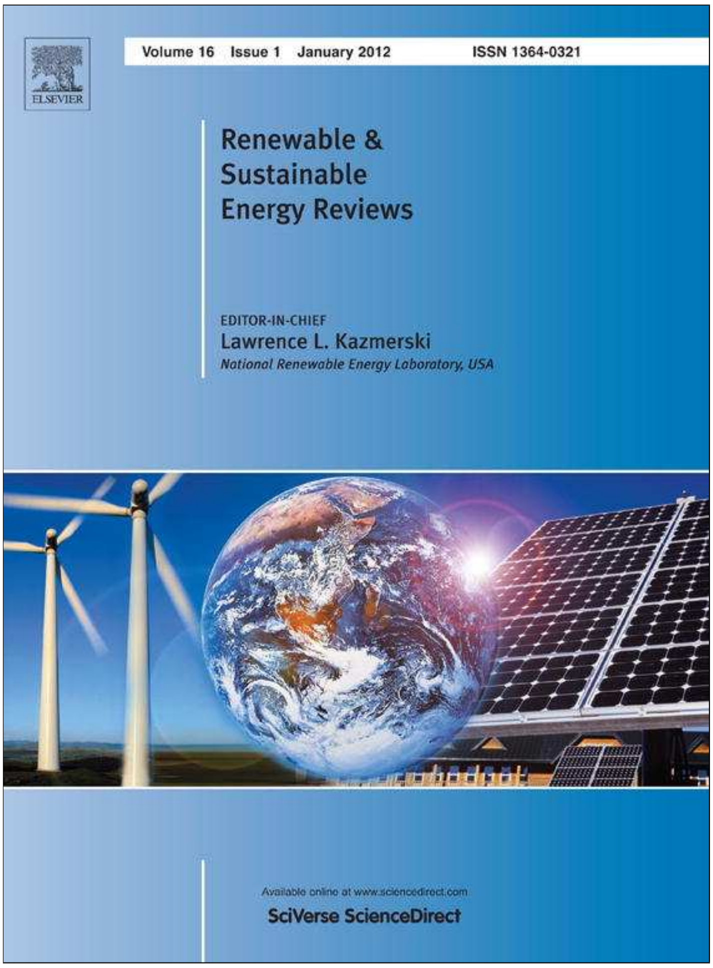
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Perspective of the preparation of agrichars using fossil hydrocarbon coke

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The increasing demand of fossil fuels and decreasing light oil proven reserves lead to a future scenario of abundant coke production from the refinement of non-conventional fossil hydrocarbons. This paper highlights the possibility of using coke as an agrichar for preparing fertile soils resembling Amazonian *terra preta*. It is suggested that this alternative may contribute to both the capture of greenhouse gas by afforestation and the increase of rainfall by the albedo effect. It is proposed that the ideal agrichar must function as a store of nutrients in the form of graphene substituted NPK groups at the micropore molecular structure, providing habitat for plant friendly microorganism inside its macropores. The possibility of a sink effect connecting nutrient storage with microorganisms has also been proposed. A preliminary discussion on the possible coking procedures to improve the resulting agrichar efficacy, three options for large scale desert greening using agrichar as well as recommendations for further research are presented.

Contents

1. Introduction: biochar application in soil

One option proposed for decreasing global greenhouse effects is the land applications of biochar [1], a stable porous solid obtained from biomass pyrolysis; also referred to as black carbon [2], to indicate that it is a pyrogenic carbon. One means of biochar application to land is based on the agricultural technique "slash-and-char," probably employed by ancient Amazonian communities that created soil preserved till today in parcels of several hectares, referred to as *terra-preta* ("black earth" in Portuguese), characterized by having very high organic carbon content and sustainable fertility [3,4,5]. Soil organic carbon content, including biochar, represents the largest reservoir of carbon in most terrestrial ecosystems, and changes in this reservoir can influence the global carbon balance and therefore, the climate change [6].

Besides serving for capturing and storing carbon [7], referred to as CCS by the environmental science media, sequestering biochar in soil may also serve to improve soil fertility by preventing organic matter (particularly humus) from being rapidly mineralized and lixiviated, therefore serving as storage for plant nutrients which are eventually transferred to plant root by diffusion phenomena. In addition, biochar porosity provides space for the habitat of plant friendly microorganism such as rhizobium bacteria and mycorrhiza fungi [8,9] protecting them from grazing protozoa. Indeed, one parameter directly related to soil life: concentration of ATP (Adenosine triphosphate: $C_{10}H_{16}N_5O_{13}P_3$), is reported to increase after mixing soil with biochar [10].

