VALUABLE AND STABLE CARBON CO-PRODUCT FROM FOSSIL FUEL EXHAUST SCRUBBING

Danny Day[1], Robert J. Evans[2], James W. Lee[3], and Don Reicosky[4]

[1]Eprida, Inc., 6300 Powers Ferry Road, Suite 307, Atlanta, GA 30339, danny.day@eprida.com
[2]National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, CO, 80401, bob_evans@nrel.gov
[3]Oak Ridge National Laboratory, 4500N, A16, MS-6194, Oak Ridge, TN 37831, leejw@ornl.gov
[4]USDA-Agricultural Research Service, 803 Iowa Avenue, Morris, MN 56267 reicosky@morris.ars.usda.gov

Introduction: A Sustainable Carbon Sink With Hydrogen Production

The increasing anthropogenic CO_2 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 needs for energy while reducing greenhouse gas emissions. The need for sustainable energy with little greenhouse gas emissions has lead 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 co-products in the form of a solid sequestered carbon. This char and carbon ("C") material represent a form of sequestered C that decomposes extremely slow[2] and retains the bio-capture CO_2 for centuries. The limitation of the use of this form of carbon is a profit centric use. It was apparent that additional value needed to be added to this material that would justify large-scale handling and usage. In 1990s, C in the form of CO_2, accumulated at rates ranging from 1.9 to 6.0 Pg C/yr and increasing CO_2 levels by 0.9 to 2.8 ppm/yr. [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 as valued added carbon could significantly reduce the atmospheric loading of CO_2 while simultaneously producing hydrogen. Normally hydrogen is referred to as a zero emissions fuel, however from life cycle perspective it can be viewed as a negative emissions fuel. In order to accomplish this economically, the sequestered C must have a very large and beneficial application such as a soil amendment and/or fertilizer.

The concept of utilizing charcoal as a soil amendment is not new. Man-made sites of charcoal rich soils intermingled with pottery shards and human artifacts have been identified covering 50,000 hectares of the Central Amazon rainforest each averaging 20ha and the largest at 350ha. [5] The radiocarbon dating of the sites have shown ages dating back 740–2,460 years BP[6] and 30% of the soil organic matter is made up of pyrolytic black carbon which is 35 times higher than the adjacent poorer quality soils (Oxisols) [7]. Most terra preta sites are identified by their thick black layers of soil (40-80cm) and some have been found in layers up to 2 meters thick[8]. These soils are so rich and fertile that they are dug up and sold as potting soil[9]. The current agricultural methods of the Kayapó (an ancient people with little European contact until the 19th century) has changed little and give evidence to the man-made techniques (slow burning fieldsand biomass) for creation of this fertile and sustainable method of agriculture which can be farmed intensively for up to 11 years . [10] This ability to farm soils without fertilization for many years is an anomaly in the rainforest. Despite the abundance of rainforest growth, their red and yellow soils are notoriously poor: weathered, highly acidic, and low in organic matter and essential nutrients.

Experimental Project Description The approach [11] in our research applies a pyrolysis process that has been developed to produce charcoal like by-product and synthetic gas (containing mainly H_2, and CO_2) from biomass, which could come from both farm and forestry sources. In this novel system [12], 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, H_20 and CO_2, at atmospheric pressure and ambient temperature to form a nitrogen enriched char. The char materials produced in this process contains 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. Recent research has shown that lower temperature charcoal produced at 500°C adsorbed 95% of ammonia versus charcoal produced at 700°C and 1000°C which had higher surface areas but only adsorbed 40%[13]. Masada noted that acidic functional groups such as carboxyl were formed from lignin and cellulose at 400°C -500°C. [14,15]. Charcoals, regardless of biological source, were found to form acidic functional groups at these temperatures which will preferentially adsorb base compounds such as ammonia and that the chemical adsorption plays the primary role over surface area. This research points to the carbonization conditions as a key ingredient in optimizing a charcoal as a nutrient carrier and binding compound for ammonia. Thus when used as a carrier for nitrogen compounds (such as NH_4^+, urea or ammonium bicarbonate) and other plant nutrients, the char binding forms a slow-release fertilizer that is ideal for green plant growth. A combined NH_4HCO_3-char fertilizer is probably the best product that could maximally enhance sequestration of C into soils while providing slow-release nutrients for plant growth.

