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# Efforts to Curb NO<sub>x</sub> from Greenhouse Gases by the Application of Energy Crops and Vegetation Filters

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Additional information is available at the end of the chapter

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## 1. Introduction

Nitrogen, in a similar way to carbon, has a complex and fragile global cycle. Anthropogenic activities from the beginning of the 20<sup>th</sup> century have interfered with this fine nitrogen-balance by capturing N<sub>2</sub> from the atmosphere for fertiliser production. When stable N from the atmosphere enters the forage crop production and stock-raising cycle it returns to the environment as waste and in more reactive forms.

During the combustion of energy crops the fuel-bound N forms greenhouse gases which are liberated to the atmosphere, therefore both fertiliser applications and biomass combustion can be directly linked to nitrogen related environmental problems.

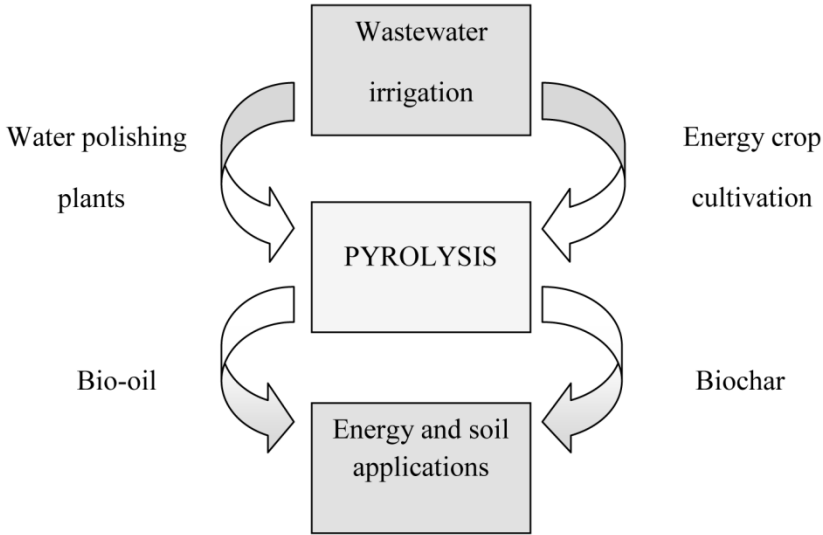
Short-rotation plantations irrigated with effluent have both high nitrogen uptake capacity [1] and also enhance growth characteristics without the application of fertilisers or competition with fresh water usage [2, 3]. Furthermore wastewater irrigation<sup>1</sup> reduces the cost of wastewater treatment while crops cultivated on the land can provide solution for the increasing energy demand of rural areas without destroying existing forestry [2].

In order to choose appropriate feedstock and design a biomass-to-energy conversion technology both the economical and environmental aspect of a project should be considered. Biomass pyrolysis, which is the thermal degradation of the biomass in an inert atmosphere, provides an advanced liquid fuel. Pyrolysis liquid (or bio-oil) is the subject of intense research and investigations for direct energy applications to provide green electric power with highest efficiency [4].

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<sup>1</sup>Throughout this chapter, the term *wastewater* will refer either to treated wastewater (effluent) or untreated (raw) wastewater. *Wastewater irrigation* can refer to both flood irrigation, spray irrigation, subsurface drains and other applications.

This chapter introduces the use of energy crops into the global nitrogen-cycle by following nitrogen from wastewater irrigation via energy conversion (biomass pyrolysis) and finally back to soil in a stable form to close the circle (Fig. 1).



**Figure 1.** General scheme showing the conversion of wastewater irrigated vegetation filters to energy and to soil amendment

## 2. Wastewater and wastewater treatments

### 2.1. Nitrogen in municipal wastewater

Nitrogen in domestic wastewater is present in both inorganic and organic forms. Organic nitrogen from human diet and metabolism is transformed into free ammonia ( $\text{NH}_3$ ) and ammonium cation ( $\text{NH}_4^+$ ) by microorganism [5, 6]. The  $\text{NH}_3$  to  $\text{NH}_4^+$  ratio in water is depending on temperature and pH. The presence of free  $\text{NH}_3$  above the concentration of 0.002 mg/L is toxic for the ecosystem [7]. Ammonia is also the source of inorganic nitrate and nitrite ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) nitrogen in wastewater [6]. Inorganic nitrogen is an essential plant nutrient. However, high concentrations in water cause *eutrophication*; an extreme bloom in the population of plants with an enhanced growth period followed by the necrosis of the biomass. The degradation of dead plant tissues increases oxygen demand of fresh water, therefore, eutrophication leads to oxygen scarcity and decreased self-cleaning ability of the biomass system [8]. The presence of nitrate and nitrite anions in drinking water is blamed for causing cyanotic conditions like shortness of breath, methemoglobinemia and blue-baby syndrome [9, 10].

