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Techno-Economic Assessment of Pyrolysis Char Production and Application – A Review

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Many organic residue streams such as pig manure are not or inefficiently used, although they can be converted into valuable materials, as well as energy, using pyrolysis. The yield of the pyrolysis products (i.e. oil, gas and char) is dependent on the process conditions and the feedstock used. Char as a soil amendment or activated carbon are interesting options for valorization of biomass residues. Here, a review is presented of the techno-economic potential of both valorization options based on literature and own experiments with wood from phytoremediation, particle board and waste from beer production.
The term “biochar” is specifically used to designate pyrolysis char that is intentionally applied to soil in order to enhance its structure and fertility. Biochar applications are often also motivated by the objective of climate change mitigation. Two main disadvantages for the economic feasibility of biochar applications have been discerned. Firstly, carbon sequestration in agricultural crops and soils is not yet eligible under the Clean Development Mechanism. Secondly, the impact of biochar on crop productivity is unclear.
Activated carbon (AC) seems to have interesting adsorption characteristics resulting in potentially high sales prices. A preliminary techno-economic assessment showed that AC production is preferred above oil production for wood from phytoremediation as long as the market price of 2 $kEUR\cdot t^{-1}$ for commercially available ACs can be attained. Whenever a feedstock with high nitrogen content is available (e.g. particle board with melamine urea formaldehyde resin), even higher market prices might be attained.
This study shows that valorization of the pyrolysis char might be an answer to the slow adoption of pyrolysis in commercial applications. Focus in research and development, for instance in future research with regard to pig manure valorization, should therefore be on sustainable products with high economic value and direct utilization potential.

1. Introduction

Pyrolysis has been extensively studied because of its potential to valorise organic residue streams (Oyedun et al., 2013) such as pig manure. Pig manure is available in large quantities (i.e. surpluses) in the provinces of Limburg (both in Belgium and the Netherlands) and Brabant (the Netherlands), so that sustainable ways of manure treatment should be investigated. One option is a three step process, in which the manure first is separated decentrally into a thick fraction which contains most of the phosphor (18 wt%), a concentrate which contains most of the nitrogen and potassium (38 wt%) and discharge water (44 wt%). In a second step the thick fraction is dried so that its dry matter content is increased from 35 wt% up to 70 wt%. In a third step the dried thick fraction is pyrolyzed. Pyrolysis is considered as a beneficial option in waste treatment largely due to the products generated and the energy recovery when compared to other methods, though the economic issue is still a concern because of the amount of energy

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used for pyrolysis (Oyedun et al., 2013).The yield of the pyrolysis products (i.e. oil, gas and char) is dependent on both the process conditions of pyrolysis (such as pyrolysis temperature and residence times) and the biomass resource used. Low heating rates and low pyrolysis temperatures result in higher yields of char, whereas intermediate pyrolysis temperatures and high heating rates maximise pyrolysis oil yields (Bridgwater et al., 1999). The pyrolysis oil can be used as a substitute for fossil fuels in industrial stoves or can be upgraded and used as a transport fuel. Besides, it has the potential to be a chemical feedstock increasing its potential economic value. The pyrolysis gas is mainly used for internal energy provision. The pyrolysis char can be used as an energy carrier (directly or after pelletising), as a soil amendment (biochar), or as active carbon (AC). AC can be used as a filter medium for gas and water treatment or in the food industry. Previous studies already indicated that char as a soil amendment or activated carbon are interesting options for valorization of biomass residues. Therefore, these options are further investigated in order to decide how the pyrolyzed dried thick fraction can best be valorised: either as a biochar, an activated carbon or a combination of both.

Here, a review is presented of the techno-economic potential of both valorization options based on literature and own experiments with wood from phytoremediation, particle board and waste from beer production.

2. Techno-economic aspects of biochar

It has been discovered that Amazonian soils contain high amounts of organic carbon that explain sustained fertility in those soils. These soils have a very dark colour and are often called “Amazonian Dark Earth” or “Terra Preta do Indio”. It is believed that biochar was intentionally buried as a soil enhancement agent by pre-Columbian inhabitants of the Amazon Basin to increase the productivity of otherwise infertile soils (Lehmann and Joseph, 2009).