A flue gas scrubbing process [16,17] utilizing hydrated ammonia was tested in combination with a low temperature char. This approach utilized a chemical process, to directly capture greenhouse gas emissions at the smokestacks by converting CO_2, NO_x, and SO_x emissions into valued added fertilizers (mainly NH_4HCO_3, ~98% and $(NH_4)_2SO_4$ and NH_4NO_3, <2%). These fertilizers can potentially enhance crop growth for sequestration of CO_2 and reduce NO_3^- contamination of groundwater. As discussed above, the low temperature charcoal forms surface acid groups, which adsorbs and binds ammonia to the porous media for nucleation of CO_2. When used as a scrubbing agent with fossil fuel exhaust, a mechanically fluidized cyclone creates a fertilizer-matrix with a commercially acceptable amount of nitrogen and a high percentage of very stable C. In addition, the inorganic carbon component (HCO_3^-) of the NH_4HCO_3 fertilizer is non-digestible to soil bacteria and thus can potentially be stored in certain soil (pH > 7.9) 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, increased crop productivity and restoration of topsoil through the return of carbon and trace minerals. The benefits of producing a value added sequestering co-product 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. [18] 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 in helping each meet Kyoto greenhouse gas reduction targets.

The char component of the material acts to provide the same benefits as in terra preta sites reducing the leaching of soluble nutrients.[19] This increases plant growth, nutrient uptake and reduces nitrogen runoff. One experimental goal of the project was to identify

process parameters that would produce a carbon material optimized for agricultural use. Since it has been shown that the that charcoal addition from 2000 years ago is still providing significant soil fertility benefits [20] and farmers report up to three times crop yields over immediately adjacent non-terra preta soils. Recent research, conducted by Steiner, on the addition of charcoal to non terra preta soils [21] showed significant crop yield increases.

Charcoal has been found to support microbial communities [22] even greater than activated carbon (which is charcoal processed at higher temperatures with steam). Prior researchers assumed that the porous structure provided safe haven but we propose that it may be the availability of microbial nutrients. The processes of pyrolysis create an intrapore deposition of organic polycondensates[23].The deposition of these materials may increase microbial activity. [24]

Experimental Set-up and Results: SEM Investigation of a Low Temperature Char

The low temperature char particles are hydrophobic in nature and grind easily. The internal gases that escape from the material during the charring help develop charcoals natural porosity. The evolution of this adsorbent material provides a porous internal structure as well. We selected 400 ^{o}C as the target temperature for the char before being discharged from the pyrolysis reactor. The resulting char was cooled for 24 hours then fed through a two-roll crusher and then sieved with a mechanized screen through 30 mesh and 45 mesh screens. The resulting fraction remaining above the smaller screen was chosen as our starting material.

Experimental Set-up & Results: SEM Investigation of an Enriched Carbon, Organic Slow-release Sequestering (ECOSS) Fertilizer

Bench scale demonstrations by Oak Ridge National Laboratory recently demonstrated the removal of flue-gas CO_2 via formation of solid NH_4HCO_3 through ammonia carbonation in the gas phase. [25] The results indicated that it is possible to use NH_3+ H_2O+CO_2 solidifying process in gas phase to remove greenhouse-gas emissions from industrial facilities such as a coal-fired power plant. A study of agriculturally optimized charcoal produced by Eprida were combined with the above process created via the sequestration of a CO2 stream. It was proposed that the char could act as a catalyst (providing more effective nucleation sites) to speed up the formation of solid NH_4HCO_3 particles and enhance the efficiency of the gas phase process. A pilot demonstration was constructed to evaluate production and material characteristics of the NH_4HCO_3-char product. The process also showed promise that it could remove SOx and NOx, enhance sequestration of carbon into soils; providing an ideal "Enriched Carbon, Organic Slow-release Sequestering" ("ECOSS") fertilizer and nutrient carrier for plant growth. The value would be enhanced if the production of NH_4HCO_3 could be developed inside the porous carbon media.

