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# Nitrogen cycle of effluent-irrigated energy crop plantations: From wastewater treatment to thermo-chemical conversion processes

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This paper reviews nitrogen (N) cycle of effluent-irrigated energy crop plantations, starting from wastewater treatment to thermo-chemical conversion processes. In wastewater, N compounds contribute to eutrophication and toxicity in water cycle. Removal of N via vegetative filters and specifically in short-rotation energy plantations, is a relatively new approach to managing nitrogenous effluents. Though combustion of energy crops is in principle carbon neutral, in practice, N content may contribute to NOx emissions with significant global warming potential. Intermediate pyrolysis produces advanced fuels while reducing such emissions. By operating at intermediate temperature (500°C), it retains most N in char as pyrrolic-N, pyridinic-N, quaternary-N and amines. In addition, biochar provides long-term sequestration of carbon in soils.

**Keywords:** Carbon and nitrogen sequestration, Intermediate pyrolysis, Nitrogen cycle, Nitrogen fixation, NOx emission, Vegetative filters, Wastewater treatment

## Introduction

Nitrogen (N) is crucial to modern agriculture and N fixated via Haber-Bosch process and from other sources is added in large quantities to soils to maintain agricultural output. Short-rotation plantations irrigated with effluent have both high N uptake capacity[1] and enhanced growth characteristics without the application of fertilizers or competition with fresh water usage[2,3]. Furthermore, wastewater irrigation reduces cost of wastewater treatment while crops cultivated at the land can meet the increasing energy demand of rural areas without destroying existing forestry[2]. A promising energy conversion technologie is intermediate pyrolysis which provides an advanced liquid fuel. Pyrolysis liquid is widely studied for direct CHP (combined heat and power) applications to provide green electric power with highest efficiency. A pyrolysis plant coupled with a high temperature gasifier unit has potential to convert biomass-to-energy with a reasonable efficiency where primary product of gasification (syngas) is a real alternative to oil for CHP feed. This review presents wastewater treatment by using effluent-irrigated energy crop plantations, N uptake in effluent-irrigated short-rotation crops and biomass-to-energy, specially using intermediate pyrolysis.

## Wastewater and Wastewater Treatments

### Nitrogen in Municipal Wastewater

In domestic wastewater, N is present in both inorganic and organic forms. Organic N from human diet and metabolism is being transformed into free ammonia ($NH_3$) and ammonium cation ($NH_4^+$) by microorganisms[4,5]. $NH_3$ to $NH_4^+$ ratio in water depends on temperature and pH. Presence of free $NH_3$ (> 0.002 mg/l) is toxic for ecosystem[6]. $NH_3$ is also the source of inorganic [nitrate ($NO_3^-$) and nitrite ($NO_2^-$)] N in wastewater[5]. Inorganic N, an essential plant nutrient, however, its high concentration in water causes eutrophication followed by thedegradation of dead plant tissues with increased oxygen demand of the fresh water. Therefore, eutrophication leads to oxygen scarcity and decreased self-cleaning ability of biomass system[7]. The presence of nitrate and nitrite anions in drinking water is blamed for causing cyanotic conditions (shortness of breath, methemoglobinemia and blue-baby syndrome)[8,9]. To protect human health and aquatic life, nitrogenous contaminants of wastewater must be controlled. Requirements have been set up by different governments and some typical N values have been

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identified as follows: typical N concentration in grey wastewater as TN[10], 0.6-74; typical N concentrations in domestic raw wastewater as TN[10], 20-80; requirement of European Council for urban wastewater treatment as TN[11], 10; general standard for effluents (India) for TN[12], 100; primary standards of National Primary Drinking Water Regulations by US Environmental Protection Agency for nitrate-N[13], 10; health value of Australian drinking water guidelines for nitrate-N[14], 11.3; and standard for drinking water (India) for nitrate-N[15] , 10.1 mg N/l. Here, TN (total N) is sum of organic N, ammonical N, nitrate-N and nitrite-N.

### Biological Wastewater Treatment

Physico-chemical removal of N from wastewater is possible, however, biological methods are more effective and less expensive treatments[16], and it is based on mixed population of live bacteria, naturally present in wastewater, which convert N compounds to other chemical forms. Mineralization (ammonification, nitrification and denitrification) of wastewater-derived organic matter provides oxygen, N and energy for bacteria to produce new cells[17]. Activated sludge formed by living microorganisms is the core of modern industrial wastewater treatment technologies. To ensure the most suitable environmental conditions for microorganisms (aerobic zone for nitrification and anoxic zone for denitrification), several industrial processes[16] (Bio-Denitro process, modified Ludzack-Ettinger process, Bardenpho Process, etc.) have been designed. When these conventional wastewater treatment facilities are not available – mostly in developing countries – stabilization ponds are the most widely used municipal wastewater treatment systems[18]. Even if climate favours microbial activity, stabilization ponds cannot reduce N concentration satisfactorily[19].

