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Economical CO₂, SO_x, and NO_x capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration

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Abstract

The objective of this project was to investigate and demonstrate production methods at a continuous, bench-scale level and generate sufficient material for an initial evaluation of a potentially profitable method of producing bioenergy and sequestering carbon. The novel process uses agricultural, forestry, and waste biomass to produce hydrogen using pyrolysis and reforming technologies conducted in a 50 kg/h pilot demonstration. The test runs produced a novel, nitrogen-enriched, slow-release, carbon-sequestering fertilizer. Seven kilograms of the material were produced for further plant growth response testing. A pyrolysis temperature profile was discovered that results in a carbon char with an affinity for capturing CO₂ through gas phase reaction with mixed nitrogen-carrying nutrient compounds within the pore structures of the carbon char. A bench-scale project demonstrated a continuous process fluidized-bed agglomerating process. The total amount of CO₂ sequestration was managed by controlling particle discharge rates based on density. The patent-pending process is particularly applicable to fossil-fuel power plants as it also removes SO_x and NO_x, does not require energy-intensive carbon dioxide separation and operates at ambient temperature and pressure. The method of sequestration uses existing farm fertilizer distribution infrastructure to deliver a carbon that is highly resistant to microbiological decomposition. The physical structure of carbon material provides a framework for building an NPK fertilizer inside the pore structure and creating a physical slow-release mechanism of these nutrients. The complete process produces three times as much hydrogen as it consumes making it a net energy producer for the affiliated power plant. See <http://www.eprida.com/hydro>. © 2004 Published by Elsevier Ltd.

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1. Introduction

Increasing anthropogenic CO₂ emissions and possible global warming have challenged the United States and other countries to find new and better ways of meeting the world's growing energy needs while, at the same time, reducing greenhouse-gas (GHG) emissions. The need for a renewable energy with few GHG emissions has led to demonstration work in the production of hydrogen from biomass through steam reforming of pyrolysis gas and pyrolysis liquids. Our research to date has demonstrated the ability to produce hydrogen from biomass under stable conditions [1]. Future large-scale, renewable hydrogen production using non-oxidative technologies will generate coproducts in the form of a solid sequestered carbon. This char and carbon ('C') material represent a form of sequestered C that will not rapidly decompose [2] or return CO₂ into the atmosphere. It was apparent that additional value needed to be added to this material that would justify large-scale handling and usage. In the 1990s, C in the form of CO₂, accumulated at rates ranging from 1.9 to 6.0 PgC/year, increasing CO₂ levels by 0.9–2.8 ppm/year. [3]. The volume of waste and unused biomass economically available in the United States is over 314 Gigatons per year [4]. Sequestering a small percentage could significantly reduce the atmospheric loading of CO₂ while producing a zero-emissions fuel, hydrogen. In order to accomplish this economically, the sequestered C must have a very large and beneficial application such as use as a soil amendment and/or fertilizer.

2. Project description

The approach [5] in our research applies a pyrolysis process that has been developed by Eprida and the National Renewable Energy Laboratory to produce a charcoal-like by-product and synthetic gas (containing mainly H₂ and CO₂) from biomass, which could come from both farm and forestry sources. In this novel system [6], a portion of the hydrogen is used to create ammonia where economical, or ammonia is purchased leaving hydrogen for fuel utilization. The ammonia is then combined with the char and CO₂ at atmospheric pressure and ambient temperature to form a nitrogen-enriched char. The char materials produced in this process contain a significant amount of non-decomposable carbons such as the elementary carbons that can be stored in soil as sequestered C. Furthermore, the carbon in the char is in a partially activated state and is highly absorbent. Thus, when used as a carrier for nitrogen compounds (such as NH₄⁺, urea or ammonium bicarbonate) and other plant nutrients, the char forms a slow-release fertilizer that is ideal for green plant growth. A combined NH₄HCO₃-char fertilizer is probably the best product to maximally enhance sequestration of C into soils while providing slow-release nutrients for plant growth.

Research work has shown [7] that activated char also provides the ability to capture farm chemical runoff. The verification of this product's capability as both a slow-release fertilizer and chemical sponge could lead to its use as an 'Approved Management Practice' under the USDA Conservation Reserve Program, a pollution prevention program that provides payment for specific land-management activities that reduce farm runoff pollution. A flue-gas scrubbing process [8,9] developed recently at Oak Ridge National Laboratory (ORNL) allowed C to be sequestered from industrial GHG emissions. This approach utilizes a chemical process that can directly capture GHG emissions at the smokestacks by converting CO₂, NO_x, and SO_x emissions into valuable fertilizers (mainly NH₄HCO₃, ~98% and (NH₄)₂SO₄ and NH₄NO₃, <2%). These fertilizers can potentially enhance crop growth for

sequestration of CO_2 into soil and subsoil layers, reduce NO_3^- contamination of groundwater, and stimulate photosynthetic fixation of CO_2 from the atmosphere. The utilization of charcoal as a medium for nucleation while scrubbing creates a fertilizer with a high percentage of very stable C. In addition, the inorganic carbon component (HCO_3^-) of the NH_4HCO_3 fertilizer is nondigestible to soil bacteria and thus can potentially be stored in certain soil and subsoil terrains as even more sequestered C. This community-based solution operates as a closed-loop process, integrating C sequestration, pollutant removal, fertilizer production, and restoration of topsoil through the return of carbon and trace minerals. The benefits of producing a value-added sequestering coproduct from coal-fired power plants and other fossil-energy-producing operations, can help bridge the transitions to clean energy systems that are in harmony with the earth's ecosystem [10]. The key step in this technology is an $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$ reaction system to form solid NH_4HCO_3 process that can remove flue-gas CO_2 emissions by ammonia carbonation throughout the porous physical matrix of charcoal. An important benefit of this approach to the power industry is that it does not require compressors or prior separation of the CO_2 . The use of biomass in combination with fossil energy production, can allow agriculture and the agrochemical industry infrastructure to assume a more holistic relationship of mutual support to help each meet Kyoto GHG reduction targets.

The goal of our research was the laboratory and pilot-scale demonstration of a slow-release sequestering fertilizer, with properties that could increase crop yields, soil carbon content, water-holding capacity, nutrient retention, cation exchange capacity and microbial activity while decreasing farm chemical runoff, nutrient leaching, and GHG emissions. The advantages of an adsorbent charcoal provided many of the characteristics we sought. An optimized porous structure with simple standard coatings that could hold a supply of nutrients and slowly release imbedded nutrients continuously to the crops or forest during the growing season was one of our first development goals.

Adding nutrients to soils does not mean that the latter becomes immediately available for plant growth [11]. Soluble nutrients can be leached from the soil; they can bind with clay materials reducing availability, or escape through atmospheric interactions. The first goal was to identify process parameters that would produce a carbon material able to act as a nutrient carrier and resist leaching. It appeared that charcoal addition from as long as 2000 years ago was providing significant soil fertility benefits [12], as noted in the research conducted on Brazilian 'terra preta' soils by Glaser, Lehman, Steiner, and research on addition of charcoal to non-terra preta soils [13]. Fig. 1 shows the plant response from the Brazilian study. The left panel shows the results of adding rice hull char to corn crop research

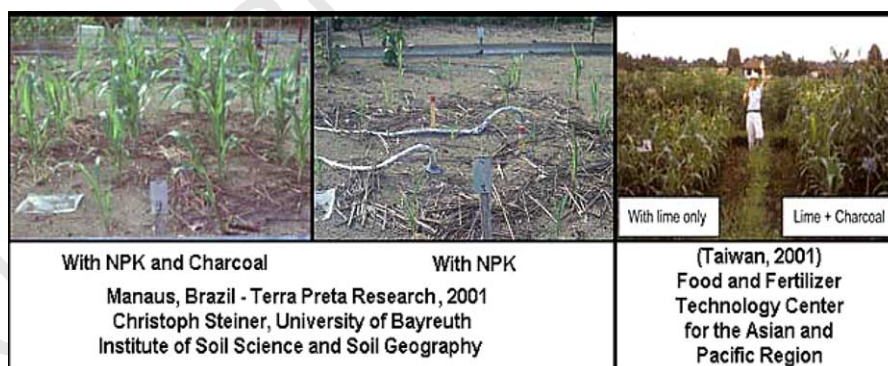


Fig. 1. Images of plant response to charcoal additions as demonstrated in Brazilian and Thailand (Taiwan report) studies.

field studies conducted by the Food and Fertilizer Technology Center for the Asian and Pacific Region in Taiwan [14].

We began our investigation by looking at charcoals made under different process conditions. We had made a number of types of char during a 100-h hydrogen demonstration experiment conducted in the summer of 2002 [15]. The goal during the run was to produce hydrogen with a coproduct.