To protect human health and aquatic life the nitrogenous contaminants of wastewater must be controlled. Table 1 contains some requirements set up by different governments and some typical nitrogen values in different types of wastewater.

	Form of nitrogen	Concentration (mg N/L)	Source
Typical nitrogen concentration in <i>grey wastewater</i>	TN <sup>a</sup>	0.6–74	[11]
Typical nitrogen concentrations in domestic <i>raw wastewater</i>	TN	20–80	[11]
Requirement of the European Council for urban <i>wastewater</i> treatment	TN	10	[12]
Primary standards of the <i>National Primary Drinking Water Regulations</i> by US EPA <sup>b</sup>	Nitrate-N	10	[13]
Health value of the <i>Australian Drinking Water Guidelines</i>	Nitrate-N	11.3	[14]

<sup>a</sup>TN: *Total Nitrogen*; Sum of organic nitrogen, ammoniacal nitrogen, nitrate-nitrogen and nitrite-nitrogen

<sup>b</sup>EPA: *Environmental Protection Agency*, U.S.

**Table 1.** Typical nitrogen values and requirements in water and wastewater

## 2.2. Biological wastewater treatment

The physicochemical removal of nitrogen from wastewater is possible, however, biological methods have proved to be more effective and less expensive treatments [15].

The biological removal of nitrogen is based on the mixed populations of live bacteria naturally present in wastewater which are able to convert nitrogen compounds to other chemical forms. The mineralization (consecutive steps of *ammonification*, *nitrification* and *denitrification*) of the wastewater-derived organic matter provides oxygen, nitrogen and energy for the bacteria to produce new cells [16].

The *activated sludge* formed by these living microorganisms is the core of modern industrial wastewater treatment technologies. To ensure the most suitable environmental conditions for the microorganisms (e.g. aerobic zone for nitrification and anoxic zone for denitrification) several industrial processes have been designed like the *Bio-Denitro process*, modified *Ludzack-Ettinger process*, *Bardenpho process*, etc. [15].

When these conventional wastewater treatment facilities are not available – mostly in developing countries – stabilization ponds are the most widely used municipal wastewater treatment systems [17]. Even if the climate favours microbial activity these stabilization ponds cannot reduce the concentration of nitrogen satisfactorily [18].

## 2.3. Vegetation filters

If the high cost of the commercial technologies discounts the use of sufficient wastewater treatment, the unregulated or poorly regulated water turns to a potential risk factor to human health and environment [19, 20]. To eliminate this risk it is crucial to reduce the concentration of nitrogen and other pollutants before any effluent reaches the environment.

The application of biological filter systems like soil and *vegetation filters* represents an alternative on-site wastewater treatment. While the first pilot tests were carried out by big companies to treat cannery effluents, the treatment of municipal water receives more and more attention now in developing countries [21, 22]. This type of wastewater management is able to reduce the concentration of organic and inorganic contaminants in the water and remove 73-97% of the *total nitrogen* [23]. This low-cost treatment also assimilates nitrogen as plant nutrients back into the environment while pathogens from the wastewater cannot compete with the natural microbial population of the soil [24, 25].

### 3. Nitrogen, the essential plant nutrient

#### 3.1. Nitrogen in soil

The role of soil in the biological-cycle is to store and supply nitrogen and other essential nutrients for plants. The average amount of organic nitrogen in soil is 3300 kg/ha, however, the available nitrogen for plants is less than 1 % of the above volume as vegetations are not able to uptake any kind of forms of soil nitrogen [26].

#### 3.2. Nitrogen uptake in plants

The synthesis of plant cell components (e.g. amino acids, nucleic acids, enzymes, chlorophyll etc.) is unachievable without nitrogen; nitrogen deficiency in plants causes slow growth which can be recognized by the pale green colour of the leaves. Without available nitrogen there are no processes in plants [26]. For the formation of new cells, plants uptake nitrogen – along with water – in the form of  $\text{NH}_4^+$  or  $\text{NO}_3^-$  during their growing period (*assimilation*), or store extra nitrogen (*immobilization*) [27].