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Consequently, and taking into account the predictions suggesting large stocks of coke by-product from the refinement of non-conventional fossil hydrocarbon (FHC) reserves such as those from the Orinoco heavy oil belt in Venezuela and the Alberta tar sands in Canada, this paper highlights the possibility of using coke as a raw material for substituting biochar application in soils, in particular for large scale *terra-preta-nova* preparation.

2. Use of FHC coke as an agrichar for substituting biochar

Originated from Sombroek's pioneering studies [11,12], the concept of *terra-preta-nova* has been used to refer to a soil artificially prepared with biochar resembling ancient terra-preta. The main problem to prepare *terra-preta-nova* is the very high amount of biomass required to prepare the biochar to achieve the organic carbon content of *terra-preta*, roughly 250 t per hectare per 1 m depth [7]. For example, one hectare of a desert soil with nearly 0 wt% organic matter would require pyrolysing about 500 t of wood or more, according to the solid yield.

Agrichar is another denomination for chars to emphasize its agricultural application and the possibility of being originated from other non-biomass materials. Recently, the possibility of using FHC coke as feedstock for agrichars to promote bioenergy has been proposed [13]. Indeed, partially replacing FHC fuels with biofuels derived from improved soil fertility by coke's agrichar application could diminish greenhouse effect due to photosynthesis, particularly if afforestation (i.e., the conversion of a nonforest land to a forest) is carried out. Sustainable global energy supply, based on lignocelluloses' harvest derived from afforestation of world's degraded areas like deserts and others undergoing desertification, may be realized in some decades [14]. Non-fertile lands represent almost one-third of total world's nonpermafrost land [15], a promising sink for atmospheric carbon if photosynthesis is activated using afforestation assisted by both agrichar application and irrigation. The latter could be introduced in dry zones from sea water desalination using renewable energy [16]. As a metaphor, bioenergy would be harvested after sowing FHC.

3. Feasibility of producing agrichars from FHC coke

The proposed use of agrichars prepared from FHC is favored by the fact that the exploitation of low H/C ratio FHC world deposits (e.g., coals, heavy oils, oil shale, oil sand, etc.) is expected to increase because of the exhaustion of the highly demanded light petroleum world reserves. Indeed, as long as upgrading low H/C FHC to obtain liquid fuels using conventional pyrolysis technologies implies large amounts of coke byproduct (e.g., about 30 kg of coke for each bbl of Venezuelan heavy oil processed), the present agrichar alternative might be strengthened in the near future. As a paradox, carbon extracted from the underground fossil deposits would be returned to ground after pyrolysis, but instead this time to the upper-ground, i.e., to the soil.

Certainly, discouragement of FHC industry because of burying a high BTU product could be offset if coke application as an agrichar is converted into a credit after carbon market consolidation. In addition, the continuous rise of renewable energies such as solar, eolic etc., besides nuclear energy, is turning the use of coke for combustion energy less attractive. Although other uses such as the recovery of valuable ash components like vanadium and metallurgy are actually in operation, a significant part of the future coke production should be expected to be surplus. Actually Venezuela and Canada produce about 40,000 t of coke daily from heavy crude oil and oil sands constituting refinery's sub-products accumulated for sale. Total world production was near 100 Mton in 2005.

It should be clarified that low H/C ratio FHC should preferably be pyrolysis feedstock rather than hydrogenation feedstock due to both economic and environmental reasons. Indeed, required hydrogen for FHC refining implies costly gasification processes emitting large quantities of carbon to the atmosphere as CO_2. In contrast, pyrolysis processes, such as destructive distillation, thermal cracking, delayed coking, flexicoking, etc., reduce the average molecular weight of the hydrocarbon fluid mixture sequestrating carbon as solid coke, resulting in a desired gasified stream for condensation.