The coproduct char was highly dependant on processing conditions. The first 10 h of our start-up phase had significant variations in operating conditions. The changes in gas flows, feed rates and heat rates eventually smoothed out to stable run conditions as we adjusted process parameters. However, these changes in process gave us an opportunity to examine the materials that were being made. After the run, we measured the density of each material (Fig. 2) stored in the sealed 55-gal drums. Each barrel had been labeled with a date and time so that we could match it up with the corresponding production data. The physical measurements of samples from each barrel's char showed that three sets of charcoal were produced. Most of the char was a low-density material produced during the long stabilized run conditions for the hydrogen experiment. The high-density material represented only a small portion of the total and, because of multiple variations in process conditions during that time, pinpointing any specific set of parameters proved difficult.

At this point, we decided to see if there were any attributes other than density that made these three materials different. We ground 40 g of each material to 30 mesh, making a small grainy powder and then added 2 g to 50 ml water. In both the high- and medium-density chars, the powders immediately sank to the bottom of the flask. The low-density char floated and had to be stirred vigorously before it sank. The higher-temperature char easily adsorbed water.

We conducted bench-scale experiments to reproduce these materials under precise controls so that we could accurately determine the temperature and conditions that created the materials and the effects on the performance of the material as a nutrient carrier. We produced five different chars, at different temperatures (900, 600, 500, 450 and 400 °C). A metal 560 ml stainless steel can with a press-in top had a 6 mm hole drilled in the lid. A 6.4 mm, 10 cm long stainless tube was tapped in to fit firmly in the hole as an exhaust port. The biomass samples (peanut hull pellets) were weighed and placed in the can and the top sealed. A Thermolyne model 1400 box furnace was preheated to each temperature for 10 min before

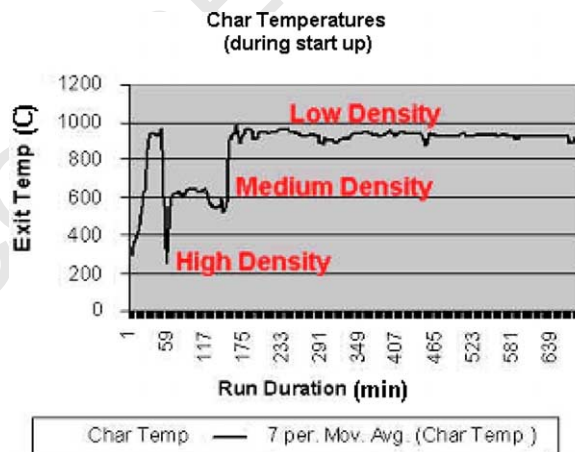


Fig. 2. Densities of char formed at process temperatures.

177 the stainless steel container was inserted. The exhaust tube was fed out through a 75 mm port in the back of
178 the furnace. An external thermocouple inserted into the free space between the can and the wall of the
179 furnace interior operated a separate controller to give precise control of the temperature experienced by
180 each sample. Within a few minutes after placing the container in the furnace, the pyrolysis vapors began to
181 escape. At 10 min intervals, a 1.5 mm thermocouple was inserted through the exhaust tube and a
182 temperature of the material was taken directly. After several experiments, we were able to gauge that until
183 the high volatile gas evolution slowed, the readings would not exceed 350 °C in the material. Therefore,
184 we changed our method and began taking internal sample temperatures after the gas flows had slowed to
185 minimal amounts, generally around 370–380 °C. Once the temperature was at 50 °C, the thermocouple
186 would be left in the sample. In each case, the samples were brought to the target temperature for 1 min.

187 After reaching the target temperature, we removed the container from the furnace and turned it upside
188 down on a smooth surface metal table to cool. We found that the material still evolved some CO₂ and,
189 because of the small tube, no oxygen could get to it until it had cooled to a point where it no longer
190 oxidized. All our samples were produced using this technique. Next the materials were ground and
191 sieved to a particle size less than 30 US mesh and greater than 45 US mesh and 20.0-g samples prepared.
192 We mixed an aqueous solution of 48% NH₄NO₃ (ammonium nitrate). Each sample was soaked for
193 5 min, then poured through cone filter paper and allowed to air dry for 24 h. We then poured rinses of
194 100 ml of tap water (pH 8) through the cone filter. The pH of each resulting rinse was measured showing
195 a decreasing pH commensurate with the leaching rates of each material.

196 In these experiments, there was very little difference until the last one. After three or four rinses, the
197 materials would stabilize at the pH 8 of the rinse material (Fig. 3). The 400 °C char showed very little
198 change and it was only after the ninth rinse that it began to drop a little faster; even after 12 rinses,
199 however, it had still not stabilized. This strong binding and slow release made the 400 °C chars a good
200 candidate for further testing.

201 The material could be considered comparable to those that have been made in a smoldering forest fire.
202 Chars have been found to support microbial communities [16]. The breakdown of plant matter, the
203 adsorption of these nutrients by a layer of char below and a niche for microbes to grow, Pietikainen
204 suggests, are the reason for the success of microbial communities in char in her study. However, char
205 exposed to high temperature, as we have seen above, may adsorb but may not provide the same levels of
206 retention that could offer a superior material for long-term slow release of nutrients.

207 If the hypothesis is that we want to adsorb, store (reduce leaching effects) and provide a safe haven
208 and an environment for microbial communities to flourish, then an examination of the science of char
209 production may help.

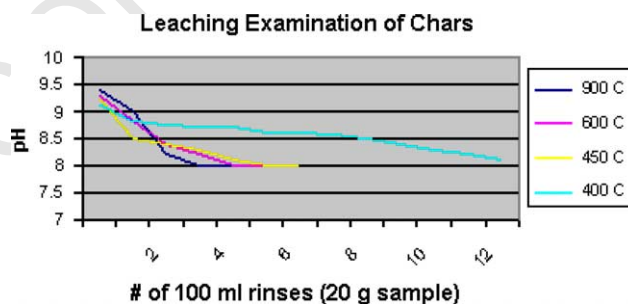


Fig. 3. Leaching examinations.

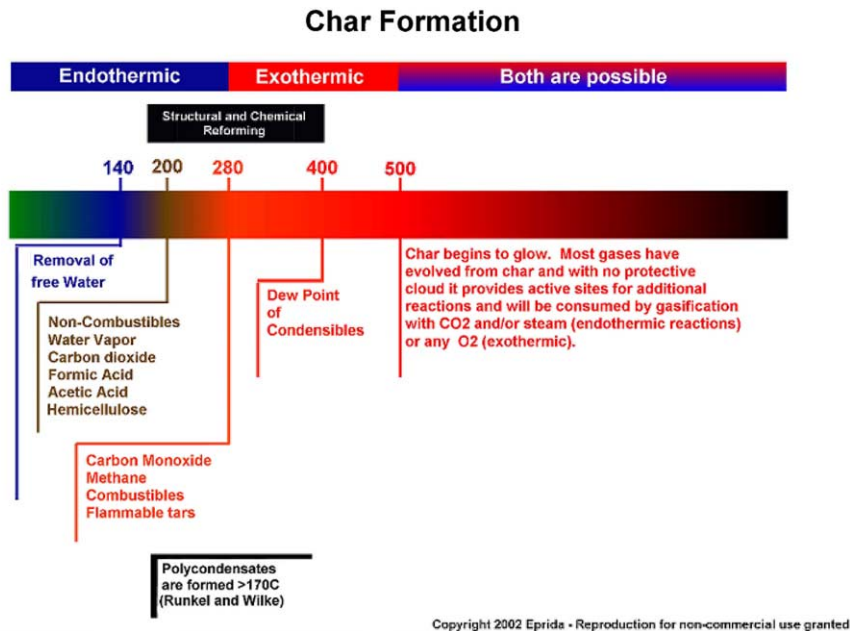


Fig. 4. Illustrative chart of temperature zones of pyrolysis.

An illustrative chart shows properties of char formation, which can vary according to the composition of the originating biomass. In Fig. 4, the material is shown entering a phase from 280 to 500 °C that is exothermic. Once started, it continues without additional heat. If oxygen is present or if the material is left in its exothermic environment it will continue past the structural and chemical reforming zone and become normal char. In certain temperature ranges of pyrolysis, reactive low molecular weight products will further react to form polycondensates [17], which will eventually volatilize and leave the char as the temperature increases. The deposition of condensables in a char bed is well known and generally the issue has been how to keep these materials from building up on downstream process. Our pyrolysis reactor was designed and developed specifically with this in mind. However, intra-particle condensation leads to increased char mass and a modification of the surface structures. The deposition of these materials may increase microbial activity [18].

3. SEM investigation of char and enriched carbon, organic slow-release sequestering (ECOSS) fertilizer

Fig. 5 is a scanning electron microscope image (SEM) of the 400 °C char. This picture is taken at 70×. As can be seen in the bottom right-hand corner and the image below, the physical structure of the cellulose material is apparent. The char particles are a hard carbon that has more strength than the higher-temperature chars, but grinds easily. These particles are hydrophobic in nature and differ from char made at high temperatures.