### Vegetative Filters

If high cost of commercial technologies disables the performance of a sufficient wastewater treatment, unregulated or poorly regulated water turns to a potential risk factor to human health and environment[20,21]. To eliminate this risk, it is crucial to reduce concentration of N and other pollutants before any effluent reaches the environment. Application of vegetative filters represents an alternative on-site wastewater treatment[22.23]. This type of wastewater management is able to reduce concentration of organic and inorganic contaminants in the water and remove 73-97% of total N[24]. This low-cost treatment also assimilates N as plant nutrients back into the environment, while pathogens from wastewater cannot compete with natural microbial population of the soil[25,26].

## Nitrogen, the Essential Plant Nutrient

### Nitrogen in Soil and Nitrogen Uptake in Plants

Role of soil in biological-cycle is to store and supply N and other essential nutrients for plants. Average amount of organic N in soil is 3300 kg/ha, however, available N for plants is less than 1% of it, as vegetations are not able to uptake any kind of forms of soil N[27].

Synthesis of plant cell components (amino acids, nucleic acids, enzymes, chlorophyll etc.) is unachievable without N; deficiency of N in plants causes slow growth, which can be recognized by pale green leaves. Without available N, there are no processes in plants[21]. For the formation of new cells, plants uptake N along with water in the form of $NH_4^+$ or $NO_3^-$ during their growing period (assimilation), or store extra N (immobilization)[28]. N is absorbed from soil during the whole life of plants but N use efficiency of plants is varied with the stage of maturity, seasons, environmental conditions of site and fertility status of the soil as well[27,29]. The latter factor is particularly important in terms of crop yield as N supply is a main limitation factor to plant growth[30].

### Synthetic Nitrogenous Fertilizers

If N supply of soil is not sufficient, land productivity can be improved by organic and inorganic (synthetic) macronutrient plant fertilizers such as ammonia-based products[31]. The source of N in these fertilizers is atmosphere containing molecular N (78%). The direct reaction of molecular N and molecular hydrogen to $NH_3$ is the base of widely applied Haber-Bosch process[32], which provides > 140 million tonnes of $NH_3$ to farmers around the world every year[33,34]. To sustain growing population, industry produces millions of tonnes of fertilizer, which is responsible for > 1% of the world's energy consumption. Since hydrocarbon combustion is the main energy source of $NH_3$ production, fertilizer industry is a major contributor to greenhouse gas (GHG) emission[35]. Besides the production related energy consumption, transportation of fertilizer materials also contributes to the world's GHG emission with several teragrams $CO_2$ per year[36].

### Nitrogen Uptake in Effluent-Irrigated Short-Rotation Crops

Similar to inorganic fertilizers, wastewater is a source of supplemental N. Plants have enhanced growing characteristics due to wastewater, grey water or effluent irrigation[38-40]. Total Kjeldahl N (sum of organic and ammonical N) in wastewater and sullage is as follows[3]: wastewater from sewage treatment, 32-36; domestic sullage from a pond, 28-32; and domestic sullage from a household, 35-37 mg N/l. During wastewater irrigation, plants uptake N for their growth and polish water. N uptake of rain-fed eucalyptus in New Zealand is reported[1] to be 30-80 kg/ha/y, while uptake in effluent-irrigated plantations is one magnitude higher.

#### Nitrate-Leaching

Even though vegetations have potential to store wastewater-derived N, nutrient uptake is not the only limitation factor of land applications of wastewater. Due to metabolism of microorganisms, N in soil and wastewater is predominantly present in the form of $NO_3^-$ and $NH_4^+$, which are readily available plant nutrients. Surface charge, which is negative of clay minerals in soil, attaches wastewater derived $NH_4^+$ ion to soil matrix, but ions with negative charge are carried by water[40]. Due to heavy rains or improper agricultural activities, $NO_3^-$ can leach below the root system of plants to groundwater with a negative effect both on environment and drinking water quality. $NO_3^-$ concentration in groundwater can reach extreme high values; one of the reported[41] Indian samples had 1500 mg $NO_3^-$ / l water, which is 150 times higher than permitted value of WHO. $NO_3^-$ is a primary pollutant of groundwater. Although chemical reduction, biological denitrification and other *in-situ* treatments of groundwater are feasible [42], $NO_3^-$ 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 soil. Without an effective prevention system, the only groundwater protection is source control, which means the limitation of wastewater loading.

