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### BIO-OIL PRODUCTION FROM AGRICULTURAL CROP RESIDUE BY PYROLYSIS PROCESS

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**Abstract:** Fossil fuels are finite, expensive and not globally distributed. Moreover, their use is associated with GHG emission such as CO<sub>2</sub>, CH<sub>4</sub>, SO<sub>2</sub> and NO<sub>2</sub>. Since 1990, considerable focus has been placed on the development of technologies for the conversion of biomass into biofuels as alternative liquid transportation fuels to gasoline and diesel oil (Shi *et al.*, 2009). Among the major reasons cited for the development of biofuel technologies are high crude fuel prices, reduction of dependence on fossil fuels, growing concerns about GHG emissions, which contribute to climate change, potential contribution to sustainable development and rural revenue generation (Worldwatch, 2006). Globally, about 60% of fossil fuels produced is utilized for transportation. Approximately 98% of transportation fuels used is produced from crude oil. However, the availability, economic sustainability and GHG emissions associated with their utilization pose major problems with transportation fuels (Bertuccio, 2008). Transportation including GHG emissions from the production of transportation fuels, constitutes about 25% of global energy-related GHG emissions, and this is gradually increasing (Worldwatch, 2006). Biofuel presents itself as a suitable option and has received considerable attention in recent years. The production of first-generation biofuels competes with global food crop production. Fast pyrolysis is a viable option since it uses a non-food renewable resource, which is low cost and globally available unlike fossil fuels, which are finite and located in just a few regions in the world. Bio-oil production as replacement or supplement would reduce the dependence on fossil fuels for transportation and consequently contribute to the national economy through foreign earning savings, job creation and rural development. Moreover, the use of bio-oils would result in reduced GHG emissions compared to conventional fossil fuels.

**Keywords:** Bio-Oil, Pyrolysis Process



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## INTRODUCTION

Biomass refers to organic matter that may be converted to energy. Biomass may take the form of energy crops, agricultural wastes, domestic and industrial waste which include sewage sludge and Municipal solid waste. Energy from biomass, does however pose a challenge as most forms of biomass have low energy contents, high moisture contents and a wide range of variability in terms of size and shape translating into problems of feed handling. Issues of transportation of feedstock to the point of production also pose a challenge to the production of energy from biomass. These issues have led researchers to seek means of mitigating these problems and increase the attractiveness of biomass as a sustainable source of energy production.

First generation biofuels are currently produced in large commercial quantities in many countries from agricultural crops such as sugarcane, maize and jatropha through well-established technologies such as hydrolysis, fermentation and trans-esterification (UNEP, 2009). Bioethanol and biodiesel are the two most well-known examples of first-generation biofuels used in the transport sector and account for over 90% of global biofuel usage. Other first-generation biofuels include vegetable oil and biogas. These are globally produced for the replacement of conventional fossils gasoline or fossil diesel oil or as additives in the transport sector and feedstock in the chemical industry. Bioethanol is produced by fermenting sugar extracted from feedstocks such as sugarcane, sugar beets, sugar extracted from starch contained in maize, wheat, sweet sorghum, cassava and potatoes (FAO, 2008).

Biodiesel such as fatty acid methyl ester is produced from fatty acids obtained from feedstocks such as rapeseed, soybean, sunflower, coconut, oil palm, *Jatropha curcas*, recycled cooking oil and pure plant oils through trans-esterification usually with methanol in the presence of catalysts such as sodium hydroxide, potassium hydroxide or acids (Schuchardt *et al.*, 1998). Glycerol results as a by-product. Acid catalysts give very high yields of biodiesel, but the reactions are slow and require temperatures above 100 oC and more than 3h to reach complete conversion. Current industrial processes, therefore, are usually carried out using base catalysts (Schuchardt *et al.*, 1998). Trans-esterification reduces long-branched molecules, which are less suitable as fuels to short straight-chained fatty acid methylesters of lower viscosity, which are readily combustible (Heywood, 1988)

Second-generation biofuels may be produced from lignocellulosic biomass such as agricultural crop residues, forestry and wood processing wastes, organic components of municipal solid waste (MSW) and energy crops such as *Mischantus giganteus*, using either thermochemical or biochemical processes (Vantomme, 2006). However, they are currently not produced on a commercial scale because of the high cost of the processes. Cellulosic ethanol or ethyl alcohol