The next image (Fig. 6) was taken at 350× and provides more detail of the char's surface. The image reflects some of the biomass origin as the physical structure had been broken up by the mechanical



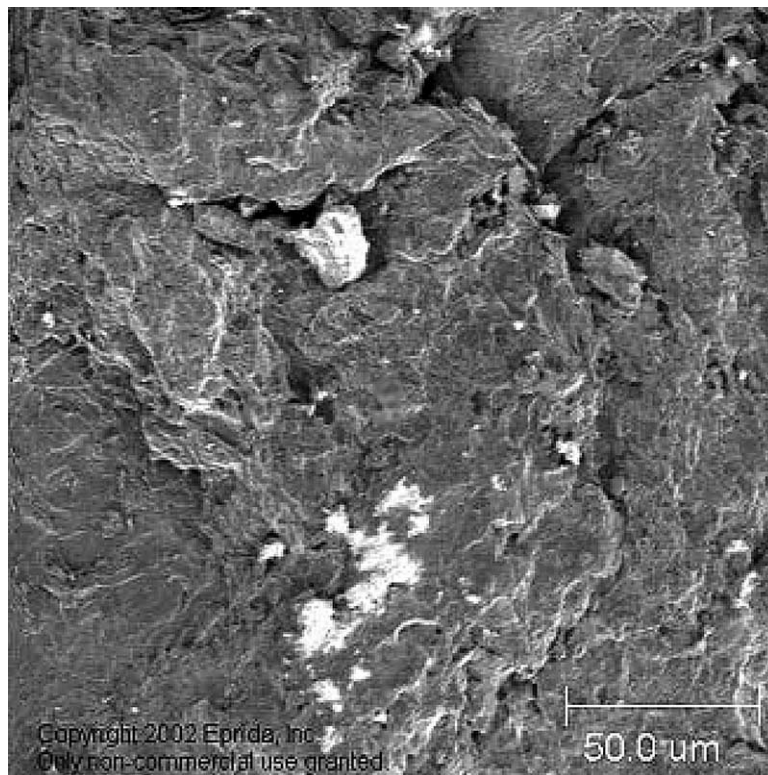
286 Fig. 5. Scanned electron microscope (SEM) image of the 400 °C char with a magnification of 70×.

287 actions of pelletizing. Its surface shows evidence of the cellulose layers. The internal gases that escape
288 from the material during the charring help develop charcoal's natural porosity. However, at this level of
289 magnification, the pore structure is not visible.

290 Fig. 7 is taken at 3270× and clearly shows pore structures. The evolution of this adsorbent material
291 also provides a porous internal structure. Using the parameters established in the bench-scale char
292 production, we selected 400 °C as the target temperature for the char to reach before being discharged
293 from our pyrolysis reactor. The material was fed into the preheated reactor and the gases that evolved
294 were flared. No external heat source was utilized and the dry material rapidly moved into an exothermic
295 reaction. The continuous process system was automatically fed material by a level indicator, and it
296 discharged into a nitrogen purged 55-gal drum upon reaching 400 °C. The resulting char was cooled for
297 24 h then fed through a two-roll crusher and sieved with a mechanized screen through 30 mesh and 45
298 mesh screens. The resulting fraction remaining above the smaller screen was chosen as our starting
299 material (Fig. 8).

300 Bench-scale demonstrations at ORNL recently demonstrated that the removal of flue-gas CO₂ can be
301 achieved via formation of solid NH₄HCO₃ through ammonia carbonation in the gas phase [19]. The
302 results indicated that it is possible to use the NH₃ + H₂O + CO₂ solidifying process in the gas phase to
303 remove GHG emissions from industrial facilities such as coal-fired power plants. A joint ORNL
304 and Eprida, Inc. study of specifically designed char materials produced by Eprida, Inc. from a biomass
305 pyrolysis process, indicated that it might also be possible to use those char particles for sequestration of
306 power plant GHG exhaust. It was assumed that the char could potentially be used as a catalyst
307 (providing more effective nucleation sites) to speed up the formation of solid NH₄HCO₃ particles in
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332 Fig. 6. Scanned electron microscope (SEM) image of the 400 °C char with a magnification of 350 \times .

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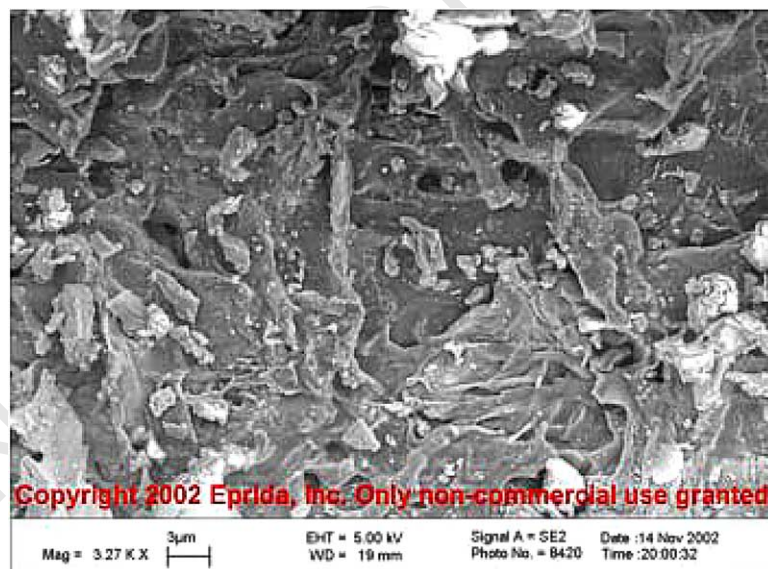


Fig. 7. Scanned electron microscope (SEM) image of the 400 °C char with a magnification of 3270 \times .

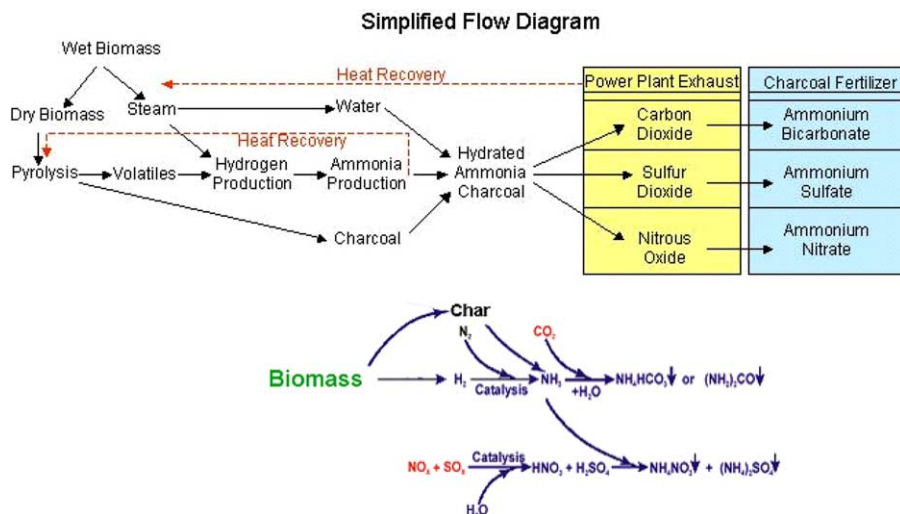


Fig. 8. Simplified flow chart of how biomass releases energy as it captures CO₂ as NH₄HCO₃.

the NH₃–CO₂-solidifying NH₄HCO₃ production process, thus potentially enhancing the efficiency of the NH₃–CO₂-solidifying technology. Furthermore, the integrated process technology could produce a valuable NH₄HCO₃-char product to maximally enhance sequestration of carbon into soils and remove SO_x and NO_x while providing an ideal ECOSS (Enriched Carbon, Organic Slow-release Sequestering) fertilizer and nutrient carrier for plant growth if the production of NH₄HCO₃ could be developed inside the porous carbon media.

The affinity of low-temperature charcoal (< 500 °C) for the adsorption of ammonia has been shown by Asada. This work offered that the formation of acidic functional groups at the lower temperatures, rather than surface area, porosity, or raw material, was the largest contributor to adsorptive capability of low-temperature char for ammonia [20]. The question of whether the NH₄HCO₃ fertilizer could be created in the low-temperature chars' ammonia-saturated, internal pore structures in an environment similar to what might be produced in an industrial environment required an experimental setup. A preliminary design was built. While the process can apply to many configurations, the development of a simple production technique was important at this stage in our research efforts and commercial implementation. In this case, we used a mechanical fluidized bed easily adaptable to any gas stream and injected CO₂ and hydrated ammonia (Fig. 9).

