free carbonhydrates)	0.5

A 24-hours operation has been performed for this plant. Figure 11 shows the temperature and pressure trend graphs at different locations inside the catalytic reformer and inside the preheater, during the start up and around catalyst fluidization period. When forming the fluidized bed, the temperatures at different locations approach uniform from the bottom to the top of the reformer. At the normal operation, the temperature inside the reformer stays around 800°C - 850°C.

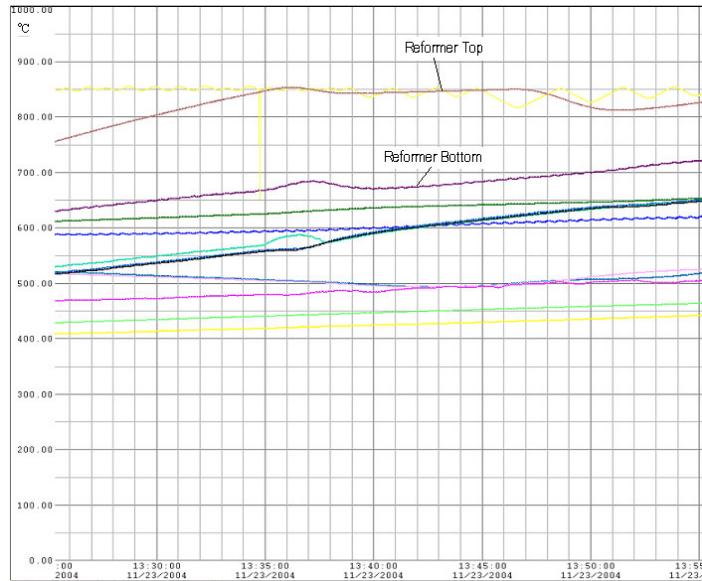


Figure 11. Reformer temperature trend

The outcome of prolysis process is shown in the table 2. It typically consists of 32wt% activated carbon, 36wt% prolysis gas and water as remaining.

Table 2 Typical product composition/yields

Pyrolyzer (Yields)	%
Pyrolysis Gases	36
Char	32
Water	32

Figure 12 illustrates the dry N₂-free basis gas composition during a 24-hours operation. It is the final output gas that excludes nitrogen and water. The nitrogen is input from outside to form the reforming fluidized bed and kept inside pressure. Excessive steam (10:1) is employed to reform the pyrolysis gas. During the 24-hours continuous operation of experiment, about 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.

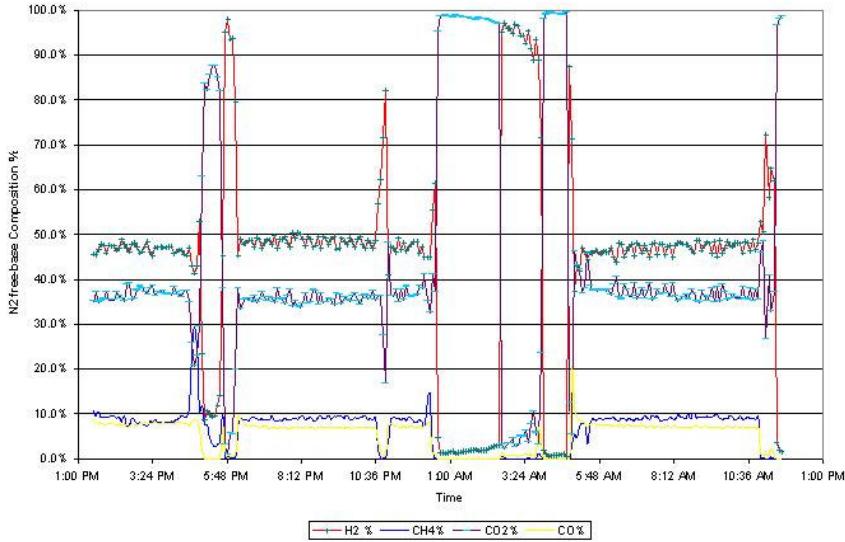


Figure 12 Dry N₂-free basis gas compositions via Time

Our initial work focuses on integrating the process of pyrolysis and reforming, and increasing production rate of hydrogen and charcoal. This integrated hydrogen and char production process through pyrolysis of biomass and reforming of the pyrolysis is based on hydrogen production process from biomass with the bench scale experiment via fast pyrolysis and reforming, investigated by National Renewable Energy Lab (NREL). This pilot scale plant is built for the process and a hydrogen production rate of 50 kg/day with continuous stable operation of more than 24 hours has been successfully demonstrated.

