Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO_2 problem?

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A chemical process, hydrothermal carbonization (HTC) of low value biomass, is discussed as a tool for the sequestration of atmospheric CO_2. *Via* the available biomass, CO_2 can be transformed into an efficient deposited form of carbon, *i.e.* hardly degradable peat or carbonaceous soil.

Currently, world crude oil production amounts to about 4 billion tons or 4 km^3 per year (official energy statistics of the US Government, http://www.eia.doe.gov/ipm/supply.html).

Assuming a price of US-\$70 a barrel, this corresponds to a value of US-\$1.76 trillion. As, essentially, all oil ends up—sooner or later—as CO_2 in the earth's system, the opposite side of this economy is the generation of an excess 12.5 billion tons of CO_2 per year, with the known implications on the world climate.

The conventional discussion for handling this problem is to replace a minor part of the fuel and/or energy production by biomass schemes. This considers—beside direct combustion—the fermentation of carbohydrates to ethanol fuels, the cultivation of oil seeds ("biodiesel"), or the generation of biogas *via* anaerobic digestion.[1] A very detailed analysis of the energy efficiencies, costs and biological impacts of such procedures was published by Gustavsson *et al.* as early as 1995.[2] For many years, sugarcane has been converted into ethanol in Brazil, replacing oil as a car fuel, which, however, turned out to be a highly inefficient process. Other countries, *e.g.* Sweden, try to become completely independent of oil imports through "second generation" biomass use, thus not only meeting their energy demand, but also significantly improving their CO_2 liberation footprint. However, in this context, it should be stated that biological fuel production schemes can only lower future increases in CO_2 emission, and cannot compensate for past and currently emitted CO_2 from fossil resources.

Concerning climate change and the role of CO_2 therein, it would therefore be highly desirable to not only slow down further CO_2 emissions but also invert current development by sequestering the atmospheric CO_2 of past years of industrialization. Not only is biomass a "zero emission" energy source, it also has the potential to generate a new chemical "CO_2 disposal" industry. This thought, as simple as it is, is only rarely accepted as a prerequisite for discussion. It also means that the search for new and efficient carbon deposits has to be perpetuated from a chemistry point of view.

The biggest carbon converter, with the highest efficiency to bind CO_2 from the atmosphere, is certainly biomass. A rough estimate of terrestrial biomass growth amounts to 118 × 10^9 tons per year, when calculated as dry matter.[3,4] Biomass, however, is just a short term, temporary carbon sink, as microbial decomposition liberates exactly the amount of CO_2 formerly bound in the plant material. Nevertheless, as biomass contains about 0.4 mass equivalents of carbon, removal of 8.5% of the freshly produced biomass from the active geosystem would indeed compensate for the complete CO_2 liberation from oil, all numbers calculated per year. To make biomass "effective" as a carbon sink, the carbon in it has to be fixed by "low-tech" operations. Coal formation is certainly one of the natural sinks that has been active in the past on the largest scale.

Natural coalification of biomass takes place on a timescale of some hundred (peat) to hundred million (black coal) years. Due to its slowness, it is usually not considered in renewable energy exploitation schemes or as an active sink in CO_2 cycles. Nevertheless, it is obvious that carbon fixation into coal is a lasting effort, as brown or black coal (on the contrary to peat) are obviously practically not biodegradable. The question of coalified carbon destabilization is, however, currently accessed in more detail.[5] Sufficient condensation of the carbon scaffold is, in any case, mandatory for the purposes of carbon fixation.

It is therefore the purpose of this contribution to discuss the feasibility of turning coal formation into an active element of carbon sequestration schemes, simply by accelerating the underlying coalification processes by chemical means. The natural process of peat or coal formation is presumably not biological but chemical in its nature.[6] As "coaling" is a rather elemental experiment, coals and tars have been made and used by mankind since the Stone Age, and one can find trials to imitate carbon formation from carbohydrates with faster chemical processes in the modern scientific literature. In this context, it is an exciting observation of soil research that the Indians of the Amazon basin used locally generated charcoal for the improvement of soil quality for hundreds of years (*i.e.* improving the water and ion binding of "rich black" soil) and that this carbon fraction was not easily decomposed.[7,8]