A 250 g charge of 30–45 mesh 400 °C char was fed in at regular intervals varying from 15 to 30 min. A higher rotor speed increased the fluidization and suspended the particles until they became too heavy from the deposition of NH₄HCO₃ to be supported by fluidized gas flows. The longer durations produced significantly larger particles.

The image on the left in Fig. 10 is the initial char. The image in the center is a material produced after 15 min and the one on the right after 30 min.

Carbonized structures from the shell material are visible in the center of the left panel of Fig. 11. The development of the NH₄HCO₃ has clearly coated the char, but the next analysis was to determine if predicted reactions occurred inside the carbon structures. We crushed the ECOSS-15 min material to examine any internal formations.

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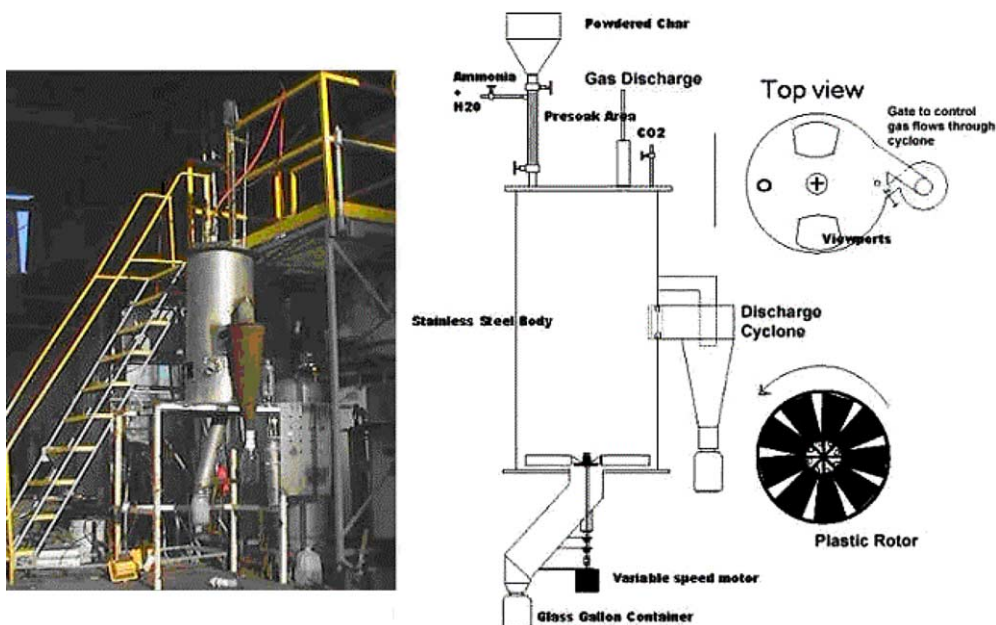


Fig. 9. Diagram of the mechanical fluidized bed used to easily adapt any gas stream and injected CO₂, and hydrated ammonia into powdered char.

4. A SEM investigation of the interior of an ECOSS-15 char particle

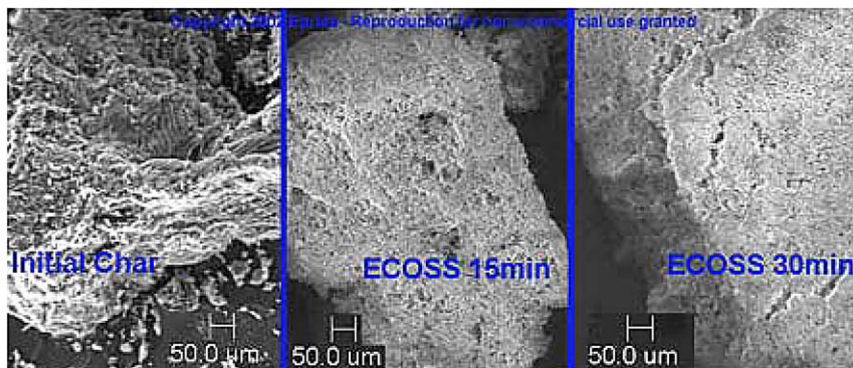
Fig. 12 is a char particle at 422×, which has been crushed and a piece was broken off in the process. The ammonium bicarbonate formed in the fractured areas between the main body of the particle and the broken piece.

Fig. 13 shows where the very small molecules of NH₃H₂O (hydrated ammonia) are adsorbed into the char fractures and internal cavities. As CO₂ enters, it converts the NH₃H₂O into the solid NH₄HCO₃, trapping it inside the micro-porous material. The internal flat-top, volcano-like structures demonstrate the impact of hydrated ammonia and carbon dioxide meeting in a pore where the ammonia bicarbonate builds up on the inside, closing the larger pore from the inside.

Fig. 14 is a closer look at the crushed material (2000×); we can see small deposits beginning to form inside the carbon framework. There appear to be plenty of open spaces for microbial interaction.



Fig. 10. Images of char; initially, after 5–15 and 20–30 min in the fluidized bed.



452 Fig. 11. Images of the initial char, the enriched carbon, organic slow-release sequestering (ECOSS) 15 min material, and
453 ECOSS-30 min material.

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455 Additionally, reformation of polycondensates on the carbon structures may contain nutrient sources for
456 enhancing microbial activity.

457 Fig. 15 is a 1000 \times image of the interior of a crushed particle of ECOSS produced with a 20–30 min
458 residence time. The SEM shows that the interior of the char is filled. A column of carbon is shown
459 broken off at the top of the picture. The exact duration for ultimate delivery and release of nutrients
460 solidified deep in these internal pore structures need further testing both in bench-scale and soil-plot
461 testing. Future testing and analytical work will, it is hoped, discover ways of enhancing the process and
462 material. Yet, the simple physical solidification of a nutrient material and sequestered CO₂ inside the
463 char structure can be seen with the fibrous NH₄HCO₃ deposits. This demonstration of the process shows
464 that we can deposit nutrients inside the porous media using a low-cost gas phase application.

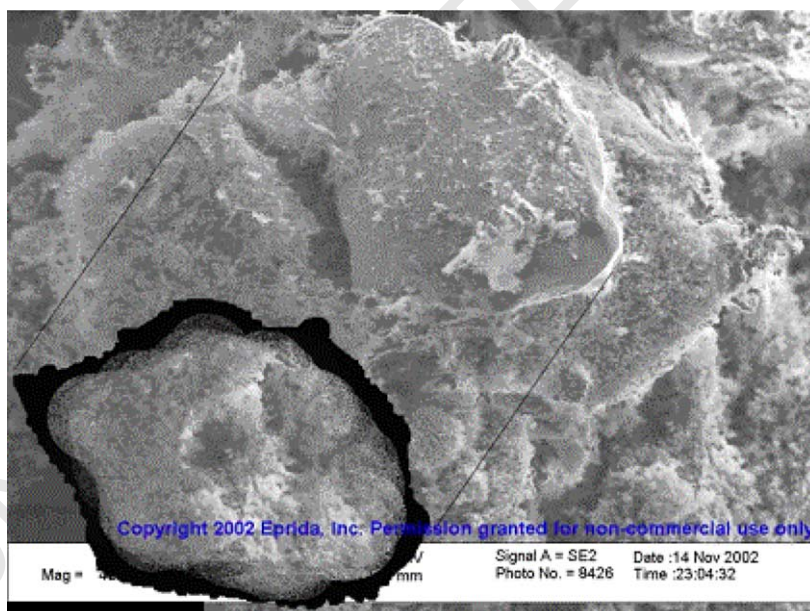


Fig. 12. Image of a broken char particle with a magnification of 422 \times .

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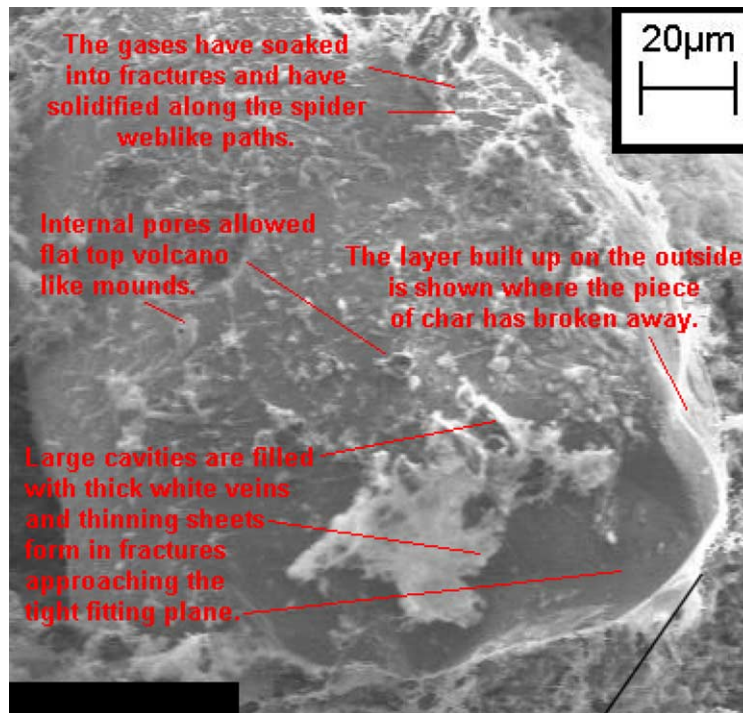


Fig. 13. Image of $\text{NH}_3\text{H}_2\text{O}$ (hydrated ammonia) molecules as adsorbed into the char fractures.