During the 24-hours continuous operation of experiment, 48% (at dry N₂-free basis) of hydrogen is obtained from the integration system. Meanwhile, the exit gas still includes 9% methane. After adjusting the reforming condition (increasing steam-to-carbon molar ratios etc.) and reducing catalyst, most of this 9% methane could be transferred into hydrogen. Using peanut shells as feedstock, the overall yield from this system is up to 6wt% hydrogen and 32wt% charcoal/activated carbon.

In this study, an assessment of the technical and economic potential of producing hydrogen from biomass is made. The resource base is assessed to determine process scale potential from information on feedstock costs and availability. Capital costs were scaled from Mann using 0.84 exponents. This exponent was derived from the three cases presented in the report. Fixed operating costs and working capital were also based on the report. Variable operating costs were determined from the material balance.

For a sized facility of daily hydrogen production rate of 50 tons hydrogen, the total capital investment is \$24 million. The feedstock cost \$16.5/T and operating cost is \$5.9/GJ. The overall yield from this process is 7wt% hydrogen and 32wt% charcoal/activated carbon of feedstock (peanut shell). The value of co-product activated carbon is \$1.1/GJ and this coproduct reduced the selling price of hydrogen. So the selling price of hydrogen is estimated to be \$6.95/GJ.

Part B Char evaluation

The pyrolysis unit has produced char samples, which planed to use as the sequestration material. Figure 13 is the photo of sample char material. Figure 14 illustrates the formation of Ammonium Bicarbonate (NH_4HCO_3) Char Production.



Figure 13 Char material produced by the Pyrolyzer

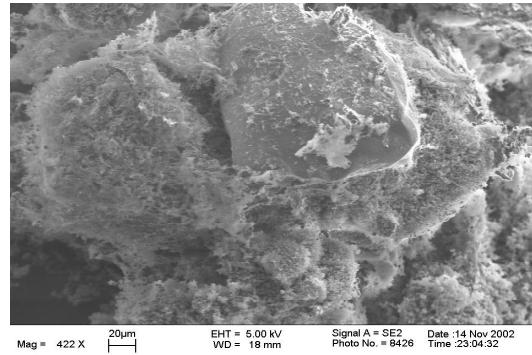


Figure 14 Photo of formation of Ammonium Bicarbonate

Figure 15 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.

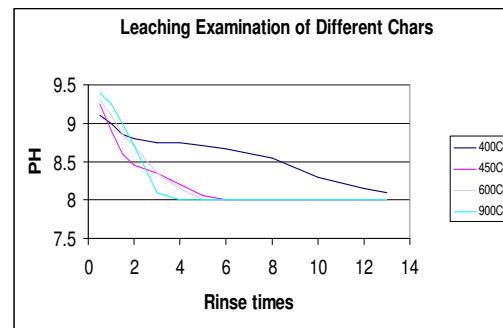


Figure 15. Leaching examination of different chars.

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 15 shows that the 380°C-420°C chars have similar absorbability and 400°C char is little better.

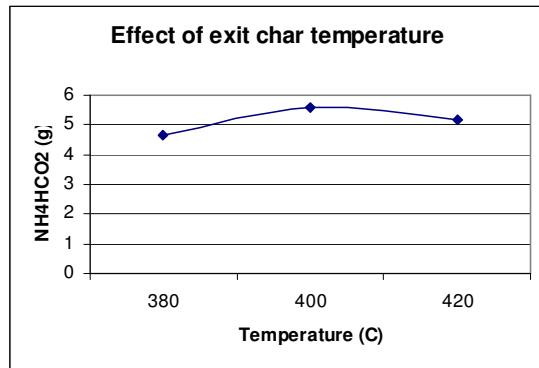


Figure 16 Effect of exit char temperature

The effect of char without and with fertilizers on plants is evaluated .