Nitrogen is being absorbed from soil during the whole life of the plants but the nitrogen use efficiency of plants varies according to the stage of maturity, seasons, environmental conditions of the site and the fertility status of the soil as well [26, 28]. The latter factor is particularly important in terms of crop yield as nitrogen supply is a main limitation factor to plant growth [29].

#### 3.3. Synthetic nitrogenous fertilisers

If the nitrogen supply within the soil is not sufficient, land productivity can be improved by organic and inorganic (also known as synthetic) macronutrient plant fertilisers. The most widely used synthetic fertilisers are ammonia-based products [30]. The source of nitrogen in these fertilisers is the atmosphere containing molecular nitrogen in 78 %. The direct reaction of molecular nitrogen and molecular hydrogen to  $\text{NH}_3$  is the base of the widely applied Haber-Bosch process [31] which provides more than 140 million tonnes of ammonia to farmers around the world every year [32].

Modern soil fertility management in the 20<sup>th</sup> century has made a significant contribution to the growth of Earth's population which has almost quadrupled since 1900s. To sustain this

growing population industry produces millions of tons of fertiliser which is responsible for more than 1% of the world's energy consumption. Since hydrocarbon combustion is the main energy source of ammonia production, the fertiliser industry is a major contributor to greenhouse gas emission [33]. In addition to the energy consumed during production transportation of the fertilisers is also contributing to the world's greenhouse gas emission with 37 Tg CO<sub>2</sub>-eq per year [34]. There is also an estimated 2.5-4.5 Tg N emitted from the nitrogen-fertilised soil to the atmosphere each year [35].

### 3.4. Nitrogen uptake in effluent-irrigated short-rotation crops

If the cost or availability of the technology does not make it possible to apply inorganic fertilisers, alternative – and possibly more sustainable – nitrogen sources should be considered to increase the productivity of agricultural land.

Similar to inorganic fertilisers, wastewater is a source of supplemental nitrogen. According to studies, nitrogen uptake of rain-fed Eucalyptus in New Zealand is in the range of 30-80 kg/ha/year while the uptake in effluent-irrigated plantations is one magnitude higher [1]. During wastewater irrigation, plants uptake nitrogen for their growth and polish the water. The absorbed N nutrients are converted to amino acids and stored in wood [36] or transferred from roots to shoots for protein synthesis [37]. Research results have also proved that plants have enhanced growing characteristics as a result of wastewater, grey water or effluent irrigation [38-40]. Table 2 shows the increments in storage and transport amino acid concentrations due to wastewater irrigation.

Free amino acid ( $\mu\text{g} / \text{mg}$ )	Arginine	Asparagine	Aspartic acid	Glutamine	Glutamic acid
Control willow	0.054	0.141	0.066	0.002	0.048
Wastewater irrigated willow	0.404	0.177	0.102	0.013	0.103

Sample: Willow (*Salix*) from the bioremediation programme of Agri-Food & Biosciences Institute (ABFI, Hillsborough, N. Ireland). Trees were in their second year of re-growth after coppicing and plantations were irrigated with farm wastewater (TN: 100 mg N/L); Source: Chapter authors

**Table 2.** Free amino acid content of willow from wastewater irrigated plot and from a control plot

### 3.5. Nitrate-leaching

Even though vegetation has the potential to store wastewater-derived nitrogen, nutrient uptake is not the only limitation factor of the land applications of wastewater.

Due to the metabolism of microorganisms, nitrogen in soil and wastewater is predominantly present in the form of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, which are readily available plant nutrients. The surface charge of clay minerals in soil is negative which attaches the wastewater derived ammonium ion to soil matrix, but ions with negative charge are carried by water [41]. Due to heavy rains or improper agricultural activities nitrate nitrogen can leach below the root system of plants into the groundwater with a negative effect both on the environment and

drinking water quality. Nitrate concentration in groundwater can reach extremely high values; one of the reported Indian examples was 1500 mg nitrate in one litre of water, 150 times higher than the permitted value by the WHO [42].

Nitrate is a primary pollutant of groundwater. Although chemical reduction, biological denitrification and other in-situ treatments of groundwater are feasible [43], nitrate leaching is still the main limitation factor of wastewater irrigation; treatments cannot prevent the formation of groundwater contamination or solve the problem of nutrient loss of the soil. Without an effective prevention system the only groundwater protection is source control which means the limitation of wastewater loading.