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5. Production chemistry calculations and carbon utilization

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Calculating the amounts of ECOS and hydrogen that can be made from a standalone system would begin with a typical initial biomass composition of: [21]

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C 46.0%
H 6.3%
O 42.5%
N 2.2%
Ash 3.0%.

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Yield of charcoal is 32% on a dry biomass basis (ash and nitrogen are totally sequestered in charcoal). Typical composition on an ash- and nitrogen-free basis is:

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C 82%
H 3.4%
O 14.6%.

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While charcoal production may go up or down, the above number reflects a reasonable dry weight estimate.

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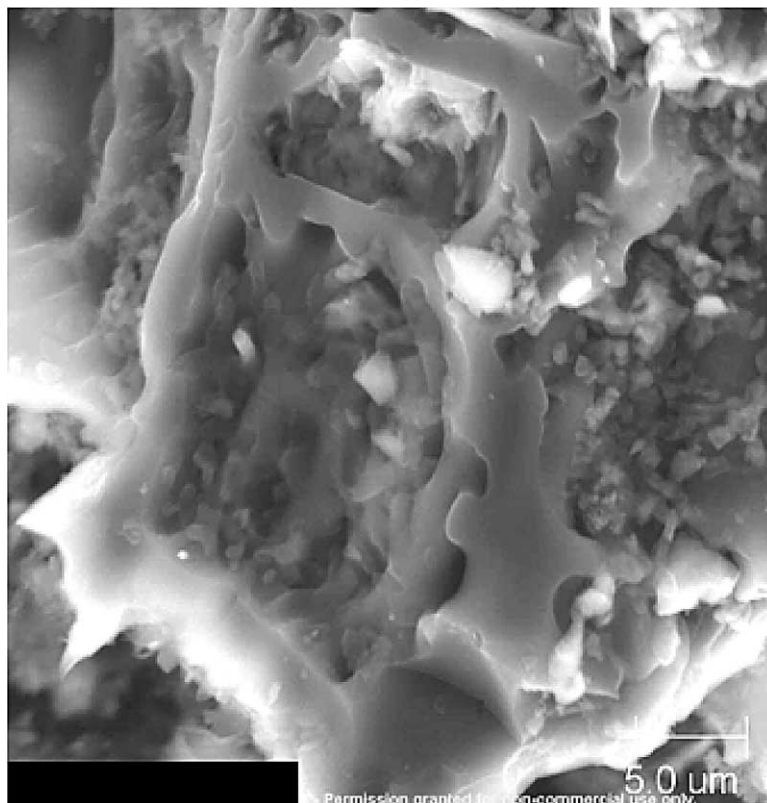


Fig. 14. Hydrated ammonia molecules as adsorbed into char (2000 \times).

ECOSS (containing 10% nitrogen from NH_4HCO_3) is a mixture of 56.4% NH_4HCO_3 (at 17.7% N resulting in the end ratio netting 0.1/0.177) and 43.6% charcoal. This actually produces a 12%+ N fertilizer, as char has approximately 2–4% N trapped in the char. For the purposes of this analysis, however, it is not utilized as its availability is unknown and the rate of release of this N has not been verified. Based on the above, from 100 kg of biomass, $(32/43.6) \times 100 = 73.4$ kg ECOSS can be produced for which 41.4 kg NH_4HCO_3 is needed. For 1 mole (79 g) NH_4HCO_3 , 5 g of hydrogen is needed, while for 41.4 kg $(5/79) \times 41.4 = 2.64$ kg hydrogen is needed.

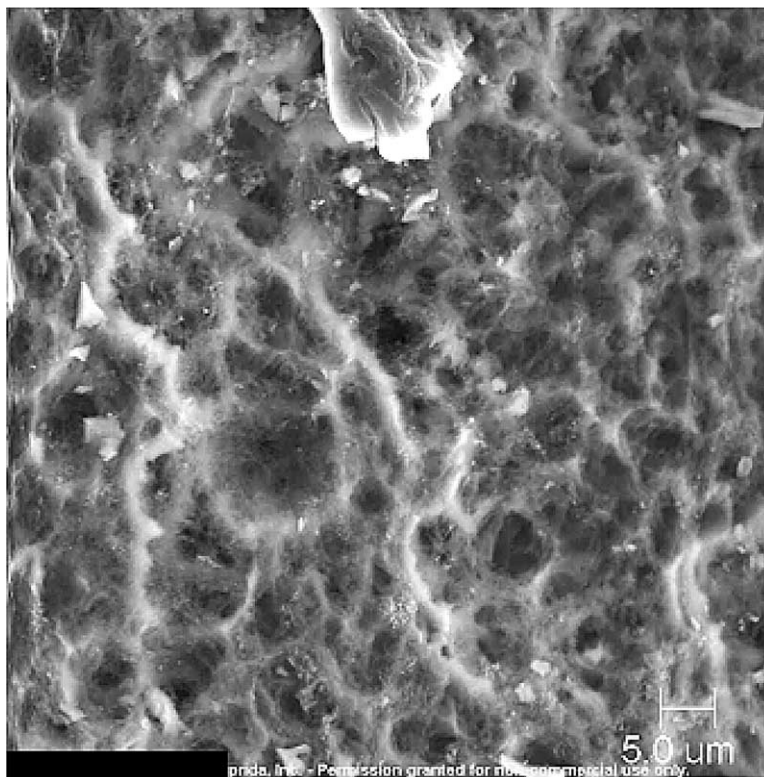
By pyrolysis of 100 kg of biomass, 32 kg charcoal and 68 kg gas and vapor will be produced. Considering the composition of charcoal, the elemental balance will be as follows: [22] (Table 1)

The 22 kg of C represents the stable form of sequestered carbon used as the framework for building a new type of fertilizer.

Reforming (assuming total conversion of carbon to CO_2) will require (stoichiometrically) 28.35 kg steam and will produce 88 kg CO_2 and 8.35 kg hydrogen. As only 2.64 kg H_2 is necessary for ECOSS (using all charcoal available from the process) 6.78 kg (68.4% total production) of hydrogen will remain for every 100 kg of biomass.

The amount of C converted from atmospheric CO_2 is equal to 12 kg for each 79 kg of NH_4HCO_3 or 15.2% of the sequestered carbon as ammonium bicarbonate. For each 100 kg of biomass, therefore, we will produce $(12/79) \times 41.4$ kg, or an additional 6.29 kg of C, or a total of 28.3 kg of utilized carbon.

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596 Fig. 15. 1000 \times image of the interior of a crushed particle of ECOS produced with a 20–30 min' residence time.
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598 In acid soils, this part of the carbon will convert to CO₂ but in alkaline soils, (pH > 8) it will mineralize
599 and remain stable. According to USDA reports, 60–70% of worldwide farmland is alkaline; thus,
600 allowing conservatively for 50% of the bicarbonate to convert to CO₂, this will leave approximately
601 25 kg of stable carbon in our soils for each 100 kg of biomass processed. This carbon represents 91.5 kg
602 of CO₂, of which 88% is stored as a very beneficial and stable charcoal.
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604 A different way of looking at this is to compare the amount of energy produced and the resulting CO₂
605 impact. With an extra 6.78 kg hydrogen produced per 100 kg of biomass, then $25/6.78 = 3.69$ kg C/kg H
606 or $3.66 \times 3.69 = 13.5$ kg CO₂/kg of hydrogen produced and used for energy. From a power perspective,
607

608 Table 1
609 Elemental balance of pyrolytic conversion

In		Out	
100 kg of biomass		32 kg of charcoal	68 kg of gas + vapor
C	46	22	24
H	6.3	1.1	5.2
O	42.5	3.7	38.8
N	2.2	2.2	
Ash	3.0	3.0	

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617 that is 13.5 kg CO₂/120,000 kJ of hydrogen consumed as a renewable energy or 112 kg/GJ of utilized
618 and stored CO₂.

6. Global potential

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622
623 The large majority of increases in CO₂ will come from developing countries as their burgeoning
624 entrepreneurial populations industrialize. A sustainable technology needs to be able to scale to meet the
625 growing needs of this large segment of the population. Developing an economic size that offers a
626 profitable platform may require certain minimums, and it may be that the lower limit of economic
627 production is larger than that of typical biomass conversion systems. A 1–2 MW facility could be the
628 lower limit yet two factors are important to note here. The first is that the low relative efficiencies
629 required by both the hydrogen separation and the ammonia production may allow a smaller footprint
630 system to be developed using new technologies. Future research efforts in separation technologies and
631 ammonia catalyst technology could offer developments leading to systems for even very small farming
632 communities.