Several definitions of biochar can be found in literature. According to Lehmann and Joseph (2009), biochar is “the carbon-rich product obtained when biomass, such as wood, manure or leaves, is heated in a closed container with little or no available air. In more technical terms, biochar is produced by so-called thermal decomposition of organic material under limited supply of oxygen (O_2), and at relatively low temperatures (<700 °C) …”. Brown et al. (2011) define biochar as “a carbon-rich material capable of resisting chemical and microbial breakdown, allowing the carbon to be sequestered for periods of time approaching hundreds or thousands of years” produced by pyrolysis of plant material). Finally, Shackley et al. (2011) define biochar as the “porous carbonaceous solid produced by thermochemical conversion of organic materials in an oxygen-depleted atmosphere that has physiochemical properties suitable for the safe and long-term storage of carbon in the environment and, potentially, soil improvement.”

Lehmann and Joseph (2009) state that the term “biochar” is specifically used to designate pyrolysis char that is intentionally applied to soils in order to improve soil characteristics and to distinguish it from charcoal which is used as fuel for heat, as a filter, as a reductant in iron-making or as a colouring agent in industry or art. The application of pyrolysis char to soils has also been explicitly mentioned in the biochar definitions by Brown et al. (2011) and Shackley et al. (2011).

Four complementary objectives are identified which motivate biochar applications for environmental management which individually or in combination must have either a social or financial benefit or both (Lehmann and Joseph, 2009):

- Soil improvement by amelioration of soil structure and fertility (e.g. by better water retention, improving soil pH, reduction of nitrate leaching, better conservation of nutrients such as N, P and K), thereby improving biomass yields and possible savings by reduced fertiliser use;
- Waste management as an alternative conversion route for organic waste disposal, which significantly reduces the volume and weight of the waste (hence influencing transport costs) and decreases methane emissions from landfills;
- Climate change mitigation as a means of sequestering atmospheric carbon dioxide (CO_2) because biochar decomposes much more slowly (opinions range from centennial to millennial timescales according to Lehmann (2007)) than plant biomass that is formed on an annual basis, so that carbon is diverted from the rapid biological cycle into a much slower biochar cycle while reducing emissions even further than the fossil fuel offset in its use as fuel;
- Bioenergy (e.g. syngas, pyrolysis oil or heat) production in addition to biochar production so that besides carbon sequestration, also emissions are reduced.

Using biochar as a soil amendment aids carbon sequestration and might result in increased crop productivity. The impact of the use of biochar as a soil amendment on crop productivity in terms of biomass yield however is not very clear: it depends on the types of biochar used, soil type, climate and type of crop amongst others (Galinato et al., 2011). Shackley et al. (2011) confirm that many of the potential biochar benefits remain highly uncertain to date, but they state that carbon sequestration is the most certain benefit and that there is reasonably good evidence that biochar increases pH (see also Galinato et al. (2011)).

However, carbon sequestration in agricultural crops and soils are currently not eligible yet as tradable "carbon offsets" or "certified emission reductions" (CERs) under the Clean Development Mechanism of the Kyoto Protocol (Galinato et al., 2011). In any case, the potential of carbon storage in greenhouse gas accounting should be calculated by life cycle carbon assessments and depends on the feedstock for biochar production, the amount of biochar produced (during slow versus fast pyrolysis) and the current conventional (waste) treatment or disposal context (i.e. the reference scenario or system in life cycle analysis) of the biochar feedstock (Ibarrola et al., 2012). Ibarrola et al. (2012) calculated net carbon abatement for wood waste: wood that can be incinerated has a carbon abatement potential of 0.50 t of CO_2 per t of feedstock produced by slow pyrolysis, whereas biochar production from wood that otherwise should be landfilled can save up to 1.25 t of CO_2 equivalents per t of feedstock from slow pyrolysis. In the latter reference system of landfilling, fast pyrolysis has a net carbon abatement potential of less than 0.9 t of CO_2 equivalents per t of feedstock. Brown et al. (2011) calculated the amount of CO_2 equivalents that can be sequestered by biochar production from corn stover: they assumed that fast pyrolysis would result in 0.47 t of CO_2 equivalents saved per tonne of corn stover, whereas slow pyrolysis augments CO_2 abatement to 0.99 tonnes CO_2 per tonne of corn stover. So it can be concluded that slow pyrolysis results in the highest carbon offset potential for any feedstock. The remaining question is whether the economics of slow pyrolysis are sufficient in order to make it a viable biochar production route (compared to fast pyrolysis). According to the references cited below this is unfortunately not the case. Fast pyrolysis appears to be the most profitable conversion technology, even for biochar applications.