The technology involved in such refining processes was originated by old coal gasification technologies to produce either fertilizers by the ammonia synthesis or gasoline by Fisher Tropsh synthesis, employing rotary hearth and kiln furnaces, fluidized beds, etc. The use of oxygen instead of air as fuel combustor is a key for the direct heating of the gaseous reactant mixture (H_2O, CO_2) in order to improve gasification kinetic by the absence of nitrogen gas diluent. The recently developed reactor heated by concentrated solar power (CSP) [17] is intended to reduce the need of heating fuel.

Notice that the above cited gasification technologies are also employed for the production of activated carbons worldwide used as adsorbents. Agrichars and activated carbons may have some common characteristics as considered in the text below.

4. Functional structure for agrichar efficacy

Following the above preliminary considerations on the perspective of agrichar applications, physical chemistry factors for modeling efficient agrichars, and preliminary results with petroleum coke, are revised below.

4.1. Chemical structure and texture

Porous solid carbons could be obtained from both biomass and other carbonaceous materials such as FHC. However, there is lack of information on the land use of agrichars prepared from FHC, though physical chemistry characteristics of coke produced from pyrolysis of FHC (also referred to as coking or thermal cracking) could be similar to those of chars obtained by pyrolysis of biomass, particularly if some procedures are adopted in the coking process. Indeed, the highest micropore surface area known (around 3000 m^2/g) has been obtained in activated carbons produced from petroleum coke [18]. In addition, the presence of a gasification catalyst such as potassium appears to be a necessary condition to produce very large surface areas in activated carbons from coke [19,20].

Notice that apart from biochar or agrichar, other porous soil rocks like alumino-silicates (e.g., zeolites) and biorock (animal skeletons: hydroxyapatite: $Ca_5P_3O_{13}H$ and calcium carbonate: $CaCO_3$) would also provide storage space within their porous structure for microorganisms and nutrients. However, from surface science it is known that highest surface areas (i.e., above 1000 m^2/g) are mainly represented in activated carbons featuring a micropore framework of distorted and defected sheets of molecular graphene with slit spacing greater than that in graphite (0.34 nm), as depicted in Fig. 1.

The arrangement of graphene sheets may also constitute small micro (or nano) particles and aggregates as depicted for pyrogenic black carbons (Fig. 2).

Two pore sizes (wide and narrow) can be differentiated forming bimodal pore size distributions [23]; one with wide widths of the order of 10^{-6} m (namely macropores), and another

Fig. 1. Slit micropore structure showing high surface area available for adsorption (minimum slit width = 0.34 nm) [21].

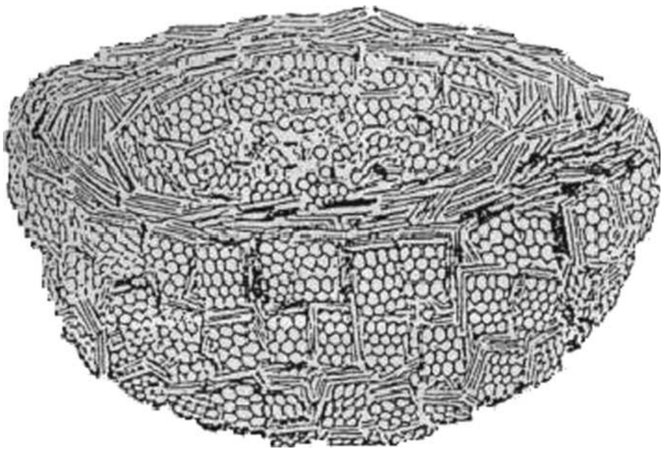

Fig. 2. Model of black carbon texture [22].

with narrow widths of the order of 10^{-9} m (namely nanopores). In case of biomass raw materials, its capillary framework may be preserved forming macropore volume after pyrolysis as shown by microscopy elsewhere [24]. Notice that in conventional nomenclature, nanopores are referred to as micropores, the mesopores being another intermediate class of pores. Slit mesopores as wide as 50 nm have been identified in activated carbon by microscopy [25].

In the case of FHC raw materials, a variety of artifact structures result from pyrolysis involving various mechanisms and plastic steps such as mesophase formations (aromatic liquid crystalline particles), stretching, coalescence, forming lamellar and grained mosaic structures [26]. Possibility of filament growth is also possible when metal nanoparticles (e.g., Ni) are present [27].