## Energy from Biomass

#### Heating Values

Higher heating value (HHV: kcal/kg; MJ/kg or Btu/lb) is the energy available from fuel[43]. Quality characteristics of biomass have a significant effect on the yield of energy during a biochemical or thermochemical conversion process[44]. Typical heating values of some Indian wood species and other solid fuels are as follows: *Eucalyptus tereticornis*[45], 19.4; *Melia azedarach*[46], 20.7; charcoal from rice husk[47], 17-18; high quality charcoal[48], 28-33; general purpose coal[49], 32-42; and petrol[49], 45-47 MJ/kg. High oxygen, carbon and N content favours combustion and increases heating value[45,50]. Elements of biomass have environmentally safe relevancies as well as original composition of biomass will determine composition of the products of thermochemical conversion processes.

#### Biomass Combustion and Nitrogen Liberation

Biomass combustion is a $CO_2$ neutral energy conversion technology. Combustion converts fuel-N to nitric oxides (NOx) and nitrous oxide ($N_2O$)[51-58], which are contributors to acid rain formation[59,60]. $N_2O$ is also a GHG with a global warming potential (GWP) of 289, where 1 unit represents GWP of $CO_2$ over 20 years[61]. In trees, N present is 0.3-1%[62] but N content in short-rotation plants is generally higher and significant differences can be found between species. Increasing N content in biomass also means increase in emission of NOx during combustion[63]. Even though presence of N in wood is relatively low and calculated NOx emission for wood combustion is not > 150-300 mg/m$^3$, NOx emission from biofuel combustion only in India was estimated to be one tera g a few decades ago[63,64]. Since energy demand and biomass fuel consumption of India are increasing[65], NOx emission must be even more significant now and need to be decreased drastically. Emission of NOx contributes to acidification and it also causes eutrophication and ground-level ozone formation[66]. To control harmful effects of combustion plants' pollutants, Environmental Protection Agency of the United States (US EPA) or Intergovernmental Panel on Climate Change (IPCC) have elaborated guidelines and emission criterias[67,68]. 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)[63] but these technologies add cost, particularly in small bioenergy facilities. Another effective way to reduce environment impact of biomass-derived NOx pollution is the application of alternative energy conversion technologies with better emission characteristics.

#### Pyrolysis

#### *Intermediate Pyrolysis*

Pyrolysis is the thermal degradation of macromolecules and biopolymers in the absence of oxygen, and leads to solid, liquid and gaseous products. Slow and fast pyrolysis of woody biomass has been extensively investigated[69,70]. The ratio of gases, vapours and solid pyrolysis products depend on temperature,

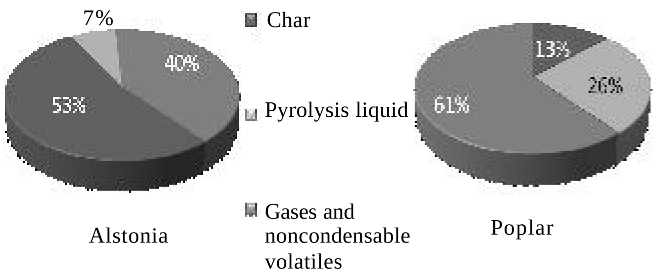

Fig. 1—Product distribution of intermediate pyrolysis (raw material, short-rotation energy crops from a wastewater-irrigated plot of Palwal, Northern India; pyrolysis temperature, 500°C; heating rate, 25°C/min)

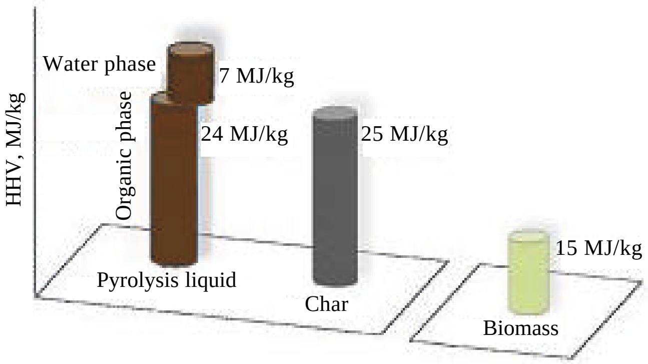

Fig. 2—Energy content of biomass (straw) and its solid and liquid pyrolysis products[73] (raw material, straw pellet; pyrolysis temperature, 500°C; feeding rate, 50 kg/h)