To test the production of a charcoal- NH_4HCO_3 fertilizer, we used a mechanical fluidized cyclone, easily adaptable to any gas stream and injected CO_2, and hydrated ammonia. A 250g charge of 30-45 mesh 400 ^{o}C char was fed in at regular intervals varying from 15-30 minutes. A higher rotor speed increased the fluidization and suspended the particles until they became too heavy from the deposition of NH_4HCO_3 to be supported by fluidized gas flows.

SEM Investigation of the Interior of an ECOSS-15 Char Particle

The material produced was evaluated by scanning electron microscopy. The examinations revealed The very small molecules of $NH_3.H_2O$ (hydrated ammonia) are adsorbed into the char fractures and internal cavities. As CO_2 enters, it converts the $NH_3.H_2O$ into the solid NH_4HCO_3, trapping it inside the microporous material. The SEM's of the original char and the resulting product clearly evidenced the intra-pore development of the fibrous NH_4HCO_3 inside the carbon-charcoal framework. The material accumulated as internal flat-top volcano like structures. This demonstration of the process showed that we can deposit nutrients inside the porous media using a low cost gas phase application. We analyzed the required amounts of hydrogen, reformed from biomass, which would be required as ammonia and calculated that 31.6% of the H_2 would be necessary for ECOSS production leaving (using all charcoal available from the process) leaving 68.4% of the hydrogen for use as a fuel.

The amount of C, directly converted from exhaust CO_2 is equal to 15.2% of the total sequestered carbon as a ammonium bicarbonate and for each 100kg of biomass, we will produce a total of 28.3kg of utilized carbon. In acid soils, this part of the carbon will convert to CO_2 but in alkaline soils, (pH>8) it will mineralize and remain stable. According to USDA reports, 60-70% of worldwide farmland is alkaline, so conservatively allowing for 50% of the bicarbonate to convert to CO_2, this will leave us with approximately 25 kg of stable carbon in our soils for each 100kg of biomass processed. This carbon represents 91.5 kg of CO_2 of which 88% is stored as a very beneficial and stable charcoal. A different way to look at this is to compare the amount of energy produced and the resulting CO_2 impact. With 6.78 kg hydrogen extra produced per 100 kg of biomass, then 25/6.78 = 3.69 kg C/ kg H or 3.66x3.69=13.5 kg CO_2 / kg of hydrogen produced and used for energy. From a power perspective, that is 13.5kg CO_2 / 120,000 KJ of hydrogen consumed as a renewable energy or 112 kg/GJ of utilized and stored CO_2.

Global Potential

The large majority of increases in CO_2 will come from developing countries and a sustainable technology needs to be able to scale to meet the growing population needs. The second point is that The energy from a total systems point of view could create a viable pathway to carbon negative energy as detailed in the IIASA focus on Bioenergy Utilization with CO_2 Capture and Sequestration (BECS) [26]. The effects (i.e. providing 112kg of CO_2 removal for each GJ of energy used) could allow major manufacturers to offset their carbon costs. For a quick test of reasonableness, if we take the atmospheric rise of 6.1GT and divide by 112kg/Gj = 54.5EJ. This number falls amazingly along the 55EJ estimate of the current amount of biomass that is used for energy in the world today. [27] While the potential reaches many times this for the future utilization of biomass, this shows that there is a chance that we can be proactive in our approach. Economic projections of a study based on the ORNL process were compared to this process. Equivalent 20% CO_2 reductions and credits needed to return a 33% ROI was estimated to cost $46 million for a 700MW facility utilizing purchased ammonia. However, if the market for nitrogen were an upper limit, and renewable hydrogen were used for producing the worlds ammonia, and all the world's N fertilizer requirements were met from NH_4HCO_3 scrubbed from power plant exhaust, then the total carbon capture at (1999 N levels) then coal combustion CO_2 could be reduced by ~39.9%. The factors of increased biomass growth with the addition of charcoal as found by Mann[28], Hoshi[29], Glaser[30], Nishio[31], and Ogawa[32] show increase biomass growth from 17% to as 280% with non-optimized char. The direct utilization of an optimized char plus slow release nitrogen/nutrients may allow the increase biomass growth targets worldwide. A portion of this increased biomass growth will be converted to soil organic matter, further increasing C capture (especially if no-till management practices are adopted).