## 4. Energy from biomass

### 4.1. Heating values

Treating contaminated water by vegetation filters require fast-growing plants, like willow [44]. Willow is also a widely cultivated fuelwood for energy applications with an annual yield of 9-13 t/ha in Europe [45].

An important feature of fuelwood and other energy crops is their composition which determines their heating (or calorific) value [46, 47]. The higher heating value (HHV) is the energy available from the fuel and it is generally given in units of energy per unit of weight (cal/g; J/g or Btu/lb). Table 3 contains some typical heating values of fuelwood and other solid fuels. Energy crops can displace approximately 0.44 tonnes of oil equivalent when converted to electricity [48] and contribute to the reduction of greenhouse gas emission by 100-2070 Mt CO<sub>2</sub>-eq/year [49].

The quality characteristics of the biomass have a significant effect on the yield of energy during a biochemical or thermochemical conversion process [50]. For example high oxygen and carbon content favours combustion and increases the heating value [51] while the general model of heating values predicts a slight decrease in HHV when nitrogen content of biomass increases [52].

	HHV (MJ/kg)	Source
<b>Fuelwood</b>		
Softwood (average)	20.0	[53]
Hardwood (average)	18.8	[53]
Straw (maize silage)	20.0	[49]
<b>Charcoals</b>		
Charcoal from rice husk	17–18	[54]
“High quality” charcoal	28–33	[55]
<b>Fossil fuels</b>		
General purpose coal	32–42	[56]
Petrol	45–47	[56]

**Table 3.** Heating values of energy crops, charcoals and fossil fuels

## 4.2. Biomass combustion and nitrogen liberation

Nitrogen content of trees ranges between 0.3 and 1 % [57]. Nitrogen in short-rotation plants is generally higher and significant differences can be found between species. Short-rotation plants represent a cheap and renewable energy source with high energy potential. The combustion of these plants is also a CO<sub>2</sub> neutral energy conversion technology, however, combustion converts fuel-nitrogen to nitric oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) [58-63] which are contributors to acid rain formation [64]. N<sub>2</sub>O is also a greenhouse gas with a *global warming potential* (GWP) of 289 where 1 unit represents the global warming potential of CO<sub>2</sub> over 20 years [65]. The emission of NO<sub>x</sub> contributes to acidification and it also causes eutrophication and ground-level ozone formation [66].

Increased nitrogen content in the biomass also means increased emission of NO<sub>x</sub> during combustion [67]. The estimated emission of NO<sub>x</sub> from biomass combustion was 5-5.9 TgN in 2000 [35] and based on the fact that the energy demand and the biomass fuel consumption are increasing [68], this NO<sub>x</sub> emission must be even more significant now and need to be decreased drastically.

To control the harmful effects of combustion plants' pollutants, organisations like Environmental Protection Agency of the United States (US EPA) or the Intergovernmental Panel on Climate Change (IPCC) have elaborated their guidelines and emission criteria [69, 70]. The most common way to fulfil these regulations is the application of flue gas cleaning systems (primary reduction with excess air, secondary catalytic reduction, etc) [67] but these technologies add cost, particularly in small bioenergy facilities. Another effective way to reduce the environment impact of biomass-derived NO<sub>x</sub> pollution is the application of alternative energy conversion technologies with better emission characteristics.

## 5. Pyrolysis

### 5.1. Biomass conversion to solid, liquid and gas products

Pyrolysis is a thermochemical process where the biomass (e.g. energy crop) is being converted into more effective energy sources. During the pyrolysis process the macromolecules and biopolymers of the biomass undergo a thermal degradation in the absence of oxygen, which leads to solid, liquid and gaseous products.

The thermal decomposition and conversion can be interpreted as the independent degradation of the three main organic woody biomass compounds, cellulose, hemicellulose and lignin [71, 72] which have an average ratio of 45/24/28 wt % in softwood and 45/31/21 wt % in hardwood, respectively [53]. The few parentage of wood inorganics remains in the solid product of pyrolysis while the lignocellulosic compounds undergo thermal degradation.

The biomass conversion at different pyrolysis temperatures can be followed by the thermal degradation and the weight loss of the main wood compounds on Fig. 2. The

ratio of the gases, vapours and solid products depend on the temperature, residence time and heating rate of pyrolysis [73, 74]. Increasing the highest treatment temperature of pyrolysis increases the liquid and gas yields and decreases char yield (Fig 3). Due to secondary reactions of vapours liquid yield has a maximum which is followed by a reduction at higher temperatures and the gas yield increases at the expense of biochar yield [73, 75].