Generally, FHC coke and black carbon materials have significant smaller micropore volume and surface area ($\sim$10 m^2/g) than activated carbons ($\sim$1000 m^2/g). The relative low surface areas are ascribed mainly to macropore volume, whereas activated carbon high surface area is mainly related to micropore volume.

In contrast with high surface area activated carbons, petroleum coke has significant graphitic crystallinity as inferred from X-ray diffraction (Fig. 3). On the other hand, biochar and other black carbons generally have no graphitic crystallinity.

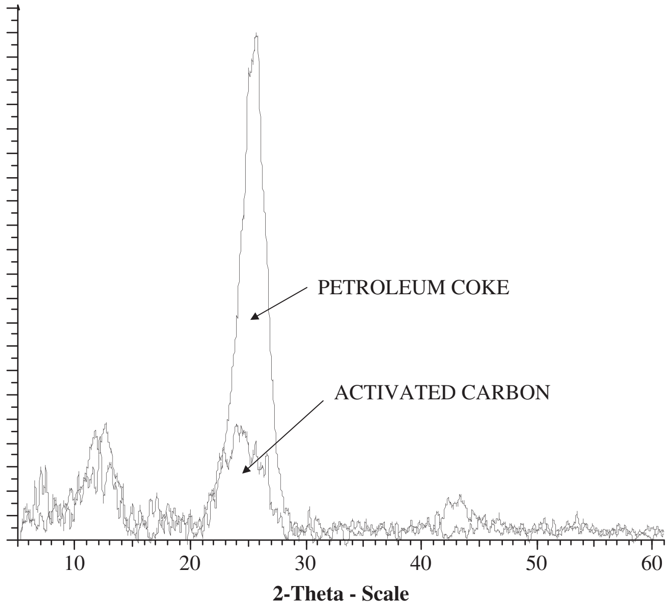

Fig. 3. X-ray diffraction patterns (CuKα) of petroleum coke from delayed coking of Venezuelan heavy oil, and of activated carbon (Merck pro-analysi, Art. 2186).

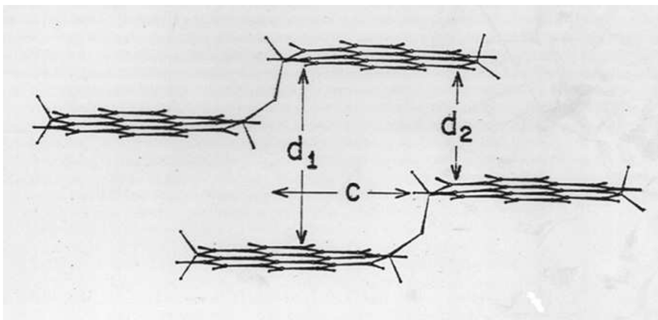

Fig. 4. Scheme of optimal configuration of a pair of PAH units in model activated carbon (micropore dimensions: d_1 = 0.8 nm, d_2 = 0.5 nm and c = 0.7 nm) [28].

Gasification of coke to produce high surface area activated carbon involves partial oxidation reactions:

$C + CO_2 \rightarrow 2CO$, and $C + H_2O \rightarrow CO + H_2$, probably diminishing graphite crystallite sizes and creating surface polycyclic aromatic hydrocarbon (PAH) containing oxygen bonding small crystallites to each other creating microporosity as shown in Fig. 4.

Based on earlier works on the infrared spectra of high surface area of activated carbons [29], a hypothesis is proposed for agrichar acting as a fertilizer as a result of the formation of substituted graphene sheet molecules with chemically exchangeable functional groups, containing N, P, and K elements (Fig. 5). Soil leaching and percolation creates the access to chemisorptions of the nutrients into the carbonaceous porous structure; N (and S) oxides originated from acid rains, as well as from the direct conversion of atmospheric nitrogen into nitrogen oxides and ammonia by soil microorganisms such as rhizobium bacteria, and many others. Other nutrient elements (P, K, etc.) could be chemisorbed after lixiviation from biorock (animal skeletons), as well as from ashes originated by application of slash-and-char procedures. Graphene NPK functional groups would improve plant nutrition by the assistance of the friendly microorganisms inhabiting the porous medium.