Part C Evaluation of char effect on plants

Figure 17 and figure 18 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 produced 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 17 Comparison of con plants with different chars applied as fertilizer

Corn plants were used as samples in figure 17. Figure 17 (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.17 (a)) is approximately 2 feet, the char group (fig.17 (b)) made with a slow burning in the barrels at low temperature is approximately 3 feet and the char group (fig.17 (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 18 Comparison of vegetable plants with different chars applied as fertilizer

Vegetable plants were used as samples in figure 18. Figure 18 (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.18 (a)) is approximately 12 inches, the plant with char (fig.18 (b)) made with a slow burning in the barrels at low temperature is approximately 20 inches and the plant with char (fig.18 (c)) made from integrated hydrogen production process is almost 28 inches.

These comparison experiments hints that the char with traditional slow burning process can help the growth of plant comparing with no char applied, while the char with our integrated process is much more effective the growth of plants.

Part D Evaluation of char time-releasing fertilizes effect on plants

1. Materials:

In this experiment, we chose three different plants (radish, flower and grass) to investigate the effect of the char-fertilizer on the plants growing.

1.1 Seeds:

Radish seeds (#1353) and Marigold (#1083) were obtained from Ferry-Morse Seed Co.

Dense Shade lawn seed mixture was obtained from Pennington seed Co.

1.2 Fertilizer:

Vigaro Blood meal (12-0-0) was obtained from Division of United Industries Cooperation.

1.3 Soil:

Organic Compost (0.05-0.05-0.05) was obtained from Smith Garden Products.

And regular soil was obtained from local field.

1.4 Pot

The 8" pots were obtained from Home Depot.

1.5 Carbon

The char produced from our pilot process was powdered as the fertilizer absorbents.

2. Procedure

2.1 Preparation of soil

Blank soil: The blank soil was prepared by mixing 4 cups of the organic compost and 8 cups of regular soil with volume ratio of 1.0 (organic compost): 2.0 (regular soil).

Soil + Fertilizer: 5g fertilizers were mixed to blank soil.

Soil + Carbon with absorbed fertilizer: 5g fertilizers and various amount of carbon powder were mixed homogenously to blank soil. The detail information was listed in table3.

Table 3. List of the sample composition

	Organic soil (cup)	Regular soil (cup)	Fertilizer (g)	Carbon (g)
Blank soil	4	8	0	0
Soil + Fertilizer	4	8	5	
Soil + Carbon with absorbed fertilizer	4	8	5	10
Soil + Carbon with absorbed fertilizer	4	8	5	20
Soil + Carbon with absorbed fertilizer	4	8	5	40
Soil with carbon which absorbed fertilizer	4	8	5	100

2.2 Planting

2.2.1 Affection of various soils for the growth of various plants

All the planting were performed batchwise in 8" pot. A total of 27 pots were divided into three groups (radish, flower and grass) evenly, with each group of 9 pots. Each group includes three pots of blank soil, three pots treated with 5g of fertilizer, and the other three pots treated with the mixture of 5g fertilizer and 10g carbon. For the planting procedure, about 1" soil was removed from the top, the seeds were placed on the surface of soil, then the removed soil was put back to pot and cover the seeds. About 300ml water was sprayed to each pot initially. And watering the samples was applied for every 3 days afterward with 100ml water each time. All the plants grew up at room temperature under artificial lights. Variable transformer was set at 60 Volts.

2.2.2 Affection of soils containing different carbon quantity for the growth of plants

All the plantings were performed batchwise in 8" pot. A total of 15 pots were divided into two groups (radish and grass), with 6 pots for radish group, 9 pots for grass

group. Grass group includes three pots with 20g of carbon that absorbed 5g of fertilizer, three pots treated with 40g of carbon which absorbed 5g of fertilizer, and the other three pots treated with the mixture of 5g fertilizer and 100g carbon. For radish groups, three pots treated with 40g of carbon that absorbed 5g of fertilizer, the other three pots treated with 100g of carbon that absorbed 5g of fertilizer. The plantings procedure follows the section 2.2.1.