In terms of nitrogen oxide emission, pyrolysis is a more desirable energy conversion technology than combustion; while biomass combustion releases fuel-nitrogen in the form of NO<sub>x</sub>, the inert atmosphere of pyrolysis does not favour to the formation of these or any other oxidized pollutants [76].

## 5.2. Pyrolysis liquids (bio-oil)

Pyrolysis has the ability to generate highly energetic bio-oil which represents most of the energy content of wood (Fig. 4) with the additional benefit that it can be easily pumped or transported. Another advantage of the bio-oil from energy crops and vegetation filters is the lack of jeopardy to the security of food supply, unlike the dangers of sugar-, starch- and vegetable oil-based conventional bio-fuels –which conquer valuable agriculture lands [77].

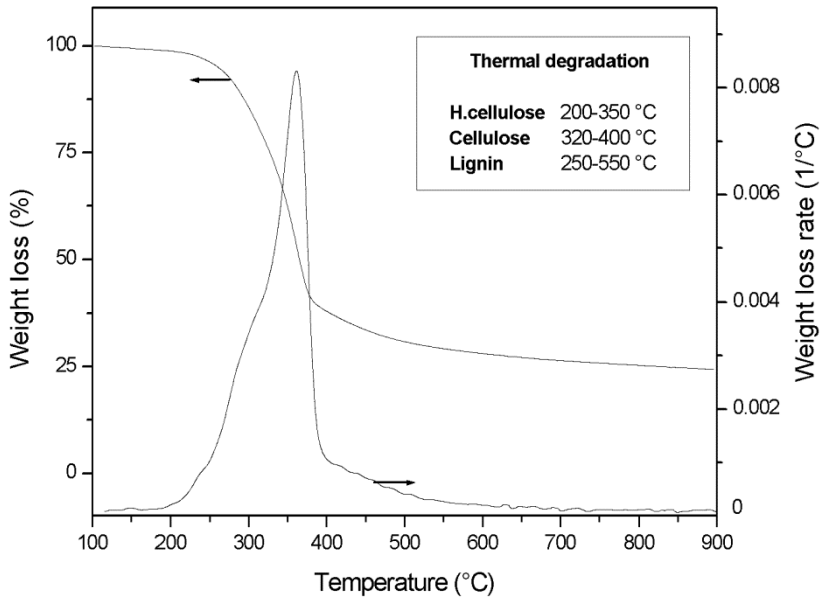
Bio-oil is still a relatively new energy source and its energy applications are still developing, but its combustion in boilers, turbines and engines has been successfully used for heat and electricity production [78, 79]. Table 4 contains some typical power output values.

<b>Hot water generation</b>	
Boiler fuelled with pyrolysis oil (BTG Biomass Technology Group BV, The Netherlands)	150 kW
<b>Electric power generation</b>	
Pyrolysis liquid combustion in diesel engine (VTT Energy, Finland)	84 kW
Pyrolysis liquid combustion in diesel engine (Wärtsilä Diesel International, Taiwan)	1.5 MW
Pyrolysis liquid combustion in gas turbine (University of Rostock, Germany)	75 kW
<b>Combine heat and power generation (CHP)</b>	
Pyrolysis liquid combustion in a Stirling CHP unit (ZSW, Germany)	10-25 kW <sub>th</sub> , 4-9 kW <sub>e</sub>

(Source: Czernik, 2004)

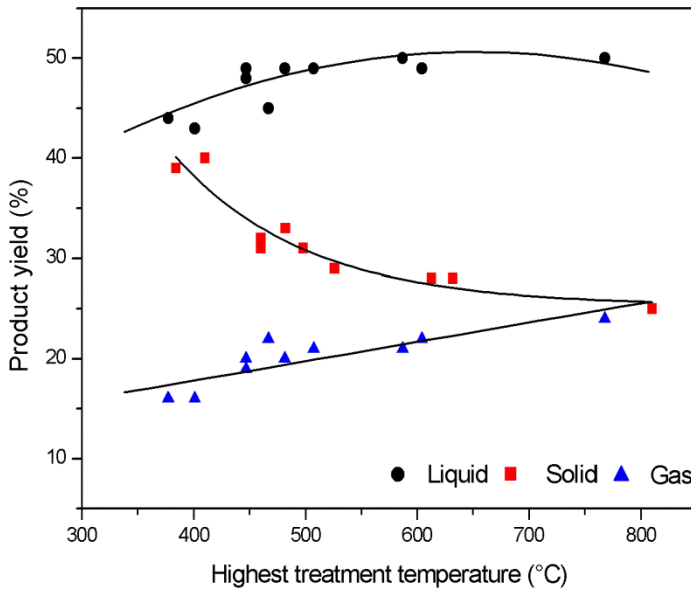
**Table 4.** Power outputs from bio-oil combustion