Lehmann (2007) calculated that biochar sequestration in conjunction with bioenergy from pyrolysis becomes economically attractive, when inexpensive feedstocks are continuously available in sufficient quantities, and when the value of avoided carbon dioxide emissions reaches 37 $USD·t^{-1}$ (or 29 $EUR·t^{-1}$). Galinato et al. (2011) calculated the profit from winter wheat production in Washington State, with and without biochar application. They considered biochar as a substitute for agricultural lime because of its consistent effect on soil pH. They stated that it may not be economically feasible for farmers to use biochar solely for pH adjustment since it would entail a relatively higher cost compared to agricultural lime. Therefore they investigated the economic potential of the additional benefit of carbon sequestration when it would have been possible to trade its carbon offsets. Because prices of traded CO_2 offset are highly volatile (cf. the Chicago Climate Exchange and the European Climate Exchange), they calculated the profits of biochar application both when the offset price equals 1 $USD·t^{-1}$ CO_2 and when a high offset price of 31 USD t^{-1} CO_2 can be attained. They concluded that biochar application is only profitable at a high carbon offset price of 31 $USD·t^{-1}$ CO_2 (or 25 $EUR·t^{-1}$) and at the same time a low biochar price of 87 $USD·t^{-1}$ biochar. The latter underpins the finding of Lehmann (2007) because a low biochar price might only be possible for inexpensive feedstocks (e.g. waste streams). Also Shackley et al. (2011) confirm that waste is the most profitable source for biochar production, although they warn for the fact that such materials will face complex regulatory issues and testing.

Shackley et al. (2011) state that the standard approach in evaluating technology costs by empirical relationships between component costs and e.g. power output is difficult in the case of pyrolysis biochar systems, as there is a lack of peer-reviewed data available on the realistic costs of slow pyrolysis (contra fast pyrolysis) at different scales. McCarl et al. (2009) used the same cost structure for slow pyrolysis and they used exactly the same fixed pyrolysis cost for 1 t of biomass. For slow pyrolysis, biomass pre-treatment costs were reduced by 50 %, whereas all other operating costs were assumed to remain the same per tonne of feedstock. Galinato et al. (2011) found that biochar application for winter wheat production is not profitable at all when the biochar has to be bought by a farmer at a price that equals the break-even price of 350.74 $USD·t^{-1}$ biochar (or 278.37 $EUR·t^{-1}$) calculated by Granatstein et al. (2009). The latter price has been confirmed by Brown et al. (2011) who quote a minimum product selling price of 346 $USD·t^{-1}$ of biochar (or 275 $EUR·t^{-1}$) for slow pyrolysis. This is quite high when compared to the revenue that can be generated by carbon offsets: one tonne of biochar from corn stover has a carbon offset value of 20 $USD·t^{-1}$ of biochar (16 $EUR·t^{-1}$) if the assumed carbon offset value is 17.33 $USD·t^{-1}$ CO_2 or 13.88 $EUR·t^{-1}$ CO_2 (Brown et al. 2011). Current prices on the market of European Union Allowances (December 2013) however are only between 4.5 and 5 $EUR·t^{-1}$ CO_2 whereas the values of Certified Emission Reductions are below 0.5 $EUR·t^{-1}$ CO_2. Even if biochar application would lead to higher crop productivity, McCarl et al. (2009) calculated that the biochar value at the pyrolysis plant (for application as a soil amendment on a maize field) equals 32.94 $USD·t^{-1}$ biochar (or 26.37 $EUR·t^{-1}$), i.e. excluding the benefit of greenhouse gas offset. Despite the higher carbon offset potential from slow pyrolysis, McCarl et al. (2009) calculated that both fast and slow pyrolysis are unprofitable (the difference with calculations by