633
634 The second point is that the total hydrogen is approximately three times the maximum that can be
635 utilized in one facility, thus every third facility could be designed to accept the charcoal that is produced
636 by two standalone energy systems. This special facility could process all of its hydrogen and the carbon
637 from two other locations and use existing industrial ammonia manufacturing techniques to create the
638 carbon fertilizer. If all the hydrogen is converted to fertilizer there is an opportunity to acquire outside
639 CO₂ (34 kg required for each 100 kg biomass processed); meanwhile, the opportunity to earn revenue
640 from SO_x and NO_x removal could provide it with another income stream and help its economics. This
641 would also fit closely into the strategies of developing areas wishing to attract and support GHG-emitting
642 manufacturing.

643 The energy, from a total systems point of view, could create a viable pathway to carbon negative
644 energy as detailed in the IIASA focus on Bioenergy Utilization with CO₂ Capture and Sequestration
645 [23]. The effects shown in the last graph (Fig. 16) (i.e. providing 112 kg of CO₂ removal for each

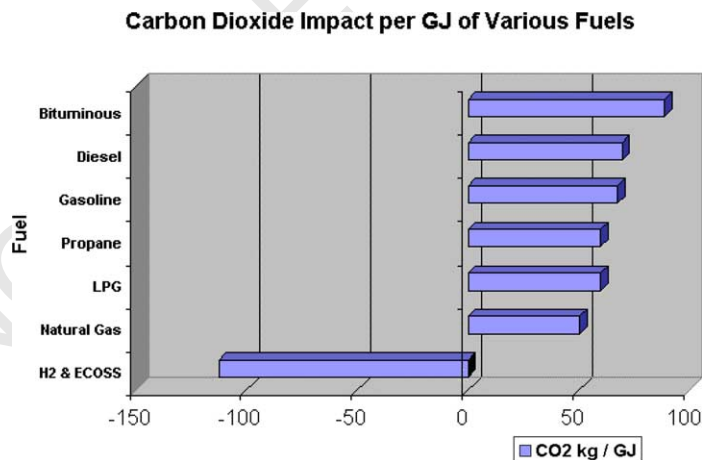


Fig. 16. Carbon dioxide impacts of various fuels per gigajoule.

CO₂ Life Cycle Analysis Budgets of Various Materials Used in Automotive Manufacturing

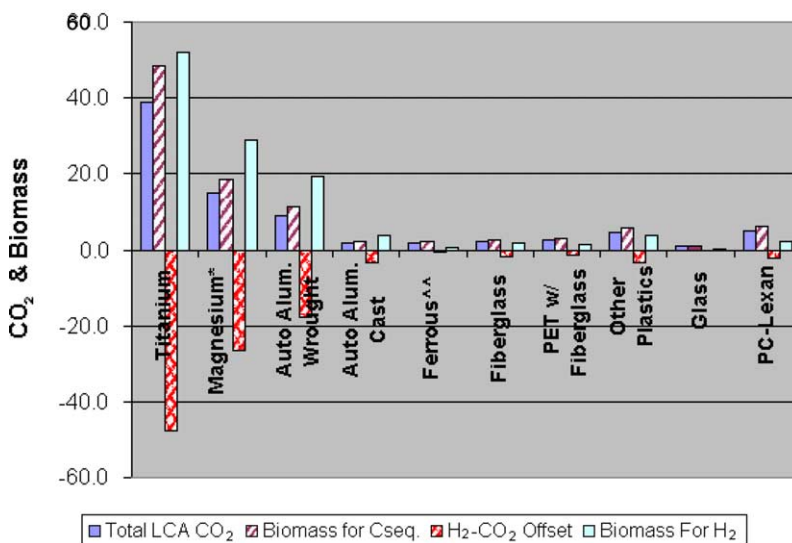


Fig. 17. Various materials used in automobile manufacturing and the life cycle analysis of carbon emissions per kilogram and biomass required to offset those emissions. Data source: ORNL-2002.

gigajoule of energy used) could allow major manufacturers to offset their carbon costs. The graph in Fig. 17 shows various materials used in automobile manufacturing and the life cycle analysis of carbon emissions per kilogram. The second bar (striped) represents the weight of biomass, using this process, that would be required to offset that carbon cost. The third bar, extending down in the checked pattern, shows the amount of sequestered carbon that would be created if the process were used to produce all the energy required for production, and the last bar represents the amount of biomass required to meet the energy needs of producing that amount of the automotive material. In some materials, the amounts needed for energy production are less than the amounts needed for carbon offset. This illustrates that energy is just one aspect of GHG production related to materials manufacturing and that methods for offsetting CO₂ release are essential.

There is an opportunity for economically developing areas with biomass to utilize their resources to help manufacturers reach carbon-negative status. If the material leaves a factory with a net carbon negative budget, then consumerism becomes an agent of climate mitigation and supports economies in side-stepping fossil-fuel pathways.

How widely could this method be applied and the areas of the earth that could make a concerted effort to reclaim eroded land and increase current farmland production are areas for future research. The positive impact of an increased soil carbon content ultimately leads to increased food and plant yields, further helping to reduce CO₂ buildup. There is very little information on the maximum rates of utilization, though 10,000 kg/ha of char have been used with very positive results and researchers have proposed that as little as 2000 kg/ha could prove beneficial for plant growth [24,25].

For a quick test of reasonableness, we saw above that 1 GJ of hydrogen produced and used represents 112 kg of utilized and stored carbon dioxide. Therefore, taking the atmospheric rise of 6.1 Gt

705 and dividing by $112 \text{ kg/GJ} = 54.5 \text{ EJ}$. This number falls amazingly along the 55 EJ estimate of the
706 current amount of biomass that is used for energy in the world today [26]. While the potential reaches
707 many times this for the future utilization of biomass, this shows that there is a chance that we can be
708 proactive in our approach.
709

711 7. Technical/economic overview and global impacts

712

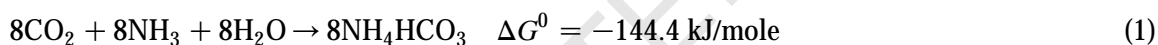
713 A proper techno-economic study has yet to be conducted of this relatively new technique, still only
714 1 year old. This simplistic economic overview can at best provide a bracket evaluation using studies
715 from comprehensive studies of constituent technologies. These include a study of the economics of the
716 ORNL process for NH_4HCO_3 production from fossil-fuel scrubbing conducted by the University of
717 Tennessee ('UT Study') [27] in 2001 and the ongoing economic evaluations of renewable hydrogen
718 production from the US National Renewable Energy Laboratory. Those studies can provide the outer
719 framework for this preliminary economic estimate, but when a dedicated and comprehensive analysis
720 is conducted, these numbers will change. The UT study in question examined the economics of
721 producing ammonium bicarbonate in the exhaust stream of fossil-fuel combustion. It assumed the use
722 of natural gas to produce ammonia and its subsequent conversion to ammonium bicarbonate. As this
723 occurred prior to the use of charcoal inclusion, it did not include any economic gains that could be
724 attributed to charcoal. Some gains benefit the fossil-fuel user. These include a single system for
725 removal of CO_2 , SO_x and NO_x , no required drying of the final product and the ability to offset income
726 from fertilizer sales. Optimally, fossil-fuel users will partner with fertilizer manufacturers to use their
727 existing market penetration. Fertilizer-manufacturing firms, which have been relegated to the sale of
728 commodity goods, can reinvent their product offerings to include service-based delivery of soil fertility
729 and management of soil carbon content. Utilizing advances in remote and satellite monitoring
730 technologies and a more in-depth local delivery of site-specific management techniques, these services
731 will offer a regional advantages that will be able to withstand competition in a way that global
732 commodity chemical production cannot.

733 More gains accrue to farmers as these fertilizers can restore soil carbon content, return trace minerals
734 to degraded lands, increase cation exchange, water-holding capacity, and microbial activity, as well as
735 decrease nutrient leaching, which all lead to increases in crop yields. Assumptions of these increases and
736 income derived cannot be made until there are more detailed yield- and cost-analyses for the amounts of
737 ECOSS utilized, yields of specific crops on representative soils, type of irrigation, and other factors
738 essential to determining farm income. The closed cycle begins with farmers entering into long-term
739 contracts to supply energy crops (which can be grown on marginal lands), forestry thinnings and other
740 sources of biomass, which will be required by this soil–food–energy–carbon management value chain.
741 These contracts will help establish revenue sources to support effective land, forest, and crop-
742 management strategies.