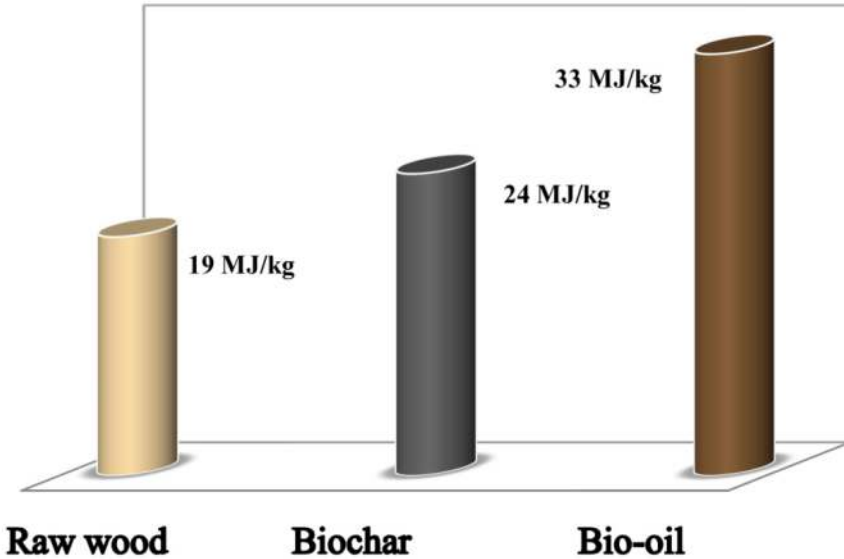
Sample: 10 mg grinded willow (*Salix*) pyrolysed in a Mettler TGA/DSC 1 Star System.  
 Heating rate: 20 °C/min. Purging gas: He (Source: Chapter authors)

**Figure 2.** Typical thermal degradation curves of wood pyrolysis



Sample: 100 g chipped willow (*Salix*) pyrolysed in a fixed bed reactor;  
 Heating rate: 30 °C/min, Purging gas: N<sub>2</sub> (Source: Chapter authors)

**Figure 3.** Effect of pyrolysis temperature on product distribution



Raw material: 100 g chipped willow (*Salix*) pyrolysed in a fixed bed reactor  
 Highest treatment temperature: 460 °C, Purging gas: N<sub>2</sub>; Source: Chapter authors

**Figure 4.** Energy content of raw wood and its solid and liquid pyrolysis products

### 5.3. Nitrogen in biochar and in pyrolysis gases

Biochar and biomass char are the solid co-products of the pyrolysis process. They are mainly made of carbon and the ash content of the biomass. Despite of their similarities, historical definitions distinguish *biochar* from *biomass char* which is also known as *charcoal*. While the latter has been produced and used as fuel for heat for centuries, the former belongs to a new concept of soil management and carbon sequestration [80]. Other names like *black carbon*, *dark earth* (terra preta) or *agrichar* can be also fined in literature.

Enrichment of the fuel-bound nitrogen of biomass occurs in the biochar independently from the applied pyrolysis technique [81]. Nitrogenous gases (e.g. ammonia, hydrogen cyanide and isocyanic acid) are released during pyrolysis, but only at high temperature. The ration of these\_main gaseous nitrogen products depending on both the type of biomass and the conditions of the pyrolysis process [76]. Nitrogen-free gases leave the system when pyrolysis temperature is increased which results nitrogen depletion in char at high temperatures [81]. However, low pyrolysis temperature does not favour the liberation of fuel nitrogen therefore most of the nitrogen (approximately 60-75 % at 500 °C) remains captured in the char [72, 76, 82].

The nitrogen functionalities in biochar are *pyrrolic-N*, *pyridinic-N*, *quaternary-N* and *amines* [83-85] and incubation tests evidenced that these stable nitrogen forms with low bioavailability [86].