Kuppens (2012) is that they do not take into account exploitation subsidies such as green power certificates or combined heat and power certificates), but that the fast pyrolysis plant is less loss making than the slow pyrolysis plant. Brown et al. (2011) confirm that a pyrolysis facility that operates primarily to generate biochar as a carbon offset (i.e. a slow pyrolysis plant) is unlikely to be profitable, whereas a pyrolysis facility that co-produces biochar for carbon sequestration and bio-oil for transportation fuel (i.e. a fast pyrolysis plant) has relatively attractive economics.

3. Techno-economic aspects of activated carbon

Activated carbons (ACs) are produced for a large number of dedicated applications and are generally used as a filter medium for air, water and gas purification, or in chemical and pharmaceutical processing, food processing, decolourisation, fillers in rubber production amongst others. The price of the AC is dependent on the demand, quality, and production costs, amongst others. Due to their adsorption properties they can often be sold at high prices on the market, whereas production costs can be decreased by using cheaply available waste streams. Some experiments and techno-economic models for the production of ACs using those waste streams are presented below.

3.1 Wood from phytoremediation

Willow and poplar are sometimes cultivated in short rotation for phytoremediation, i.e. the removal of pollution from soils by means of plants (Vangronsveld et al., 2009). The main barrier in the development of commercially viable phytoremediation is the long time period required for effective soil remediation, which can be countered by valorization of the plants (Robinson et al., 2003). For small scale conversion of short rotation coppice, fast pyrolysis is more profitable than gasification (Voets et al., 2011). During fast or flash pyrolysis, char is generated as a by-product for which a higher economic value than its fuel value is desired. Stals et al. (2013) therefore activated char from fast and flash pyrolysis of different short rotation hardwoods that have been cultivated for phytoremediation. They applied both physical (by means of steam) and chemical (by means of KOH) activation and compared the adsorptive properties of the resulting activated carbons with a commercial AC (Norit). Some of the experimental ACs showed adsorption characteristics comparable to the commercial reference.

Kuppens (2012) performed economic calculations on active coal production from willow cultivated for phytoremediation. Preliminary calculations show that the production of activated carbon is more profitable than disposal of the pyrolysis char from phytoremediating willow, even though the latter contains heavy metals resulting in higher AC production costs (for fume gas treatment) compared to non-polluted willow. As long as the AC from phytoremediating crops can be sold at market prices, the processing costs of activation and fume gas treatment (for removal of the volatilising metals during activation) are expected to be more than compensated. Revenues from AC production even outweigh potential revenues from combined heat and power production from the combustion of pyrolysis oils, so that process conditions in favour of char production are preferred above those in favour of oil production from an economic point of view.

3.2 Particle board

Several contaminated wood products such as particle board (PB) waste contaminated with aminoplasts (i.e. melamine (urea) formaldehyde, abbreviated as MF) are not or partly reused/recycled. Part of these products can be recycled in the production of new PB, but loss of mechanical properties of the final product does not allow reuse of significant quantities as an incoming wood stream for the production of PB, for which a sustainable solution is required. Combustion of this wood waste results in the production of toxic gases like ammonia, isocyanic and hydrocyanic acid and nitrous oxides. The chemical properties of these waste streams (high nitrogen content) make them ideal precursors for the production of nitrogenized activated carbon (Vanreppelen et al., 2013a). Nitrogen incorporation in activated carbon can play a significant role for the adsorption properties as well as for the catalytical activity and dispersion of carbon supported catalysts. An average char yield of 23 wt% is obtained after pyrolysis (Vanreppelen et al., 2013a). The resulting AC yield after activation depends on the mix ratio of PB and MF and lies between 11 and 22 wt%. ACs containing nitrogen have enhanced adsorption capacity towards phenol which is very toxic. The performance of the ACs produced from PB and MF are similar but somewhat lower than the commercial AC.