From previous researches [30,31], biomass (coconut shell) impregnated with NPK chemical compounds (H_3PO_4, KOH, KPO_4, or KNO_3), submitted to heating (above 400 °C) under CO_2

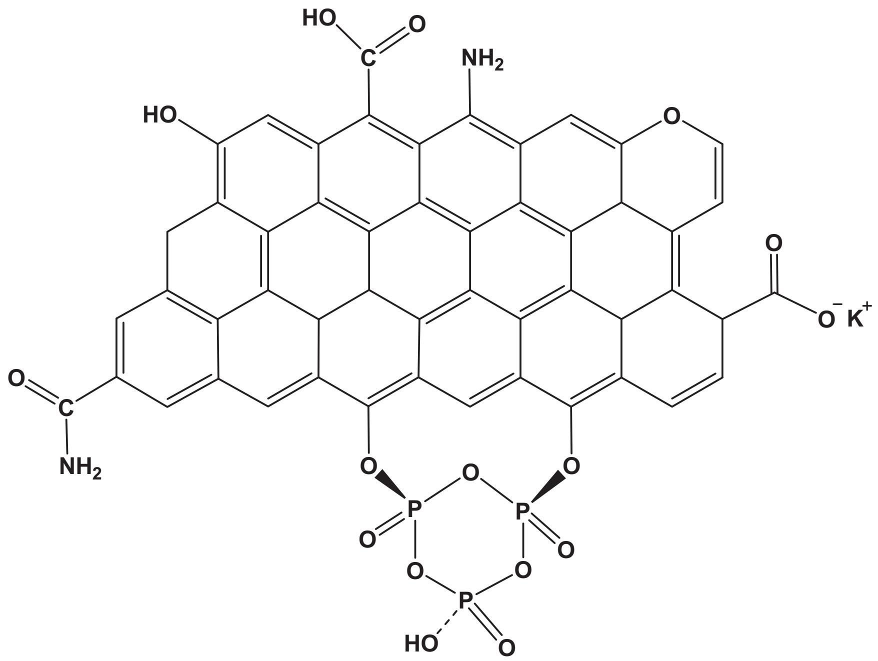

Fig. 5. A model for substituted graphene with NPK functional groups [13].

atmosphere to proceed catalytic partial carbon gasification by the reaction: $C+CO_2 \rightarrow 2CO$, leads to the generation of a porous carbonaceous structure with a large surface area (> 1000 m^2/g), compounded by interconnected PAH with NPK groups detected by infrared spectra. Accordingly, similar procedures adapted to coke instead of biomass are recommended for further research.

Previous economic evaluation of producing activated carbons [32] indicates that among all possible raw materials (wood, fruit nuts, discarded rubber tyres, etc.), petroleum coke appears to show great potential. In addition, the same industrial installation to produce activated carbon would also be suitable to produce agrichar, by means of simply removing the final step of extraction of the impregnated chemical (e.g., KOH, H_3PO_4, etc.), as long as it is plant nutrients.

4.2. Preliminary results using petroleum coke as an agrichar

Experiments have recently been carried out [33] on the effect of adding Venezuelan petroleum coke, as received from refinery, to a fertile soil to grow a typical crop: sunflower. The main elemental composition of the coke, except oxygen was (wt%): C = 71, S = 1.2, N = 0.8, H = 0.4, V = 0.9, Ni = 0.2, Ca = 0.1 (others < 0.1). It should be noted that Venezuelan crude heavy oils are characterized by high Vanadium and Nickel content; however, this appears not to have toxic effect on this application.

Mixing this petroleum coke into the previously manured soil to get 2 wt% coke (the *terra-preta* organic carbon content) did not change plant growth parameters (stem diameter and height) as compared to the same soil without added coke (see Table 1). In contrast, using a high micro-porosity activated carbon (1100 m^2/g) instead of coke impaired plant growth, probably as a result of stealing of plant nutrients caused by the great adsorptive capacity of the activated carbon. In fact, plants in soil added with activated carbon had leaves with a clear green tone different from the greener tone of all the other plants.

Therefore, these results suggest the necessity of adding nutrients if high surface area agrichars produced from FHC coke are employed for preparing *terra-preta-nova*.

Table 1
Effect of the agrichar types added to soil on sunflower (dwarf type) growth.