2.3 Analysis

After 10 days of growth, the clipped grass blades were dried and ground. At the mean time, soil samples were collected from the surface of each pot, dried and ground. The amount of total nitrogen was measured by LECO CHN 600 Element Analyzer. And the TruSpec CHN Macro is used to determine the carbon, hydrogen and nitrogen content of a variety of materials.

There are three phases during an analysis cycle: Purge, combust, and analyze. In the purge phase, the encapsulated sample is placed in the loading head, sealed, and purged of any atmospheric gases that have entered during sample loading. The ballast volume (zero volume at this point) and gas lines are also purged.

During the combust phase, the sample is dropped into a hot furnace (950°C) and flushed with oxygen for very rapid and complete combustion. The products of combustion are passed through a secondary furnace (afterburner, 850 °C) for further oxidation and particulate removal. The combustion gases are then collected in a collection vessel known as the ballast.

In the analyze phase, oxygen flows into the furnace to combust the sample. The gases from combustion are collected in the ballast. The homogeneous combustion gases

in the ballast are then purged through the CO₂ and H₂O infrared detectors and the 3cc aliquot loop. Once the gases have equilibrated, carbon is measured as carbon dioxide by the CO₂ detector and hydrogen is measured as water vapor in the H₂O detector. The gases in the aliquot loop are transferred to the helium carrier flow, swept through hot copper to remove oxygen and change NO_x to N₂ and then flow through Lecosorb and Anhydrene to remove carbon dioxide and water, respectively. A thermal conductivity cell is used to determine the nitrogen content. The final result is displayed as weight percentage as determined by the operator.

3 Results and discussion

3.1 The Total Nitrogen contents in the various soil and plant shoots were listed.

Table 4 the amount of total nitrogen in various soil and plant shoots

SAMPLES	Amount of Fertilizer (g)	Amount of Carbon (g)	Total Nitrogen (wt%) Sampling: After 15 days	Total Nitrogen (wt%) Sampling: After 25 days	
SBR			0.3073	0.2327	Soil,blank, radish
SFR	5		0.5619	0.4654	Soil, fertilizer,radish
SFCR	5	10	1.3303	0.9025	Soil,fertilizer,carbon,radish
SBF			0.3422	NA	Soil,blank,flower
SFF	5		0.3157	NA	Soil, fertilizer,flower
SFCF	5	10	0.7556	NA	Soil,fertilizer,carbon,flower
SBG			0.3586	0.2715	Soil, blank,grass
SFG	5		0.3121	0.2878	Soil,fertilizer,grass
SFCG	5	10	0.6396	0.5683	Soil, fertilizer,carbon,grass
ORGF			11.503	NA	Original fertilizer
PBG			5.0123	4.8538	Plant, blank, grass
PFG	5		6.0542	6.2084	Plant, fertilizer,grass
PFCG	5	10	6.3932	6.3892	Plant,fertilizer,carbon grass
PBR			4.2320	4.3047	Plant,blank,radish
PFR	5		5.4711	5.2546	Plant,fertilizer,radish
PFCR	5	10	6.2050	6.3803	Plant,fertilizer,carbon,radish

- S:soil; P: plant; B: blank; F: fertilizer; C: carbon; R: radish; F: flower; G: grass

From Table 4, the soils that treated with fertilizer or the mixture of fertilizer and carbon show clear distinctions in the amount of total nitrogen, twice amount of the total nitrogen was kept in soil with the mixture of fertilizer and carbon than those with fertilizer but without carbon. The results show that the samples added carbon have significant improvement ability of keeping fertilizer in soil to avoid the fertilizer leaching with water.

After 10 days, the soils and plants were collected, following the same procedure as before. From Table5, we know, after 10days, the amount of total nitrogen in soil decreased because the parts of fertilizer lose with watering. However, the amount of total nitrogen in plant was still keeping almost the same level.