743 Viewed from a global perspective, this technique simulates the interdependence we find among
744 organic species in nature. Each role is essential and rewards are evolved through market mechanisms.
745 This diversity in economic gain offers to help restore the growth opportunities to farming, forestry, and
746 small rural businesses. Instead of a transfer of wealth, this is a grass-roots development of income which,
747 quite literally, has been going up in smoke for the last two centuries. The development of opportunity
748 and broad-based growth in entrepreneurial activity, farm operations and businesses that support them,

will lead to more stable and predictable income for multinationals, medium and small businesses and lead to an increase in the rural tax base. While this is not a cure-all, it moves the world toward more sustainable growth strategies.

The economic projections of the UT study were based on a market value of the end product at US\$2.63/lb atom of nitrogen based on 1999 prices of nitrogen fertilizer. Today's prices are significantly higher due to increased natural gas prices. However, with a target of 20% CO₂ removal, the study concluded that a 700 MW facility would be optimally sized for the economic production of fertilizer and would yield an after-tax return on investment of US\$0.33. The investment required to meet this level of CO₂ capture would be US\$229 million. The same amount of carbon captured with ECOSS, where 88% of the target will be met by the carbon contained in the char, would require a production unit only one-fifth the size. This should be considered as one bracket in our assessment. While economics and scale may favor larger installations, Kyoto reduction targets can be met through smaller facilities. The revenues from fertilizers will drop as less fertilizer would need to be manufactured while more hydrogen can be produced for fuel. In the UT study, the world's consumption and demand for nitrogen became the limiting factor in how much carbon could be captured. The total market for nitrogen in 1999 was 80.95 million tons [28] which, converted at the power plant targeting 20% reductions in CO₂, leads to the conclusion that 337 fossil-fuel plants of 237 MW each would meet world fertilizer demand. Their calculations showed that this would reduce the global C output from coal combustion by 3.15%. The study also assumed the use of natural gas to make the ammonia. The total stoichiometric calculation for ammonia from natural gas and the conversion of 8 lb-moles of NH₃ into NH₄HCO₃, which captures 5 lb-moles of CO₂. With renewable hydrogen to make ammonia, no fossil-fuel-based CO₂ is released into the atmosphere when the following ammonia-carbonation reaction is applied:



Calculations using published thermodynamic data [29,30] showed that the standard free-energy change ΔG^0 is -144.4 kJ/mol , which indicates that this carbonation reaction is favored thermodynamically. The thermodynamic equilibrium constant (K) is 1459 for this ammonia-carbonation reaction. Consequently, this reaction requires no additional energy and actually releases energy as it captures CO₂ as NH₄HCO₃, as illustrated in Fig. 8. Therefore, renewable hydrogen allows a 1.6 times increase in CO₂ captured per lb-mole of NH₄HCO₃ produced. Utilizing results from the study above, a switch to renewable hydrogen to make ammonia would increase carbon capture, $3.15 \times 1.6 = 5.04\%$. However, carbon closure of biomass energy is not zero but has been calculated [31] at 95%. A more accurate number would be $5.04 \times 95\% = 4.79\%$ reduction in C from worldwide coal combustion if renewable H₂ as the source for producing ammonia and all the world's N requirements are met from NH₄HCO₃ scrubbed from power plant exhaust.

As stated, the total C captured in the combined ECOSS material was 12% from fertilizer and 88% from char. Taking the theoretical number of 4.79% and equating that to the 12% portion of ECOSS, would mean that the total carbon capture at 1999 N levels would be increased or leveraged $100/12 = 8.3$ -fold or total C from coal combustion reduced by $\sim 39.9\%$. This leveraged total theoretical potential should be seen as a second bracket. This number is not the true total. Only a more comprehensive analysis can accurately predict what that number would be. The factors of increased biomass growth with the addition of charcoal as found by Mann [32], Hoshi [33], Glaser [34], Nishio [35], and Ogawa [36] show increased

793 biomass growth from 17 to 280% with non-optimized char. The direct utilization of an optimized char
794 plus slow-release nitrogen/nutrients may allow increased biomass growth targets worldwide. A portion of
795 this increased biomass growth will be converted to soil organic matter, further increasing C capture
796 (especially if no-till management practices are adopted). Therefore, another bracket in our assessment of
797 this process is the increase in non-fossil-fuel CO₂ capture from biomass growth in addition to the
798 leveraged total.

799 The ability to slow down the release of ammonia in the soil will allow plants to increase their uptake
800 of nitrogen. This will lead to a reduction in NO₂ atmospheric release. This potent greenhouse gas is
801 equivalent to 310× the impact of CO₂. The fertilizer industry releases CO₂ during the manufacture of
802 ammonia from methane



804
805
806
807 The equation illustrates that, for each ton of nitrogen produced, 0.32 tons of C are released, and the
808 80.95 million tons of nitrogen utilized would represent 26 million tons of C. This is a small number
809 in relative terms to the amounts released by combustion of coal (2427 million tons) [37]; however, if
810 we assume [38] that 1.25% of our nitrogen fertilizer escapes into the atmosphere as N₂O, then 1.923
811 million tons of N₂O are released, with an CO₂ equivalence of 595.9 million tons or 162.5 million
812 tons of C equivalent. This has an impact equal to 6.7% of the entire world's combustion of coal.
813 Kaiser has measured N₂O flux in sugar beets, and two crops of winter wheat under three
814 recommended fertilization rates [39]. His work found that relative N₂O from the applied N
815 fertilization ranged between 0.7 and 4.1%. The highest level could equate to as much as a coal-fired
816 power plant in some areas. While this high level is not the average, the fact that a typical farm
817 fertilizer application can represent the same emissions impact as a small coal-fired plant is one that
818 many do not consider as they look across the expansive green fields of modern agriculture. This
819 bracket then demonstrates that effective efforts, such as in the slow release of nutrients, to reduce the
820 distributed release of N₂O from fertilizer can play a substantial role, in the same way as reductions
821 sought from fossil-fuel combustion.

822 The economics of hydrogen from biomass has been addressed in the 2001 report by Spath [40]. The
823 conclusion was that pyrolytic conversion of biomass offered the best economics, partly because of the
824 opportunity for coproduct production and reduced capital costs. However, this assessment was based on
825 using bio-oil for reforming, and it acknowledged the uncertainty in pricing for coproducts. The analysis,
826 at a 20% internal rate of return, provided plant-gate pricing of hydrogen from US\$9.79–US\$11.41/GJ. In
827 the UT study, hydrogen production equipment represented 23% of the total capital equipment costs and
828 utilized a US\$4/GJ expense for methane. This cost represented ~50% of total expenses and ~45% of
829 before-tax profits. If we assume that other operational costs remain the same, with the increased cost of
830 natural gas, the inside-plant cost of renewable hydrogen would no longer be 2.4–2.8 times the costs from
831 methane, but approaching 1.6–1.9 times. As net profits were based on the market price of nitrogen, then
832 increases in natural gas prices will change total income in the model as well. For simplicity, if we use
833 US\$7/GJ, then total income would increase 1.75× and expenses related to renewable hydrogen would
834 roughly equal ~50% of before-tax profits. This represents a third bracket in assessment. Intra-plant
835 usage of renewable hydrogen (i.e. no storage or transport expense) becomes significantly more
836 competitive at our current natural gas prices.

837 The last bracket comes from a review of traditional ammonia processing methods and how they
838 compare to the ECOSS process. The UT study notes that because of unfavorable equilibrium
839 conditions inherent in NH_3 conversion, only 20–30% of the hydrogen is converted in a single pass. In
840 Section 5, we determined that the ECOSS process could utilize only 31.6% of the hydrogen as we were
841 limited by the total amount of char produced and the target 10% nitrogen loading. This means that a
842 single pass NH_3 converter could be used and the expense of separating and recycling unconverted
843 hydrogen eliminated. The 68.4% hydrogen is then available for sale or use by the power
844 company/fertilizer partnership. This last bracket shows that the ECOSS process thus favors the
845 inefficiencies of ammonia production and reduces costs inherent in trying to achieve high conversion
846 rates of hydrogen.

847 With increased biomass utilization for energy and increasing demands for food production, the
848 requirements for fertilization will increase. The restoration and return of micronutrients could allow
849 substantive increases in overall soil amendment applications and the potential needs for nitrogen may
850 not be such a limiting factor as was considered in the UT study. From a global systems view, the
851 combination of topsoil restoration, desert reclamation, and the associated increases in biomass growth,
852 could allow the economics to be driven not by C capture but rather by value creation of increased
853 soil/crop productivity. Modeling of this approach is needed to examine the long-term impacts. The
854 brackets listed above describe an area of possible economic and technical performance. This area of
855 probability is sufficient in scale, impact, and comparative advantage to other carbon management
856 techniques to lead research organizations toward a critical examination. A more complete review should
857 examine barriers to commercialization, which include farm acceptance of a new type of fertilizer. Proof
858 of increased crop productivity and soil improvement will require local demonstrations and field trial
859 studies by regional agricultural universities and research facilities. Other barriers include adoption of a
860 new type of exhaust scrubbing system by fossil-fuel users, acceptance by the fertilizer industry, and
861 world acceptance of the carbon credits generated in this manner.

