Abstract: Converting fossil hydrocarbons (FHC) into agrichar would be an alternative to remediate global warming, through replacing FHC energy by bioenergy derived from improving soil fertility by agrichar application.

INTRODUCTION

Anthropogenic alterations of carbon flows between the atmosphere and the terrestrial carbon sources and sinks can affect global climate change. For example, actual emissions of CO$_2$ to the atmosphere by the combustion of fossil hydrocarbons (FHC), about 6 G ton C per year, would theoretically almost double the actual atmospheric CO$_2$ content (750 G ton C) by the end of this century, thus increasing global warming by the greenhouse effect. Therefore, the first option to offset global warming is the partial replacement of FHC fuels by other energy alternatives in order to decrease emission rates of CO$_2$. On the other hand, improving soil fertility would lead to creating new land suitable for crops and to enhance the conversion of non-forest land to forest (afforestation), tending to decrease CO$_2$ atmospheric content as a result of photosynthesis, particularly if crops in the newly-created fertile lands include biofuel raw materials for FHC fuels replacement.

Another option for decreasing the greenhouse effect promotes carbon sequestration by underground storage of CO$_2$ emitted from FHC stationary processes, as well as by land application of biochar. Biochar applications involve the agricultural technique “slash-and-char,” anciently developed by Amazonian natives who created the terra preta: a fertile soil characterized by its very high organic carbon content, as high as 250 tons of elemental C per hectare. The soil’s organic carbon, where biochar can be included, represents the largest reservoir of carbon in most terrestrial ecosystems and changes of this reservoir can influence the global carbon balance and therefore the global climate.

One problem in creating synthetic terra preta is the very high amount of biomass required to prepare the biochar to achieve such high carbon content in the soil. Agrichar is a more general denomination of bio-char to emphasize its agricultural application and the possibility of being originated from other non-biomass materials. Accordingly, the objective of this article is to consider the possibility of preparing agrichar from FHC. This would not only increase land productivity derived from higher soil fertility, but would also provide sequestration of carbon that would otherwise be emitted if using FHC as a fuel.
AGRICCHAR TO IMPROVE SOIL FERTILITY

Agrichar (or biochar) is a porous black, carbon material that may make applied fertilizers more efficient in providing nutrients and to serve as a habitat, protecting soils from grazing protozoa, for the growth of beneficial bacteria and fungi.

These chars can be obtained as by-products from the biomass processing industry, offering the opportunity to turn it into a carbon-negative bioenergy industry. By withdrawing carbon from the biomass cycle of photosynthesis-decomposition-mineralization, biochar sequestration in soil directly removes CO₂ from the atmosphere.

Figure 1. Slit micropore structure model (pore widths = 1 – 10 nm).

Assuming that the ideal structure for an agrichar is similar to that of an activated carbon synthesized from biomass, it is expected to have large pore volumes covering a variety of pore widths ranging from micropores (less than 10 nm), mesopores, and macropores (more than 100 nm). The slit-like geometry resulting from the parallel arrangement of graphene sheets (Figure 1) predominates in the micropore range, whereas most macropores preserve the capillary framework of the raw biomass material (Figure 2). Agrichar and beneficial microorganism associations improve symbiosis with plants so that refuges are available in micropores for small bacteria (e.g., rizhobium) and in macropores for larger microorganism (e.g., mycorrhize).

In addition to being a refuge for beneficial microorganisms, another hypothesis on the function of agrichar is that of the important elements for soil fertility: N, P, K, etc., are “decorating” the edges of the agrichar porous structure forming substituted graphenes with functional groups (carboxylates, amines, phosphates, etc.) as shown in Figure 3. Some of these functional groups (e.g., carboxylates) are probably involved in increasing cation exchange capacity in soil. On the other hand, agrichar may be related to humus substances within the rizosphere. (Humus is the group of organic, large-molecular-weight compounds, very important to soil fertility, resulting from the first step of decomposition of materials creating life). Accordingly, partial stabilization of humus by agrichar diminishes continuing decomposition to mineralization and eventual lixiviation.