At the same day, soil samples were also collected from the areas around root, and separated the plant into root and shoot. Following the procedure same as before. The results are listed in Table 5.

Table 5. The amount of total nitrogen in various soils around plant root

Samples	Amount of total nitrogen (wt%)	
SBRR	0.2117	Soil,blank, radish root
SFRR	0.4102	Soil, fertilizer,radish root
SFCRR	0.8398	Soil,fertilizer,carbon,radish root
SBGR	0.2513	Soil, blank,grass root
SFGR	0.2811	Soil,fertilizer,grass root
SFCGR	0.4148	Soil, fertilizer,carbon,grass root

From the data of Table 4 and Table 5, it is obviously that the amount of total nitrogen in the soils which from around the plant root are lower than the soil which from the surface.

3.2 The quantities of total nitrogen in various soils containing various amount of carbon were listed in Table 6.

Table 6 The amount of total nitrogen in various soil containing various amount off carbon

Samples	Amount of fertilizer(g)	Amount of cabon(g)	Amount of total nitrogen (wt %)	
SFCG20	5	20	0.6821	Soil, fertilizer,carbon,grass root
SFCG40	5	40	0.7637	
SFCG100	5	100	0.7712	
SFCG20R	5	20	0.5623	
SFCG40R	5	40	0.6321	
SFCG100R	5	100	0.6641	
SFCR40	5	40	0.7591	Soil,fertilizer,carbon,radish root
SFCR100	5	100	0.8104	
SFCR40R	5	40	0.6833	
SFCR100R	5	100	0.7021	
PFCG20	5	20	6.1654	Plant,fertilizer,carbon,grass root
PFCG40	5	40	6.4562	
PFCG100	5	100	6.5129	
PFCG20R	5	20	4.6123	
PFCG40R	5	40	4.5545	
PFCG100R	5	100	4.7673	
PFCR40	5	40	6.0276	Plant,fertilizer,carbon,radish root
PFCR100	5	100	6.3218	
PFCR40R	5	40	3.2473	
PFCR100R	5	100	3.7761	

Table 6 shows that the amount of total nitrogen in the soil samples was increasing with increasing the weight of carbon in the soil (both top and root). However, the increase is level off as the carbon amount increased from 40g to 100g. In addition, the amount of total nitrogen in plant shoot is significant higher than the amount of total nitrogen in root.

CONCLUSIONS

During the 24-hours continuous operation of pilot scale hydrogen and char production plant, using peanut shells as feedstock, 48% (at dry N₂-free basis) of hydrogen is obtained from the integration system. The overall yield from this system is up to 6wt% hydrogen and 32wt% charcoal/activated carbon.

The preliminary techno-economic analysis indicates that this developed integrated process has the potential of producing hydrogen at the cost of about US\$7.2/GJ with an assumed facility of a daily hydrogen production rate of 25 tons.

This primary testing to the char-fertilizer, NH₄HCO₃-Char product shows that the 400°C char has the potential of long-term slow release of nutrients, hinting good candidate for a time-release fertilizer. It also reveals that the 380°C-420°C chars have similar absorbability and 400°C char is little better.

These comparison experiments of the effect of char without and with fertilizers on plants hints that the char with traditional slow burning process can help the growth of plant and protect fertilizer from loss with watering comparing with no char applied, while the integrated process char time releasing fertilizers are much more effective for the growth of different plants.

This pilot scale plant has increased the hydrogen production rate by orders of magnitude compared with the bench scale. Meanwhile, this system also produced a co-product, char, which can be used for making time-release fertilizers (NH₄HCO₃), by absorption of CO₂ (potentially, SO_x and NO_x etc. acid gases) from exhaust flows to remove industrial greenhouse gas emissions, benefiting both agriculture and the

economy. Therefore, this system shows the potential of being cost and environmental competitive with those conventional means of hydrogen production.

The green house experimental results show that the samples added carbon-fertilizers have effectively growth increase of three different types of plants and improvement ability of keeping fertilizer in soil to avoid the fertilizer leaching with water.

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