The ability to slow down the release of ammonia in the soil will allow plants to increase their uptake of nitrogen. This will lead to a reduction in NO_2 atmospheric release. For each ton of nitrogen produced, 0.32 tons of C are released, and the 80.95 million tons of nitrogen utilized would represent 26 million tons of C. This is a small a small number in relative terms to the amounts released by combustion of coal (2427 million tons) [33], however if we assume [34] 1.25% of our nitrogen fertilizer escapes into the atmosphere as N_2O,

then 1.923 million tons of N_2O are released, with an CO_2 equivalence of 595.9 million tons or 162.5 million tons of C equivalent.

The economics of hydrogen from biomass has been addressed in the 2001 report by Spath[35]. Our analysis shows that inside plant use of renewable hydrogen would no longer be 2.4-2.8 times the costs from methane, but is approaching 1.6-1.9 times with the increase in natural gas prices. Since market price of nitrogen increases with natural gas prices and this process shows intra plant usage of renewable hydrogen (i.e. no storage or transport expense) becomes significantly more competitive at our current natural gas prices. A review of traditional ammonia processing, shows that due to unfavorable equilibrium conditions inherent in NH_3 conversion, only 20-30% of the hydrogen is converted in a single pass. We determined that the ECOSS process could only utilize 31.6% of the hydrogen as we were limited by the total amount of char produced and the target 10% nitrogen loading. This means that a single pass NH_3 converter could be used and the expense of separating and recycling unconverted hydrogen is eliminated. The 68.4% hydrogen is then available for sale or use by the power company/fertilizer partnership. This last bracket shows that the ECOSS process thus favors the inefficiencies of ammonia production and reduces costs inherent in trying to achieve high conversion rates of hydrogen.

Conclusions

This concept of biomass energy production with agricultural charcoal utilization may open the door to millions of tons of CO_2 being removed from industrial emissions while utilizing captured C to restore valuable soil carbon content. This process simultaneously produces a zero emissions fuel that can be used to operate farm machinery and provide electricity for rural users, agricultural irrigation pumps, and rural industrial parks. The use of value added carbon while producing hydrogen (or energy) from biomass can lead to energy with an associated carbon credit (ie negative carbon energy). With this development non-renewable of carbon dioxide producers can work with agricultural communities to play a significant part in reducing greenhouse gas emissions while building sustainable economic development programs for agricultural areas in the industrialized and economically developing societies.

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References

(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/

(2) Gavin, D.G., Brubaker, L.B., and Lertzman, K.P. Holocene fire history of a coastal temperate rain forest based on soil charcoal radiocarbon dates. In press for Ecology: **2003**

(3) IPCC, "Climate change 2001: the scientific basis", Intergovernmental Panel on Climate Change, **2001** (see also at http://www.grida.no/climate/ipcc_tar/wg1/index.htm.)

(4) Walsh, Marie et al., Biomass Feedstock Availability in the United States: 1999 State Level Analysis, **1999** http://bioenergy.ornl.gov/resourcedata/index.html

(5) Glaser et.al, The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics, Naturwissenschaften **2001**, 88: 37–41

(6) Saldarriaga JG, West DC, Holocene fires in the northern Amazon basin. Quat Res **1986**, 26: 358–366

(7) Glaser, et. al., Black Carbon in the Terra Preta Soils of the Brazilian Amazon Region, Proceedings 9th Annual V.M.Goldschmidt Conference, Cambridge, MA **1999**, #7391

(8) Smith NJH, Anthrosols and human carrying capacity in Amazonia. Ann Assoc Am Geogr **1980**, 70: 553–566

(9) Mann, C., The Real Dirt on Rainforest Fertility, Science **2002**; 297:920-923

(10) Hecht, S and D. Posey. "Preliminary Results on Soil Management Techniques of the Kayapó Indians." Advances in Economic Botany **1989**, 7: 174-188.