## 6. Biochar properties

### 6.1. Biochar as a fuel

Due to its high fixed carbon content biochar is a renewable energy source with a heating value up to 30-35 MJ/kg [87]. Biomass char has higher energy density and better combustibility properties than traditional biomass, and higher reactivity than coal due to its oxygen content [88] and its incoherent carbon structure [89]. The combustion of biomass char is able to displace traditional fuels, however, the combustion of biochar recycles atmospheric CO<sub>2</sub> and liberates the char-bond N in the form of NO<sub>x</sub> without the benefit of carbon or nitrogen sequestration.

According to different estimations biomass pyrolysis with soil applications of the biochar has a negative greenhouse gas emission – with a *CO<sub>2</sub> equivalent* ranging from few hundred kg up to a few tonnes of *CO<sub>2eq</sub> t<sup>-1</sup> dry biomass* – with a positive net energy [90-92]. A detailed calculation and complete life cycle assessment of biochar can be found in the work of Roberts et al [90].

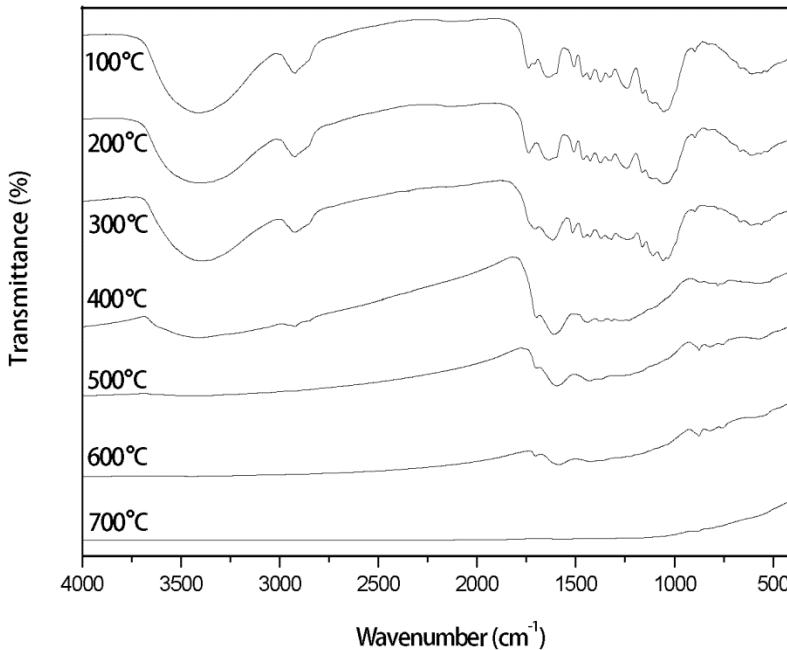
### 6.2. Biochar as a soil amendment

The most widely acknowledged benefit of biochar's soil applications is its long-term carbon sequestration potential [90, 93]. Other potentials of biochar is stimulation of N<sub>2</sub> fixation and the biological transformation of nitrogen in soil [94-96].

Biochar is also known for the ability to contribute to soil properties by changing its physical and chemical characteristics. The most important physicochemical properties of biochar are directly related to the type of the biomass used for char production and the applied temperature of pyrolysis [55, 97] therefore biochar contribution to soil quality factors can be both positive and negative [98, 99]. By selecting the right feedstock, setting the right pyrolysis conditions and elaborately characterising the physicochemical properties, char can be applied to soil as an amendment.

The pyrolysis temperature related structural changes of biochar can be seen on the infrared absorption spectra of Fig. 5. Comparing these spectra it can be seen that char gradually loses its structural complexity at higher pyrolysis temperatures as wood carbonisation becomes more completed. Char samples prepared at 300 °C and 400 °C show dramatic decreases in intensity in almost all functional groups; this is the temperature range in which the majority of the pyrolysis mass loss of wood occurs due to the degradation of cellulose, hemicellulose and lignin. Hemicellulose peak at 1736 cm<sup>-1</sup> becomes undetectable in char prepared at 400 °C but the O – H (3413 cm<sup>-1</sup>) and CH<sub>n</sub> related vibrations (2956, 2924, 2851 cm<sup>-1</sup>) show dramatic decreases in char prepared at higher temperatures (400 – 600 °C) where the thermal degradation of cellulose is already completed. Pyrogenic char (prepared at 700 °C or over)

has no measured transmittance due to the lack of organic functionalities and the disordered carbon structure.