Growth parameter	Soil with activated carbon as agrichar	Soil with petroleum coke as agrichar	Soil without added agrichar
Number of plants grown-up (20 seeds)	16	17	18
Total dry weight (g)	35	51	52
Average stem diameter (mm)	3.6	4.2	4.2
Average height (cm)	21	22	23

Another possibility is to allow enough land fallows in order to facilitate natural charge of nutrients and microorganism within coke's porosity; however, this may require several years or decades. In connection with this, maize grain yield was not found to be significantly increased in the first crop after adding biochar (20 t/ha), but yield reached a 140% increase after four years [34].

It should be remarked that there are few published reports dealing with the interactions of petroleum coke with biological systems [35]; though it is probable that certain microbes which are active to bio-restore contaminated lands where oil spills occurred might also interact with petroleum coke in soil.

From the above reviewed results, it might be suggested that narrow and wide pores are both required for nutrient availability and friendly microorganism habitat respectively. Indeed, the affinity for nutrients of activated carbon cited above suggests that the capacity for NPK nutrients' storage of an agrichar is mainly related to its micro-porous surface area where friendly microorganisms or spores cannot be fitted because of the narrow width of slit micropores. Certainly, small unicellular bacteria and mycorrhiza spores have sizes larger than 1000 nm. Therefore, the presence of adjacent macropores and micropores would be another requirement to facilitate microorganisms transferring agrichar stored nutrients into rizosphere. These microorganisms could diffuse to micropore entrance as a result of a driving adsorptive force similar to that occuring in the sink effect postulated earlier for the activated carbon supported catalytic hydrodesulphurization [36]; in the present case the driving force must be the high concentration of nutrient elements NPK available at the micropore slit.

Another possibility for preparing *terra-preta-nova* may involve an agrichar combination of micro-porous coke with macro-porous biorock; the latter could be sustainably harvested from coralline exoskeletons, known to be characterized by large macropore volumes, up to 50% of its bulk volume [37]. In fact, archeologists have speculated about the connection between the Amazonian *terra-preta* fertility and biorock remaining from livestock, hunting and fishing [5].

5. Coke agrichar for desert land use change

Another effect of the application of agrichar (either made from biomass or FHC) is that it makes soil darker. Amazonian *terra-preta* color is something in between sandy yellow and carbon black as portrayed elsewhere [7]. As infrared reflection is smaller in darker soils, inter-phase heat transfer between soil and the atmosphere must be affected favoring exothermic processes, probably favoring water condensation over the darker soils. In agreement with this, numerical models indicate that rainfall would increase when albedo decreases [38,39]. Therefore, one may speculate that if the yellow tone of an arid zone is converted into a darker one by covering or mixing the soil with agrichar, this zone would, after a certain period of time, experience rainfall increases improving vegetable life. Afterwards, the zone converted into green should produce, by albedo decrease also, more rainfall than its parent yellow one. Nevertheless, this issue needs more scientific evidence; for example, experimenting with two adjacent lots of several hectares of desert with different soil color (e.g., one sandy yellow and another darkened by adding agrichar) to measure data such as moisture transfer at the atmosphere–soil interphase, development of ATP, etc. One question that has to be investigated first is what is the minimum size area over which the albedo should be altered to create a noticeable effect in re-vegetation [40].

Afforestation, a concept that can also be referred to as desert greening [8], is one of the most dominating terrestrial options to offset greenhouse gas emissions [41,42]. Two important factors are necessary for dessert greening: one is irrigation and the other is to introduce enough organic carbon (e.g., agrichar) into the soil. Therefore, afforestation programs with and without timber harvesting [14] could be considered as a first option for the present *terra-preta-nova* proposal. As an example, the agrichar needed to completely transform North Africa Sahara desert (about 1 Gha) into *terra-preta-nova* should be near to 200 Gton C, equivalent to about 20% of the actual FHC in world's proven conventional reserves; about 1000 Gton C [43], a percentage that would be reduced significantly if considering the total exploitable FHC from the geological point of view.

