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

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Introduction: A Sustainable Carbon Sink With Hydrogen Production

The increasing anthropogenic CO₂ emissions and possible global warming have challenged the United States and other countries to find new and better ways to meet the world’s increasing 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 charcoal. This char and carbon (“C”) material represent a form of sequestered C that decomposes extremely slow[2] and retains the bio-capture CO₂ 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 CO₂, accumulated at rates ranging from 1.9 to 6.0 Pg C/yr and increasing CO₂ 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 CO₂ 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] The study noted that acidic functional groups can potentially be stored in certain soils (pH > 7.9) and component (HCO₃⁻) from biomass, which can directly capture greenhouse gas emissions at the smokestacks by converting CO₂, NOₓ, and SOₓ emissions into valuable fertilizers (mainly NH₄HCO₃, -98% and (NH₄)2SO₄ and NH₄NO₃, <2%).[7] These fertilizers can potentially enhance crop growth in sequestration of CO₂ into soil and subsoil layers, reduce NOₓ contamination of groundwater, and stimulate photosynthetic fixation of CO₂ from the atmosphere. As discussed above, the low temperature charcoal forms surface acid groups, which allow efficient binding of ammonia and provide a porous media for nucleation of CO₂. When used as a scrubbing agent with fossil fuel exhaust, it 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 (HCO₃⁻) of the NH₄HCO₃ 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 charcoal 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. [19] The key step in this technology is an NH₄+CO₃+H₂O reaction system to form solid NH₄HCO₃ process that can remove flue-gas CO₂ emissions by ammonia carbonation through out 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 CO₂. 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.

Adding nutrients to soils does not mean that they become immediately available for plant growth[20]. 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 that could act as a nitrogen-nutrient carrier and resist leaching. It appeared that charcoal addition from even 2000 years ago is still providing significant soil fertility benefits[21] as farmers report up to three in research conducted on Brazilian terra preta soils by Glaser, Lehmann, Steiner, which included the addition of charcoal to non terra preta soils[22]. The material could be considered comparable to those that have been made in a smoldering forest fire. Chars have been found to support microbial communities.[8] The breakdown of plant matter, the adsorption of these nutrients by a layer of char below and a niche for microbes to grow. An illustrative chart shows properties of char formation, which can vary according to the composition of the originating biomass. 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, 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 for this
reason. 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.

Experimental Set-up and Results: SEM Investigation of a Low
Temperature Char
The physical structure of the cellulose material is apparent. The char
particles are a hard carbon with more strength than the higher temperature
chars, but grinds easily. These particles are hydrophobic in nature and
differ from char made at high temperatures. Its surface shows evidence of
the cellulose layers. 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. Using the
parameters established in the bench scale char production, we selected 400
°C as the target temperature for the char to reach before being discharged
from our pyrolysis reactor. The material was fed into the pre-heated reactor
and the gases that evolved were flared. No external heat source was needed
and the materials rapidly moved into an exothermic reaction. The continuous process system was automatically fed material by a level
indicator and discharged into a nitrogen purged 55-gallon drum upon
reaching 400 °C. 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 CO₂ can be achieved via formation
of solid NH₄HCO₃ through ammonia carbonation in the gas phase. The
results indicated that it is possible to use NH₄+ H₂O+CO₂ solidifying
process in gas phase to remove greenhouse-gas emissions from industrial
facilities such as a coal-fired power plant. A joint ORNL and Eprida, Inc.
study of specifically designed char materials produced by Eprida, Inc. from
a biomass pyrolysis process, indicated that it might also be possible to use
those char particles for sequestration of power plant greenhouse gas
exhaust. It was assumed that the char could potentially be used as a catalyst
(providing more effective nucleation sites) to speed up the formation of
solid NH₄HCO₃ particles in the NH₃+CO₂-solidifying NH₄HCO₃ production
process, thus potentially enhancing the efficiency of the NH₃+CO₂-
sequestration technology. Furthermore, the integrated process technology
could produce a valuable NH₄HCO₃-char particle that could maximally
enhance sequestration of carbon into soils and remove SOX and NOX while
providing an ideal “Enriched Carbon, Organic Slow-release Sequestering
(“ECOSS”) 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. The question of
whether the NH₄HCO₃ fertilizer could be created in the low temp char
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. A 250g charge of 30-45 mesh 400 °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 NH₄HCO₃ to be supported by fluidized gas flows. The longer durations produced significantly larger particles.