The first strong broad band between 3700 and 3000  $\text{cm}^{-1}$  of dried willow (100 and 200  $^{\circ}\text{C}$ ) is the stretching vibrations of O – H functional groups. In the region of 2975–2840  $\text{cm}^{-1}$  the unresolved group of medium weak bands is related to C – H stretching vibrations of  $\text{CH}_n$  groups. The peak at 1736  $\text{cm}^{-1}$  is assigned to the absorption of free carbonyl groups, therefore it is a typical hemicellulose marker [112, 113]. Bands around 1600 and 1500  $\text{cm}^{-1}$  are generally considered as lignin markers as this is the region of the skeletal vibrations of aromatic rings [114].

Sample: 2 mg grinded wood or biochar blended with 200 mg KBr and pressed into pellet

Spectra: recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer, 4 scans per experiments, resolution: 4  $\text{cm}^{-1}$

Source: Chapter authors

**Figure 5.** Changes in the infrared spectra of biochar obtained at different pyrolysis temperatures

The functional groups on biochar surface determine the pH and the cation exchange capacity and the nutrient retention in soil [100, 101]. The pH also has an impact on the mobility of ions and affects soil microbial activity [102].

As well as the changes of biochar surface, the increasing pyrolysis treatment temperature also increases C content, decreases H and O content and increases the ash content in char [103]. These changes in char composition increase hydrophobicity [99] and aromaticity [103]. Hydrophobicity and aromaticity play a major role in the future stability of biochar in soil [103] and the estimated half-life of char with O/C over 0.2 is 100–1000 year and greater than 1000 years in case of char when O/C is smaller than 0.2 [104].

The composition changes in the carbonised char is also accompanied by changes in the physical appearance of the biochar; Pyrolysis vapours can develop pores in biochar [105]

The increased porosity affects the water-holding capacity of soil and the surface area – a shelter for microorganism [97]; bulk density, which affects the pore size distribution of soil and the conditions for gas exchange [106]; and total dissolved solids, which give an estimation on the amount of the mobile charged ions, migrating from char to soil [80].

Due to the high specific surface and adsorbent capacity, biochar can increase the water and nutrient retention capacity of the soil [107, 108] while a biochar buffer layer in soil can reduce both nitrate leaching and gaseous loss of soil nitrogen [107, 109]. Improved nitrogen recovery in soil will directly result in increased plant growth.

Biochar properties are strongly affected by the pyrolysis temperature [97, 110] which makes possible to design biochar, remediate specific soil issues and realise a new type of soil management [99, 111].

## 7. Conclusions

Nitrogen always has been the “weakest link” in the food chain and agriculture. Without additional nitrogen the present capacity of Earth’s topsoil is not able to satisfy our hunger for biomass for food or energy.

Wastewater is a valuable source of nitrogen but nitrate leaching is harmful for groundwaters and results in nutrient lost from the soil. Plants cultivated for wastewater treatment can be considered as energy crops and bring land back into economic use.

To obtain an economically attractive feedstock for energy conversion applications, efforts should be made to maximise the utilisation of the sources (land, irrigation water etc) and the energy gained from the biomass with a minimum environmental impact. Pyrolysis of wastewater irrigated energy crops offers the advantages in both fields, therefore it is an excellent candidate to supply green energy for rural areas in developing countries while the soil application of biochar can retain and assimilate the wastewater derived nitrogen back into the environment.

- In terms of the nitrogen-cycle, biomass combustion liberates 5-5.9 Tg of NO<sub>x</sub>-N each year into the atmosphere. However, the cultivation of wastewater irrigated energy crops and the pyrolysis of the vegetation filters have the potential to reduce the emission of NO<sub>x</sub>-N and other greenhouse gases the following ways:
- Vegetation filters reduce the concentration of water contaminants and lower nitrogen content by 97%. Wastewater can provide nitrogen and nutrients for plants and increase biomass yield without the application of inorganic soil fertilisers.
- Energy crops can uptake wastewater derived nitrogen and double the concentration of the storage amino acids.
- Compare to traditional combustion the pyrolysis of energy crops does not favour the formation of NO<sub>x</sub>.
- Pyrolysis captures 60-75% of the biomass derived nitrogen in the biochar. The soil applications of the biochar provide a long-term nitrogen sequestration and reduce the amount of the reactive nitrogen forms which accompany the traditional water treatment processes.

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