Besides "charcoal formation," which is performed with high quality, dry biomass only, hydrothermal carbonization (HTC)

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is an especially promising process. The first experiments were carried out by Bergius, who, in 1913, had already described the hydrothermal transformation of cellulose into coal-like materials.[9] More systematic investigations were performed by Berl and Schmidt in 1932, which varied the biomass source and treated the different samples, in the presence of water, at temperatures between 150 and 350 °C.[10] The latter authors summarized, *via* a series of papers in 1932, the knowledge of those days about the emergence of coal (*e.g.* ref. 11). Later, Schuhmacher *et al.* analyzed the influence of pH on the outcome of the HTC reaction and found serious differences in the decomposition schemes, as identified by the C/H/O composition.[12] A review of the current knowledge on coal structure and its origin is found in ref. 13.

A renaissance in such experiments was started with reports on the low temperature hydrothermal synthesis of carbon spheres (≤200 °C) using sugar or glucose as precursors.[14,15] Recently, our group has found that the presence of metal ions can effectively accelerate the hydrothermal carbonization of starch, which shortens the reaction time to several hours and directs the synthesis towards various metal/carbon nanoarchitectures, such as Ag@carbon nanocables,[16] carbon nanofibers[17] and spheres.[13,16] Iron ions and iron oxide nanoparticles were shown to effectively catalyze the hydrothermal carbonization of starch and rice grains under mild conditions (≤200 °C), and gave exciting nanostructures.[18] It was also revealed that the presence of ternary components in complex biomass (such as orange peel or oak leaves) seriously alters decomposition schemes.[19] Unexpectedly, an improvement in properties of the carbonaceous structures for certain applications was found, *i.e.* smaller structural size of carbon dispersions and porous networks, higher hydrophilicity of the surfaces, and higher capillarity.

For completeness, it must also be mentioned that, beyond coalification, the conversion of biomass under hydrothermal conditions is a widely examined process. These approaches aim for the recovery of liquid,[20,21] or gaseous[22,23] fuel intermediates (like glucose, 5-hydroxymethylfurfural, methane, hydrogen *etc.*) from biomass, while the solid residues were, up until now, mostly treated as undesirable side products.

However, the described acceleration of HTC for coalification by a factor of 10^6–10^9 under rather soft conditions, down to a scale of hours, also makes it a considerable, technically-attractive alternative for the sequestration of carbon from biomass on large and ultra-large scales. Finally, to summarize the outcome of the optimization trials, catalyzed HTC required only the heating of a biomass dispersion under weakly acidic conditions in a closed reaction vessel for 4–24 h to temperatures of around 200 °C. This is indeed an extremely simple, cheap and easily scalable process. Besides that, HTC has a number of other practical advantages. HTC inherently requires wet starting products or biomass, as effective dehydration only occurs in the presence of water, plus the final carbon can be easily filtered from the reaction solution. This way, complicated drying schemes and costly isolation procedures can be conceptually avoided. In addition, under acidic conditions and below 200 °C, most of the original carbon stays bound to the final structure. Carbon structures produced by this route—either for deposit or materials use—are therefore the most CO_2-efficient.

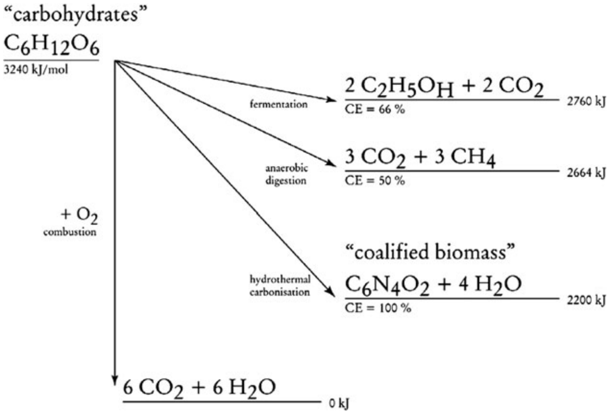

Fig. 1 Comparison of different energy and carbon exploitation schemes from carbohydrates, based on the stored combustion energy and the "carbon efficiency" of the transformation (CE). The "sum formula" of the coalified plant material is a schematic simplification.