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

SEM Investigation of the Interior of an ECOSS-15 Char Particle
The very small molecules of NH₃,H₂O (hydrated ammonia) are adsorbed into
the char fractures and internal cavities. As CO₂ enters, it converts the
NH₃,H₂O into the solid NH₄HCO₃, trapping it inside the microporous
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.

Next small deposits begin to form inside the carbon framework. There
appear to be plenty of open spaces for microbial interaction. Additionally,
reformation of polycondensates on the carbon structures may contain
nutrient sources for enhancing microbial activity.

The exact duration for ultimate delivery and release of nutrients solidified
deep in these internal pore structures need further testing both in bench
scale and soil plot testing. Future testing and analytical work will
hopefully, discover ways to enhance the process and material. Yet, the
simple physical solidification of a nutrient material and sequestered CO₂
inside the char structure can be seen with the fibrous NH₄HCO₃ deposits.
This demonstration of the process shows that we can deposit nutrients
inside the porous media using a low cost gas phase application.

Reforming (assuming total conversion of carbon to CO₂) will require
(stoichiometrically) 28.35 kg steam and will produce 88 kg CO₂ and 8.35
kg hydrogen. Because only 2.64 kg H₂ is necessary for ECOSS (using all
charcoal available from the process) 6.78 kg (68.4% total production) of
hydrogen will remain per every 100 kg of biomass.

The amount of C, converted from atmospheric CO₂ is equal to 12 kg for
each 79 kg of NH₄HCO₃ or 15.2% of the sequestered carbon as a
ammonium bicarbonate. Therefore for each 100kg of biomass, we will
produce (12/79)*141.4 kg or an additional 6.29 kg of C or a total of 28.3 kg
of utilized carbon. In acid soils, this part of the carbon will convert to CO₂
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 CO₂, 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 CO₂ 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
delivered and the resulting CO₂ impact. With 6.78 kg hydrogen extra
produced per 100 kg of biomass, then 256.78 = 3.69 kg C/ kg H
and 66.63x3.69=13.5 kg CO₂ / kg of hydrogen produced and used for energy.
From a power perspective, that is 13.5 kg CO₂ / 120,000 J of hydrogen
consumed as a renewable energy or 112 kg/GJ of utilized and stored CO₂.

Global Potential The large majority of increases in CO₂ will come from
developing countries as their burgeoning entrepreneurial populations
industrialize. A sustainable technology needs to be able to scale to meet the
growing needs of this large segment of the population. Developing an
economical size that offers a profitable platform may require certain
minimums and it may be that the lower limit of economical production are
larger than typical biomass conversion systems. A 1-2 MW facility could be
the lower limit yet there are two factors that are important to note. The first is
that the low relative efficiencies required by both the hydrogen separation
and the ammonia production may allow a smaller foot print system to be
developed using new technologies. Future research efforts in separations
technologies and ammonia catalyst could offer developments that lead to
systems for even very small farming communities.

The second point is that the total hydrogen is approximately three times the
maximum that can be utilized in one facility, so every third facility could be
designed to accept the charcoal that is produced by two standalone energy
systems. This special facility could process all of its hydrogen and the
charcoal from two other locations and use existing industrial ammonia
manufacturing techniques to create the carbon-fertilizer. If all hydrogen is
captured and converted to fertilizer then there is an opportunity to acquire outside CO₂
(34 kg required for each 100 kg biomass processed) and the opportunity to

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earn revenue from SOx, NOx removal could provide it with another income stream and help its economics. It would also fit closely into strategies of developing areas that wish to attract and support GHG emitting manufacturing.

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 CO2 Capture and Sequestration (BECS) [32]. The effects (i.e., providing 112kg of CO2 removal for each GJ of energy used) could allow major manufacturers to offset their carbon costs. 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.

For a quick test of reasonableness, we saw from above that 1GJ of hydrogen produced and used will represent 112kg of utilized and stored carbon dioxide. Therefore, taking the atmospheric rise of 6.1GT and dividing 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. [35] 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.