862 If these barriers can be overcome, the concept of biomass energy production with agricultural carbon
863 utilization may open the door to removing millions of tons of CO_2 from industrial emissions while
864 utilizing captured C to restore valuable soil carbon content. This process simultaneously produces a
865 zero-emissions fuel that can be used to operate farm machinery and provide electricity for rural users,
866 agricultural irrigation pumps, and rural industrial parks. Future developments from the global research
867 community will produce a range of value-added carbon containing coproducts from biomass. With this
868 development and future use of inventions like this, both the producers of carbon dioxide and agricultural
869 community have the capability of becoming a significant part of the solution to the global rise in GHG
870 emissions while building sustainable economic development programs for agricultural areas in the
871 industrialized and economically developing societies.

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875
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References

- 881
882
883 [1] Day D. Activities web report of a 100 hour production run of hydrogen from biomass in Blakely, GA, USA; 2002. <http://www.eprida.com/hydro/>.
- 884
885 [2] Gavin DG, Brubaker LB, Lertzman KP. Holocene fire history of a coastal temperate rain forest based on soil charcoal radiocarbon dates. Ecology 2003 in press.
- 886
887 [3] IPCC. Climate change 2001: the scientific basis, intergovernmental panel on climate change. Cambridge, UK: Cambridge University Press; 2001. http://www.grida.no/climate/ipcc_tar/wg1/index.htm.
- 888
889 [4] Walsh M, et al. Biomass feedstock availability in the United States: 1999 state level analysis; 1999. <http://bioenergy.ornl.gov/resourcedata/index.html>.
- 890
891 [5] Yeboah Y, et al. Hydrogen from biomass for urban transportation. Proceedings of the US DOE Hydrogen Program Review 2002.
- 892
893 [6] Day D, Evans R, Lee J. US Patent Application; 2002.
- 894
895 [7] Yelverton F. The use of activated carbon to inactivate agricultural chemical spills North Carolina Cooperative Extension Service; March 1996. <http://www.bae.ncsu.edu/bae/programs/extension/publicat/wqwm/ag442.html>.
- 896
897 [8] Lee JW, Li R. A novel strategy for CO₂ sequestration and clean air protection Proceedings of First National Conference on Carbon Sequestration, Washington, DC; May 14–17 2001. http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/p12.pdf.
- 898
899 [9] Lee JW, Li R. Method for reducing CO₂, CO, NO_x, and SO_x emissions, 1998. Oak Ridge National Laboratory Invention Disclosure, ERID 0631; 2002. US Patent No. US 6,447,437 B1.
- 900
901 [10] Lee JW, Li R. Integration of coal-fired energy systems with CO₂ sequestration through NH₄HCO₃ production. Energy Convers Mgmt 2003;44:1535–46.
- 902
903 [11] Schleppi P, Bucher-Wallin I, Siegwolf R, Saurer M, Muller N, Bucher JB. Simulation of increased nitrogen deposition to a montane forest ecosystem: partitioning of the added N. Water Air Soil Pollut 1999;116:129–34.
- 904
905 [12] Glaser B, Lehmann J, Zech W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. Biol Fertil Soils 2002;35:219–30.
- 906
907 [13] Wardle DA, et al. The charcoal effect in Boreal forests: mechanisms and ecological consequences. Oecologia 1998; 115(3):419–26.
- 908
909 [14] International Cooperation in Agriculture and Forestry. Application of Rice Hull Char, Taiwan; 2002. Leaflet 03-01. <http://www.agnet.org/library/article/pt2001004.html>.
- 910
911 [15] Day D. Activities web report of a 100 h production run of hydrogen from biomass in Blakely, GA, USA; 2002 <http://www.eprida.com/hydro/>.
- 912
913 [16] Pietikäinen J. Soil microbes in boreal forest humus after fire. Thesis; 1999. <http://ethesis.helsinki.fi/julkaisut/maa/mekol/vk/pietikainen/soilmicr.html>.
- 914
915 [17] Runkel ROH, Wilke K. Chemical composition and properties of wood heated at 140C to 200C in a closed system without free space. Part II. Holz Roh Werkst 1951;9:260–70 [in German].
- 916
917 [18] Godsy EM. Impact of human activity on groundwater dynamics Proceedings of a Symposium Held during The Sixth IAHS Scientific Assembly at Maastricht, The Netherlands, July IAHS Publication no. 269; 2001. p. 303–9.
- 918
919 [19] Li R, Hagaman R, Tsouris C, Lee JW. Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase. Energy Fuels 2003;17:69–74.
- 920
921 [20] Asada T, et al. Science of bamboo charcoal: Study of carbonizing temperature of bamboo charcoal and removal capability of harmful gases. J Health Sci 2002;48(6):473–9.
- 922
923 [21] Gaur S, Reed TB. Thermal data for natural and synthetic fuels. New York: Marcel Dekker; 1998. p. 200–44.
- 924
[22] Czernik S. Personal correspondence and emails. Golden, Colorado, USA: National Renewable Energy Laboratory; March 2003.
- [23] Obersteiner M, et al. Biomass energy, carbon removal and permanent sequestration—a real option for managing climate risk, report no. IR-02-042. Laxenburg, Austria: International Institute for Applied Systems Analysis; 2002.
- [24] Glaser B, Lehmann J, Zech W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. Biol Fertil Soils 2002;35:219–30.
- [25] International Cooperation in Agriculture and Forestry. Application of Rice Hull Char, Taiwan; 2002. Leaflet 03-01. <http://www.agnet.org/library/article/pt2001004.html>.

- 925 [26] Hall DO, Rossillo-Calle F, Williams RH, Woods J. Biomass for energy: supply prospects. In: Johansson TB, Kelly H,
926 Reddy AKN, Williams RH, editors. Renewable energy: sources for fuel and electricity. Washington, DC: Island Press;
927 1993. p. 593–652.
- 928 [27] Athon, et al. CO₂ sequestration from coal fired power plant flue gas, (a pre-patent confidential design project study for co-
929 author James Lee). University of Tennessee; 2000. See also [http://www.eprida.com/hydro/ecoss/background/
CO2seqeconomics.pdf](http://www.eprida.com/hydro/ecoss/background/CO2seqeconomics.pdf).
- 930 [28] The Fertilizer Institute. World fertilizer use; 2003. <http://www.tfi.org/Statistics/worldfertuse.asp>.
- 931 [29] Handbook of chemical engineering art and design. Shanghai: China National Chemical Engineering Industry Press; 1985.
932 p. 722–5 [in Chinese].
- 933 [30] Lide DR, Frederikse HP. CRC handbook of chemistry and physics, 75th ed. London: CRC Press; 1994. p. 5-1-5-47.
- 934 [31] Mann M. Life cycle assessment of a biomass gasification combined-cycle system National Renewable Energy Laboratory
Report, Golden, Colorado, USA; 1997.
- 935 [32] Mann C. The real dirt on rainforest fertility. *Science* 2002;297:920–3.
- 936 [33] Hoshi T. Web report of growth studies with charcoal amendments on green tea yields; 2002. [http://www.fb.u-tokai.ac.jp/
WWW/hoshi/cha](http://www.fb.u-tokai.ac.jp/WWW/hoshi/cha).
- 937 [34] Glaser, et al. Potential of pyrolyzed organic matter in soil amelioration 12th ISCO Conference, China, vol. 3; 2002. p. 421.
- 938 [35] Nishio M. Microbial fertilizers in Japan Bulletin by National Institute of Agro-Environmental Sciences, Japan; 1999.
- 939 [36] Ogawa M. Effect of charcoal on the root nodule and VA mycorrhizal formation of soybean Proceedings of the Third Inter-
940 national Mycology Congress, Tokyo, Japan 1983 p. 578.
- 941 [37] World Carbon Dioxide Emissions from the Consumption of Coal; 1992–2001. [http://www.eia.doe.gov/emeu/iea/tableh4.
942 html](http://www.eia.doe.gov/emeu/iea/tableh4.html).
- 943 [38] Mosier, et al. Closing the global N₂O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient
944 Cycl Agro Ecosystems* 1998;52:223–45.
- 945 [39] Kaiser, et al. Nitrous oxide release from arable soil: importance of N fertilization, crops and temporal variation. *Soil Biol
946 Biochem* 1998;30(12):1553–63.
- 947 [40] Spath, et al. Update of hydrogen from biomass—determination of the delivered cost of hydrogen National Renewable
948 Energy Laboratory, Milestone Report for the US Department of Energy’s Hydrogen Program 2001, Golden, Colorado,
949 USA 2001.
- 950
- 951
- 952
- 953
- 954
- 955
- 956
- 957
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