(11) Y. Yeboah,et al., Hydrogen from Biomass for Urban Transportation, Proceedings of the **2002** US DOE Hydrogen Program Review

(12) Day, Danny; Robert Evans, James Lee U.S. Patent Application, **2002**

(13) Asada, T. et al, Science of Bamboo Charcoal: Study on Carbonizing Temperature of Bamboo Charcoal and Removal Capability of Harmful Gases, Journal of Health Science **2002**, 48(6) 473-479

(14) Matsui, T. et al, Preparation and Analysis of Carbonization Products from Sgi, Cryptomra japonica D. Don) Wood. Nippon Kagakukaishi **2000**; 1:53-61 (Japanese)

(15) Nishimaya, K. et al., Analysis of Chemical Structure of Wood Cjrcoal by X-ray photoelectron spectroscopy **1998**, Journal of Wood Science,44, 56-61

(16) Lee, J. W.; 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

(17) Lee, J. W.; Li, R, Method for Reducing CO2, CO, NOx, and SOx Emissions, 1998 Oak Ridge National Laboratory Invention Disclosure, ERID 0631; **2002** U.S. Patent No. US 6,447,437 B1.

(18) Lee, J. W., and R. Li, Integration of Coal-Fired Energy Systems with CO2 Sequestration through NH4HCO3 Production, Energy Conversion Management **2003**; 44: 1535-1546.

(19) Schleppi P., Bucher-Wallin I., Siegwolf R., Saurer M., Muller N. & Bucher J.B., Simulation of increased nitrogen deposition to a montane forest ecosystem: partitioning of the added N; Water Air Soil Pollution **1999**; 116: 129-134

(20) Glaser B., Lehmann J., Zech W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. Biology and Fertility of Soils **2002**; 35: 219-230.

(21) Wardle, D. A. et al., The charcoal effect in Boreal forests: mechanisms and ecological consequences**,** Oecologia **1998**; Volume 115 Issue 3: 419-426

(22) Pietikäinen, Janna, Soil microbes in boreal forest humus after fire (thesis **1999**) http://ethesis.helsinki.fi/julkaisut/maa/mekol/vk/pietikainen/soilmicr.html

(23) Runkel, R.O.H and Wilke, K, Chemical composition and properties of wood heated at 140C to 200C in a closed system without free space. Part II Holz als Roh und Werkstoff **1951**; 9: 260-270 (Ger.)

(24) Godsy, E. Michael, Impact of Human Activity on Groundwater Dynamics (Proceedings of a symposium held during the Sixth IAHS Scientific Assembly at Maastricht, The Netherlands, July 2001). IAHS Publication no. 269, **2001**, pp. 303–309.

(25) Li, E. Hagaman, et al., "Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase," Energy & Fuels **2003**; 17: 69-74.

(26) Oberstiener, 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**.

(27) Hall, D.O., F. Rossillo-Calle, R.H. Williams and J. Woods,: Biomass for energy: Supply prospects. In: Renewable Energy: Sources for Fuel and Electricity [Johansson, T.B., H. Kelly, A.K.N. Reddy, and R.H. Williams (eds.)]. Island Press, Washington, D.C., **1993**:593-652
(28) Mann, C., The Real Dirt on Rainforest Fertility, Science **2002**; 297:920-923
(29) 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
(30) Glaser, et.al, Potential of Pyrolyzed Organic Matter in Soil Amelioration, 12th ISCO Conference, China, **2002**; 3:421
(31) Nishio, M., Microbial Fertilizers in Japan, Bulletin by National Institute of Agro-Environmental Sciences, Japan, **1999**
(32) Ogawa, M., Effect of charcoal on the root nodule and VA mycorrhizal formation of soybean, Proceedings of the Third Inter-national Mycology Congress, Tokyo, Ja-pan, **1983**: 578
(33) World Carbon Dioxide Emissions from the Consumption of Coal, 1992-2001 http://www.eia.doe.gov/emeu/iea/tableh4.html
(34) Mosier, et.al, Closing the Global N2O budget: Nitrous Oxide Emissions through the Agricultural Nitrogen Cycle, Nutrient Cycling and in Agro Ecosystems **1998**, 52: 223-245
(35) Spath, et al, Update of Hydrogen from Biomass -Determination of the Delivered Cost of Hydrogen, National Renewable Energy Laboratory, Milestone Report for the U.S. Department of Energy's Hydrogen Program **2001**, United States