Another effect of agrichar applications in soil is that it makes soil darker. It has been debated that the anthropogenic establishment of the Amazonian terra preta (translated from Portuguese: black earth), is essentially similar to what it would be in an inorganic soil artificially enriched with about 250 tons of elemental C per hectare. As infrared reflection is smaller in darker soils, inter-phase heat transfer between soil and the atmosphere must be affected, probably decreasing evapotranspiration and favoring water condensation over darker soils. Therefore, one may speculate that if the yellow tone of an arid zone is converted into a darker one, for example covering or mixing the soil with agrichar, this zone would, after a certain period of time, experience rainfall changes that would improve the vegetable life. However, the linkage between darker soils and local/regional water cycles is not comprehensive in regards to the relevant literature associated with climate change.

Research on Amazonian terra preta suggests that biochar may remain in soils for several hundred years, allowing extraordinary fecundity. This is probably connected to the recalcitrant properties of biochar which grant it to be a significant pool of stable organic carbon (e.g., humus) in soils. For example, many sugarcane plantations in tropical America have been continuously harvested since colonial times with the only addition of burnt crop residues (i.e., biochar) plus ash recovered from a nearby “Ingenio” (sugar cane processing factory). Nevertheless, there is a need for long term information on the efficacy of biochar-induced crop benefits.

The original terra preta recipe of ancient Amazonian natives included bones besides the biochar. Bones contain calcium phosphate having a macro-porous structure with large pore volumes (up to 50 % vol) similar to coralline exoskeletons (see Figure 4). In fact, corals are used as a bone graft substitute for some surgeries. These natural materials can be referred to as biorock, and the macro-pore structure of the biorock would certainly add more room for the beneficial micro-organisms in the terra preta. Today’s livestock bones are recycled into food and not into soil as Amazonian natives did. Therefore, the use of coralline biorock may be an object of further studies as a soil conditioner, particularly the biorock that could be obtained from bleached coral reef barriers.

The main problem associated with the preparation of synthetic terra preta to induce soil fertility would be the enormous amount of biomass that must be pyrolyzed to produce the agrichar required. As an example, assuming that 250 tons of agrichar are required to prepare one hectare of terra preta soil in the extreme case of starting with an inorganic desert soil; this is equivalent to about 700 tons of wood. Therefore, one alternative would be to use agrichar prepared from FHC, particularly those with a low H/C ratio (i.e., coal and heavy oils, rather than light petroleum and natural gas).

Figure 3. A model for substituted graphene with NPK functional groups.

Figure 2. A macropore structure of carbonized biomass.
USE OF FHC COKE AS AN AGRICHAR

Charring biomass is also referred to as pyrolysis. In the FHC refining industry, pyrolysis may be referred to as thermal cracking: a process used to reduce the average molecular weight of the FHC (e.g., for upgrading coal and heavy oil into more desirable lighter fuels). In its extreme form, pyrolysis converts the FHC into \( H_2 \) plus a porous and stable carbon material: coke. Technologies for FHC pyrolysis include simple processes such as delayed coking for coal and heavy oils, some other more sophisticated technologies such as fluidized bed and flash coking, and others like the microwave plasma more recently developed for methane pyrolysis.

Coke produced from FHC serves as raw material for the metallurgical industry, but alternate uses for coke will be worth having if FHC pyrolysis is adopted on a large scale. Presently, worldwide metallurgical coke (i.e., calcined coke) is mainly produced from coal, whereas at some petroleum refineries, green coke is a by-product accumulated for sale. This scenario may become more realistic after a more intense exploitation of the world’s vast reserves of low \( H/C \) FHCs (e.g., the shale bitumen in Canada, the heavy oils in Venezuela and the many unexploited coal deposits existing in the world).

One possible alternative for the use of coke obtained from FHC pyrolysis may be one of the options cited above for carbon sequestration in terrestrial ecosystems: applications for land like a biochar. This means that carbon extracted from the underground fossil deposits are returned to the ground after pyrolysis, but instead this time toward the surface, i.e., to the soil.

However, the possible use of coke as an agrichar has apparently not been considered in detail yet, though physical-chemistry characteristics of coke could be similar to those of chars obtained by pyrolysis of biomass. More research is necessary in order to specify agrichar standards to search preparation procedures and the efficacy of agrichars produced from FHC.