Table 1—Power outputs of pyrolysis liquid combustion[80]

| | |
|---|---|
| *Hot water generation* | |
| Boiler fuelled with pyrolysis oil (BTG Biomass Technology Group BV, The Netherlands) | 150 kW |
| *Electric power generation* | |
| 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 |
| *Combine heat and power generation (CHP)* | |
| Pyrolysis liquid combustion in a Stirling CHP unit (ZSW, Germany) | 10-25 kWth, 4-9 kWe |

residence time and heating rate. Intermediate pyrolysis[71,72] (Fig. 1) combines advantages of fast and slow pyrolysis. Slow temperature and moderate residence time lead to pyrolysis liquid with low viscosity, low tar yield and high energy yield[73-78] (Fig. 2). In terms of NOx emission, pyrolysis is a more desirable energy conversion technology than combustion; while biomass combustion releases fuel-N in the form of NOx, the inert atmosphere of pyrolysis does not favour the formation of these or any other oxidized pollutants[79].

### *Pyrolysis Liquids*

Intermediate pyrolysis has already proven its ability to generate high energy pyrolysis vapours and liquids, which carry most of the energy content of original feedstock[73-78]. Even though liquids from pyrolysis generally have lower heating values than conventional fossil-derived fuel oils. This renewable fuel has higher energy density than raw biomass with additional benefit that it can be easily pumped or transported. Pyrolysis liquid is a relatively new energy source and its energy applications are still developing. However, it is already proven that pyrolysis liquid combustion in boilers, turbines and engines can be used for heat and electricity production (Table 1)[80].

### *Gas Products*

Main gaseous N products[79] of wood pyrolysis are hydrogen cyanide (HCN), ammonia ($NH_3$) and isocyanic acid (HNCO) with a ratio depending on both the type of biomass and the conditions of pyrolysis process. Nitrogenous gases are released during pyrolysis at high temperature. Low temperature of intermediate pyrolysis does not favour the liberation of fuel N, therefore most of the N (60-75% at 500°C) remains captured in char[79,81,82].

### *Solid Products of Pyrolysis*

#### *Biochar*

Biochar (mainly C and ash) is solid co-product of pyrolysis process. Johnsson[57] found N enrichment in biochar, independent of applied pyrolysis technique, because primary devolatilization products released at low pyrolysis temperature have a similar organic structure to the feedstock, therefore formation of these products cause neither an increase nor decrease in N concentration of char. By gradually increasing temperature up to 900°C, N-free gases leave system, therefore N depletion in char does not occur during intermediate pyrolysis proceseses[57]. N functionalities in biochar are pyrrolic-N, pyridinic-N, quaternary-N and amines[83-85].

Due to high fixed C content, biochar is a clean-burning fuel (heating value, 30-35 MJ/kg)[86]. However, combustion of biochar recycles atmospheric $CO_2$ and liberates char-bond N as NOx. On the other hand, char product of pyrolysis captures both C and N in a stable, solid form and biochar returned to soil makes pyrolysis a $CO_2$-negative energy conversion technology and closes loop of biomass-to-energy cycle. Biomass pyrolysis with soil applications of biochar has a negative GHG emission – with a $CO_2$ equivalent ranging from few 100 kg up to a few tonnes of $CO_2$eq $t^{-1}$ dry biomass – with a positive net energy[87-89]. A detailed calculation and complete life cycle assessment of biochar is reported[87]. The most widely acknowledged benefit of biochar's soil applications is its long-term carbon sequestration potential[87,90]. Other potentials of biochar are prevention of nitrate leaching and fertilization due to its high specific surface and adsorbent capacity. A biochar buffer layer in soil char reduces both nitrate leaching and gaseous loss of soil N[91,92] and increases water and nutrient retention capacity of soil[92,93]. Char is also able to improve efficiency of plant fertilizers and biological transformation of N in soil[94,95]. While nitrate leaching removes valuable N and nutrients from soil, an improved N recovery in soil will directly result in increased plant growth.

## Conclusions

Wastewater is a valuable source of N but nitrate leaching is harmful for groundwater and results in nutrient lost from the soil. Both vegetation selection and N management have equal importance to design an effective and sustainable wastewater-irrigated plantation field. Plants cultivated for wastewater treatment can be considered as energy crops, which can also bring land back into economic use. However, to obtain an economically attractive feedstock for energy conversion applications, efforts should be made to maximise the utilisation of sources (land, irrigation water etc.) and energy gained from biomass with a minimum environmental impact. Small scale intermediate pyrolysis of wastewater-irrigated energy crops offers advantages in both fields and is, therefore, an excellent candidate to supply green energy for rural areas of developing countries.

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