Once activated, HTC is a spontaneous, exothermic process. It liberates up to a third of the combustion energy stored in the carbohydrate throughout dehydration (due to the high thermodynamic stability of water, but see ref. 5). A schematic comparison of the energy and mass streams of HTC with those of the more common biomass processes of fermentation and anaerobic digestion is shown in Fig. 1.

It is seen that HTC is the most exothermic of the three transformation processes, explaining the ease with which it is performed chemically. It is also the most efficient for carbon fixation, as expressed by a "carbon efficiency" of close to 1.[24] Therefore, we strongly believe that the carbonization of fast growing plants is currently the most efficient process for removing atmospheric CO_2, binding it into depositable carbon or even as useful solids.

For a negative atmospheric CO_2 balance, the generated carbonaceous materials have to be deposited on a large scale, and potential carbon landfills may lay the foundations for chemical starting materials of the next century. Another quite attractive application with immediate impact is their use as water- and ion-binding components to improve soil quality. This is a chemical process that is also found in nature, and "carbonaceous soil" is presumably the largest active carbon sink on earth. The proposed "terra preta", *i.e.* artificial coal-enriched soil as a potential carbon sink of global dimensions, has already been mentioned in soil research, improving soil quality and plant growth at the same time.[25] Instead of clearing the rainforest for questionable palm oil production,[26] such a "carbon-reinforced turbo-rainforest" would produce at least 10 times the energy, but stored in carbon, whilst also being CO_2-negative for the climate and supporting biodiversity at the same time. Spending just 10% of our oil expenses on global CO_2 sequestration would compensate for carbon fixation costs of US-$44 per ton, a target which can, in our opinion, be quite easily met (HTC is essentially just heating an aqueous dispersion, where even the energy is generated by the process itself) and does not even consider the added value for the geosystem or agriculture.

Even in industrial countries such as Germany, only the treatment of highly defined waste biomass, such as from

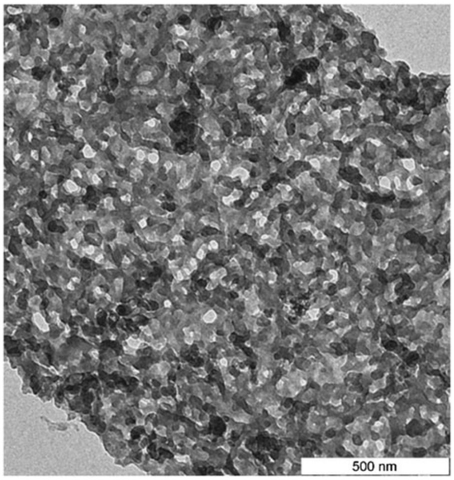

Fig. 2 TEM picture of the local structure of HTC-treated oak leaves, indicating the complete change of nanostructure towards a sponge-like cubic porous system, with structural elements in the 20–50 nm range.

sugar-beet (4.3 Mt sugar per year), rapeseed production (3.5 Mt oil per year), or clarification sludge (3.0 Mt per year), has the potential to lower German CO_2 output by about 10%. The low-tech processing of fast growing plants into non- or weakly-degradable peat-type carbon scaffolds by hydrothermal reaction cascades is therefore, in our opinion, a realistic "artificial" instrument for reducing atmospheric CO_2.

For final material use, *e.g.* as a fertilizing soil additive, the carbonaceous material has to not only have a distinct chemical structure (at a molecular level) but also have a specific structural texture, *i.e.* nanoarchitecture and surface chemistry. For soil- or sorption use—besides being free of toxic or carcinogenic compounds—the carbonaceous product has to be water-wettable and highly porous. This is an attractive task for hydrothermal carbon chemistry, involving a mindset where carbonization is nothing but a polycondensation procedure (the "chimie douce" of carbon) that is still full of novel possibilities and tasks. Fig. 2 shows, for illustration, the HTC product obtained from oak leaves,[19] which exhibits an almost perfect sponge-like cubic mesoporosity with a highly functional surface, ideal for water sorption, ion binding, or as a catalyst support.

In that sense, HTC can be seen as much more than just a technique for making carbon-rich substances.

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