Assuming that suitable methods are developed combining agrichar's coke application and irrigation to carry out the Sahara desert greening with eucalyptus trees, and taking into account that this tree is able to capture 80 t C/ha by photosynthesis after about 10 years from planting the sprouts [44] allow harvesting cycles every 3–5 years to feed bioenergy industry producing electricity and biodiesel. Therefore, 8 Gton C from the atmosphere would be captured every year from green Sahara offsetting the actual global rate of CO_2 emission (6 Gton C/year) from burning fossil hydrocarbons. Nevertheless, eucalyptus plantings may be subject to many criticisms, particularly as a result of its propensity to catch fire; consequently, prospective tree species should be studied more in detail for desert greening. For example, Mallee species are hardy trees that are well suited as a perennial crop because of their ability to re-sprout from the large lignotuber after the upper ground mass has been lost due to fire or harvesting. Fully operational plants for integrated wood processing (IWP) could potentially produce 5 MW of electricity, 1000 t of eucalyptus oil and 3500 t of charcoal from 100,000 t of mallee feedstock material supplied annually from some 10 million harvested oil mallees [45].

Fig. 6. Aerial view of 'alleys' of Mallee–Eucalyptus established in Australia [44].

Instead of planting the Sahara with tree species as in the example above, a second option would be to plant sugar cane, African palm, or other annual crop for biofuel production. A sugar cane plantation can produce an average of 5 t of sugar per hectare yearly equivalent to 20–30 bbl of biofuels [15]; therefore, a volume of about 20–30 Gbbl of bioethanol could be obtained from the Sahara sugar cane plantations, nearly substituting the actual world petroleum production (30 Gbbl/year). One particular and interesting crop, the Tequila plant cultivated in Mexico appears to be a promissory raw material for arid biofuels source [46].

A third option involving the two proposed above, actually experimented in large scale at the dry lands of Western Australia [44,47], is to combine both annual food harvesting (e.g., wheat, sunflower, etc.) and afforestation, by means of establishing crop's parcels separated by alleys featuring various parallel files of planted trees (see Fig. 6). In this establishment, charcoal from alleys IWP has being used for soil application [47].

The permanent tree root system at the alleys may contribute to reduce undesirable excess recharge of saline groundwater, and also help protect soil against wind erosion; therefore reversing long term desertification. Besides Mallee, the specie *Gliricidia sepium*, a common tree employed for alleys in Central America, Colombia, Venezuela and the Guyanas [48], could be another promissory material for this option.

Agrichar from FHC coke could be used to sprout trees in irrigated alleys of other dry lands nearby petroleum coke producers. After capturing enough carbon from atmosphere the trees can be given to nearby IWP factory, and the biochar returned to be added to the parcels.

Besides adding agrichar to transform the desert into *terra-preta-nova*, it is of paramount importance for any of the three options of desert greening, to introduce irrigation either using sea water desalination or artifact alterations to promote rainfall (e.g., cloud seeding, albedo changes). In the first case, solar energy received in each square kilometer of Sahara is sufficient to desalinate an amount of 60 mm^3 of sea water per year using high temperature CSP collector technology [49]. Therefore, CSP plants to desalinate sea water in the Pacific and Mediterranean coasts adjacent to desert areas of North Africa, California, Peru–Chile, and Australia supplying fresh water throughout the coast inland using irrigation channels might be interesting future projects.

Nevertheless, to produce enough fresh water (e.g., 1000 mm yearly) for irrigating a Sahara desert it would be necessary to have solar collectors covering an enormous area (i.e., about one hundred thousand square kilometers). In addition, energy for pumping water from sea to the irrigation zones will be also necessary. Consequently, desert greening would be very difficult particularly due to irrigation requirements. Theoretically, improving rainfall as a result of albedo alteration by land application of agrichar would facilitate desert greening, but experimental confirmation in larger geographical areas will be necessary.

6. Conclusions

The perspective reviewed in the present communication focuses on the possible use of agrichars derived from fossil hydrocarbon coke, to prepare a *terra-preta-nova* to convert degraded areas into green areas that could be productive to substitute fossil hydrocarbon energy by bioenergy, offsetting the increase of atmospheric CO_2. Further research has been recommended to verify the effect of the preparation of *terra-preta-nova* on climate change due to the albedo effect, as well as to introduce FHC coke modifications by catalytic gasification with NPK compounds to increase agrichar micro-porosity and nutrient availability. It is suggested that the capacity for nutrient storage of an ideal agrichar is directly related to its micro-porous surface, whereas the presence of adjacent macropore volume facilitates microorganism's accommodation for nutrient transfer within rizosphere. Three options for desert greening were considered.

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