Simple calculations show that if all the world’s proven conventional FHC reserves (about 1,000 G ton C) were processed by pyrolysis, and the coke produced were used as an agrichar at a terra preta rate of 250 ton/ha, this would suffice to cover 4 Gha: about one third of the planet’s ice-free land. Coincidentally, the world’s ice-free land (about 12 Gha) could be split into approximately three equal parts. One part is fertile land suitable for agriculture and livestock pastures; another part is forest (Amazonas, Siberia, Canada, etc.); and the third part is infertile land (deserts and other arid lands). Therefore, hypothetically 4 Gha of infertile land would be available in the world for land-cover change by additional coke produced from FHC reserves, looking toward the conversion of that infertile land to a new 4 Gha of fertile land.

Assuming a value for sugar cane plantations of 5 tons of sugar per hectare yearly, a volume of about 80 Gbbl (1bbl = 160 liters) of bio ethanol could be obtained annually from sugar cane harvest in the new fertile 4 Gha. This is equivalent to almost three times the world’s actual petroleum production (about 30 Gbbl).

Interestingly, combining sea water desalination with synthetic terra preta using agrichar from petroleum coke could be the way to create fertile land in arid scenarios like those of petroleum producing countries found in the Middle East and North Africa.

CONCLUSIONS

A development originated by the ancient Amazonian natives more than a thousand years ago, terra preta, is being rediscovered for the preparation of fertile land using agrichar. FHC coke used as an agrichar to increase the extension of fertile lands could promote bioenergy and \( CO_2 \) sequestration, aiming for both the replacement of FHC fuels and the remediation of global warming.
The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association are pleased to announce the creation of the journal, **Coal Combustion and Gasification Products**.

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Contributions should include papers describing original research results; proceedings of symposia; surveys; book reviews; overviews of recent literature; and letters to the editor. While the emphasis is on products from coal combustion and gasification, products of the co-combustion of tires, petroleum coke, biomass, etc., with coal will also be considered. Above all, a contribution accepted for publication should be a novel, original, concise, and well-written advancement in the science and/or engineering of coal combustion and gasification products.

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For more information: www.worldofcoalash.org
The growing threat of climate change caused by greenhouse gases was created by our industrial activity, but solutions to the climate crisis may lie as much with nature as with industry.

Many current proposals to reduce atmospheric greenhouse gas concentrations require dramatic progress in technologies that do not currently exist. Carbon capture and sequestration (CCS) is one such technology. CCS is not currently feasible at an industrial scale, and a huge R&D effort will be needed to determine whether it is practical. If it is proven feasible, an enormous industrial infrastructure will need to be developed to implement CCS on the scale required to create a significant reduction in emissions. Other technologies, such as replacement of liquid fossil fuels with cellulosic ethanol, are also in the formative stages.

Are there existing or nearly-mature technologies and policies that will enable us to implement emissions reductions quickly? If so, we may be able to buy time to allow other technologies to mature and become financially viable. Substantial reductions in atmospheric greenhouse gases could be obtained through changes in management of forests and soils.

**FORESTS**

The world’s vegetation holds about 600 Gt (Gigatons, or billion metric tons) of carbon, excluding soils. Most of this is in forests, both temperate and tropical. Tropical forests are extremely important in removing carbon from the atmosphere.

Tropical forests take carbon out of the atmosphere faster than previously thought. Each hectare of remaining tropical forest is removing carbon faster than it used to, due to the fertilizing effect of increased atmospheric carbon dioxide and nitrogen deposition. Current estimates are that tropical forests remove about 1.6 Gt per year from the atmosphere. Tropical forests are rapidly being lost by conversion to other land uses. Felling and burning of tropical forests currently releases about 1.8 Gt of carbon per year into the atmosphere. At present, the growth of remaining forests nearly offsets the release of carbon due to forest destruction.

Tropical forest conservation is thus a critical part of any solution to the climate problem. Money spent on avoiding further forest destruction, or better yet to encourage increased tropical forest coverage, would be well spent. Reduction of Emissions from Deforestation and Degradation (REDD) is a structure for reducing loss of tropical forests and was approved at the Bali round of climate talks in 2007. Investments of between 7 and 28 billion dollars per year could cut deforestation in half, and make tropical forests an important component in removing carbon from the atmosphere. There are problems both of enforcement and verification, to ensure that money spent in developing countries actually is used to halt deforestation, and mechanisms are being developed now.