The economic projections of the UT study were based on a market value of the end-product at $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 economical production of fertilizer and would yield a after tax ROI of $0.33. The investment required to meet this level of CO2 capture would be $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 only require a production unit one-fifth the size. This should be considered 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 be required to be manufactured, however, more hydrogen can be produced for fuel.

\[8\text{NH}_3 + 8\text{CO}_2 + 8\text{H}_2 \rightarrow 8\text{NH}_2\text{HCO}_3\]

Therefore, renewable hydrogen allows a 1.6 times increase in CO2 captured per lb-mole of NH3HCO3 produced. Utilizing the study above, a switch to renewable hydrogen would increase carbon capture, 3.15 x 1.6 = 5.04%. However, carbon closure of biomass energy is not zero but has been calculated (Spath&Mann-1997) [38] at 95%. A more accurate number would be 5.04 x 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 NH3HCO3 scrubbed from power plant exhaust. As stated before, the total Carbon 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 reduce total C from coal combustion by ~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. The factors of increased biomass growth with the addition of charcoal as found by Mann [39], Hoshi [40], Glase [41], Nishiyama [42], and Ogawa [43] 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). Therefore, another bracket in our assessment of this process is the increase in non-fossil fuel CO2 capture from biomass growth in addition to the leveraged total.

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 NO2 atmospheric release. This potential greenhouse gas is equivalent to 310x the impact of CO2. The fertilizer industry produces CO2 during the manufacture of ammonia from methane.

\[4\text{N}_2 + 3\text{CH}_4 + 6\text{H}_2 \rightarrow 3\text{CO}_2 + 8\text{NH}_3\]

The equation illustrates that 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 number in relative terms to the amounts released by combustion of coal (2427 million tons) [44] however if we assume (Mosier-1998) [45] 1.25% of our nitrogen fertilizer escapes into the atmosphere as N2O, then 1.923 million tons of N2O are released, with an CO2 equivalence of 595.9 million tons or 162.5 million tons of C equivalent. This has an impact equal to 6.7% of all the worlds combustion of coal. Kaiser has measured N2O flux in sugar beets, and two crops of winter wheat under three recommended fertilization rates. [46] His work found relative N2O from the applied N fertilizer ranged between 0.7% and 4.1%. The highest level could equate to as much as a coal fired power plant in some areas. While this high level is not the average, the fact that a typical farm fertilizer application can represent the same emissions impact as a small coal fired plant is one that many do not consider as they look across the expansive green fields of modern agriculture. This bracket then demonstrates that effective efforts, such as in the slow release of nutrients, to reduce the distributed release of N2O from fertilizer can play a substantial role just as will reductions sought from fossil fuel combustion.

The economics of hydrogen from biomass has been addressed in the 2001 report by Spath [47]. Their conclusion was that pyrolytic conversion of biomass offered the best economics due in part to the opportunity for co-product production and reduced capital costs. However, this assessment was based on using bio-oil for reforming and acknowledged uncertainty in pricing for co-products. Their analysis, at a 20% IRR, provided plant gate pricing of hydrogen from $9.79-$11.41/GJ.

In the UT study, hydrogen production equipment represented 23% of the total capital equipment costs and utilized a $4/GJ expense for methane. This cost represented ~50% of total expenses and ~45% of before tax profits. If we assume that other operational costs remain the same, with the increased cost of natural gas, the inside plant cost of renewable hydrogen would no longer be 2.4-2.8 times the costs from methane, but is approaching 1.6-1.9 times. Since net profits were based on market price of nitrogen, then increases in natural gas prices will change total income in the model as well. For simplicity if we use $7/GJ, then total income would increase 1.75% and expenses related to renewable hydrogen would roughly equal ~50% of before tax profits. This represents a third bracket in assessment. Intra plant usage of renewable hydrogen (i.e. no storage or transport expense) becomes significantly more competitive at our current natural gas prices.

The last bracket comes from a review of traditional ammonia processing methods and how they compare to the ECOSS process. Due to unfavorable equilibrium conditions inherent in NH3 conversion, only 20-30% of the hydrogen is converted in a single pass (UT) 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 NH3 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 CO2 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 (i.e 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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