Vanreppelen et al. (2011) performed a preliminary techno-economic evaluation for the production of high-value nitrogenized activated carbon by co-pyrolysis and subsequent steam activation of a mix of particle board and melamine (urea) formaldehyde waste, in order to choose promising valorization options for the conversion of PB and MF waste, which in a next step have been experimentally tested. The techno-economic evaluation has been updated in Vanreppelen et al. (2013a) based on experimental results.

Encouraging results for a profitable production of activated carbon were obtained, even though the authors assumed a rather pessimistic scenario. For instance, in Belgium a MF factory currently pays 220 EUR t^{-1} for disposing its waste to a landfill site (including transport costs). In other words, a pyrolysis and activation plant that processes PB and MF waste should receive this amount as a revenue or “gate fee”, though this gate fee has been set at 0 EUR t^{-1} in the techno-economic model so that a worst case scenario is constructed. Depending on the PB/MF-ratio, minimum required selling prices to render a profitable investment are between 1.8 $kEUR \cdot t^{-1}$ and 2.6 $kEUR \cdot t^{-1}$ of AC which are expected to be realistic market prices as such nitrogenized ACs could yield selling prices as high as 4 to 6 $kEUR \cdot t^{-1}$ (Vanreppelen et al., 2011).

3.3 Brewer’s spent grain

Brewer’s spent grain (BSG) is a low cost residue generated by the brewing industry. Its chemical composition makes BSG also very useful for the production of added value in situ nitrogenised AC (Vanreppelen et al., 2013b). Depending on the process conditions, the AC yield from dried BSG is between 17.4 and 23.5 wt% with a nitrogen content between 2.13 and 2.49 wt%. Vanreppelen et al. (2013b) investigated the economic feasibility for an AC production facility from BSG based on a techno-economic model. Two options have been investigated because breweries have two possibilities to valorise BSG as AC. The first option is to produce the AC onsite and thus build an AC production facility near the brewery. In that case the brewery process quantity for AC production is limited to its own BSG production capacity and a 0 $EUR \cdot t^{-1}$ feed cost. The second option is to sell the BSG at 38 $EUR \cdot t^{-1}$ to an external AC producer who can enjoy economies of scale by buying BSG from more breweries. The break-even selling price for AC produced in an onsite facility with a processing scale of 1 $t \cdot h^{-1}$ are between 2.2 and 2.5 $EUR \cdot t^{-1}$ which are prices one might expect to be realistic given the quality of the ACs produced from BSG. In offsite facilities no profitable production of AC from BSG is possible given the very high feedstock cost of BSG, unless the scale can be increased to an input rate of 5 $t \cdot h^{-1}$ (Vanreppelen et al., 2013b).
Besides wood from phytoremediation, particle board and brewer’s spent grain, adsorbents have also been produced from sewage sludge (Velghe et al., 2012), although no economic assessment for this feedstock has been made to date. However, De Filippis et al. (2013) mention that the manufacture of these adsorbents for the removal of metals from water and wastewater appears to be a promising low-cost alternative to the high-cost commercial carbons.

4. Conclusions for future research

From the review above, it can be concluded that valorisation of pyrolysis char might result in the production of AC with high economic value and direct utilization potential, especially when in situ nitrogenization of the AC is possible which might be relevant for the proposed pig manure treatment. Besides one can wonder whether the presence of phosphor might result in an enhanced biochar after activation because the latter might reduce leaching of nutrients to groundwater, it might make the availability of nutrients for plants more efficient while reducing the amount of fertilizers required and increasing crop productivity. Besides activated biochars might help immobilizing pollutants in soils like toxic metals or radionuclides. Future research steps for the valorization of pig manure therefore should focus on the characterization of the feedstock, experiments and process design for manure pyrolysis and subsequent char activation, characterization of the pyrolysis products (especially with respect to nutrient content), investigation of the impact of activated biochar by means of pot experiments, and a techno-economic assessment which translates experimental data into economic figures taking into account the value of biochar by estimating production costs, the economic effects on crop productivity, biomass quality and soil characteristics and the farmer’s willingness to pay for activated biochars as a soil amendment.

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