Temperate forests are more problematic. It now appears that temperate forests, while important for biodiversity, ecosystem services and commerce, do not have a huge potential to increase carbon dioxide removal from the atmosphere. At high latitudes, converting land to the dark surface of forests may actually contribute to global warming by reducing their albedo, or reflectance. This is not an argument against conservation of temperate forests, but does suggest that investments in growing more forests at high latitudes will not result in a reduction in carbon in the atmosphere.

Reforestation (restoring existing forests) and afforestation (growing forests on lands currently used for other purposes) could remove approximately 94 Gt of carbon from the atmosphere between now and 2060. This assumes that countries implement REDD schemes quickly and that we maximize the potential for forest plantations at low latitudes.

Forests are a short-term solution to the greenhouse gas problem. Trees die and decay, returning some of their carbon to the atmosphere. Over the next 100 years, increasing forest growth and avoiding further destruction of forests could contribute to solving the climate problem, but over longer time scales, other solutions will be needed. Forestry effectively buys time for other solutions.

**SOILS**

Soils hold vast amounts of carbon, mostly in the form of organic matter. Soils currently contain around 1,500 Gt of carbon, about twice what is in the atmosphere.

Agricultural practices often reduce the amount of carbon in soil. Many farming practices, such as annual plowing, gradually reduce soil organic matter, by increasing soil respiration by microbes. Since the advent of mechanized agriculture, soils have lost about 78 Gt of carbon. When soil organic matter is depleted, soils are less stable and more prone to erosion. They are also less productive. Tropical soils, which often contain little organic matter, can completely lose their productivity after only one or two crop harvests.

Modern agricultural techniques can substantially increase soil carbon storage. Converting traditional plowing to no-till agriculture could absorb about 5% of current carbon emissions. Improving animal husbandry methods and converting pastures to mixed native species can substantially increase accumulation of carbon in pasture soils. In the long run,
converting annual crops to perennial crops can make a large contribution to soil carbon storage.

The greatest opportunity to use soils for carbon storage may lie in biochar incorporation into soils. Biochar is charcoal obtained by low-oxygen burning of wood and other organic materials. Incorporation of biochar into soils was invented by ancient people of the Amazon basin, who used the method to make tropical soils more fertile. This manmade soil was known as terra preta, or black earth. Biochar enriches soils and promotes the growth of beneficial microorganisms. Carbon content of terra preta soils can be 10 times the carbon content of ordinary agricultural soils.

Biochar is produced by pyrolysis, combustion at low oxygen concentrations. Current technologies for making biochar are inefficient, losing about 50% of the dry matter in wood to the atmosphere. Recent developments in industrial biochar production allow the capture of heat, hydrogen or biodiesel fuel from the combustion process. Biochar production can become a component of biofuels production.

Worldwide implementation of biochar programs could remove up to 31 Gt of carbon from the atmosphere by 2060. Additional removal by best-practices soil management could remove an additional 20 Gt. Unlike many approaches to reducing atmospheric carbon, forestry and agriculture approaches do not require an enormous expenditure on industrial infrastructure.

The combination of preservation of existing tropical forests, recovery of previously destroyed forests, conversion of agricultural techniques to no-till and other carbon-sparing soil management, and the extensive use of biochar in soils, could dramatically reduce the rate of carbon dioxide accumulation in the atmosphere.

At relatively low cost, and with largely existing technology, agriculture and forestry could remove at least half of expected total carbon emissions by 2060. Combined with energy conservation, these solutions could buy us many decades in which to consider other technologies to reduce emissions and stabilize the atmosphere. Agriculture and forestry approaches to reduced greenhouse gases would also benefit farmers and forest owners financially, since they could sell carbon credits in a cap-and-trade market.

Forestry and agriculture offer the hope of dramatically reducing our risks due to climate change while at the same time enhancing agricultural productivity and eliminating destruction of tropical forests. These approaches can be used now, can be done cheaply, and do not require the development of major new technologies.

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