( $\text{CH}_3\text{-CH}_2\text{OH}$ ) and cellulosic butanol ( $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{OH}$ ) are two well-known examples produced from lignocellulosic biomass through biochemical processes. They can be used as alternative sources to petroleum-gasoline for transportation (OECD/IEA, 2008). While the properties of cellulosic ethanol are similar to those of first-generation bioethanol, the relative abundance and wide range of lignocellulosic biomass used as feedstock, which is non-food, give them an advantage (Vantomme, 2006; UNDESA, 2007; UNEP, 2009).

Third-generation biofuels are, however, produced from feedstocks such as micro- and macro-algae, vegetable oils and biodiesel. Green algae, in particular, produce as much as 60% of their body weight as triglycerides when deprived of key nutrients such as nitrogen and potassium. Algae fuel, also called oil-algae and referred to as a third-generation biofuel, is produced using trans-esterification (OECD/IEA, 2008; UNEP, 2009).

### Types, structure and chemical composition of lignocellulosic biomass

Lignocellulosic biomass is the major structural component of woody and non-woody plants, and represents a major source of renewable organic matter. It includes wood processing waste, forest residues, agricultural crop residues, organic portion of municipal solid waste (MSW) and special energy crops such as *Miscanthus giganteus* (Table 2). It is composed

of, depending on its origin and type, cellulose (40–50%), hemicellulose (20–30%) and lignin (20–30%) (Malherbe and Cloette, 2002; Jarvis, 2005; Mohan *et al.*, 2006; Howarth *et al.*, 2008).

Cellulose and hemicellulose are tightly bound to lignin by covalent and hydrogen bonds (Mohan *et al.*, 2006). Cellulose is a linear crystalline polymer of hexose sugars, which consists of glucose units linked by  $\beta$ -(1,4)-D-glycosidic bonds. This is in contrast to starch, which is a polymer of glucose linked by  $\alpha$ -(1,4)-D-glycosidic bonds (Duff and Murray, 1996). Chemically, glucose is a monosaccharide or a simple sugar while starch is a complex carbohydrate. Starch and glucose are also chemically different in terms of size, physical properties and uses.

The  $\beta$ -(1,4)-D-glycosidic bonds make it highly resistant to de-polymerization by either enzymatic or acidic hydrolysis. The hydrogen bonds between adjacent cellulose polymers, whilst forming crystalline structures that give plants structural strength, make them difficult to react since they prevent water penetration (Viikari *et al.*, 1991). The chain length or degree of polymerization (DP) of cellulose, which depends upon its source is 3,000–15,000. The DP affects the yields of fast pyrolysis products. During fast pyrolysis, cellulose undergoes de-polymerization and fragmentation to form bio-oil, non-condensable gas and char (Mohan *et al.*, 2006).

Hemi-cellulose is a highly branched polymer composed of five-carbon sugar, that is, pentoses ( $\text{C}_5$ ), mostly xylose, and hexoses ( $\text{C}_6$ ), mostly mannose. In general, the percentage composition of pentose sugars in hemicellulose is 6–26 %wt of dry mass, while hexose is 40–70%.

Hemicellulose is thermally less stable than cellulose due to lack of crystallinity. It is easier to extract and decompose into its constituent sugars than cellulose (Mohan *et al.*, 2006; Centi, 2009). Its molecular weight is also lower than that of cellulose. However, its exact composition depends on the type of lignocellulosic biomass (Jarvis, 2005; Centi, 2009; Sanchez, 2009).

### **Biochemical conversion of lignocellulosic biomass into biofuels**

Biochemical conversion of lignocellulosic biomass into biofuels consists of processes which include: (1) pre-treatment; (2) hydrolysis of the polymers to produce sugars such as hexose and pentose that can be readily fermented; (3) fermentation of the sugars to biofuels (4) separation and (5) purification (Lee *et al.*, 2005; Liu *et al.*, 2008; Sanchez, 2009; Joshi *et al.*, 2011). Pre-treatment changes the structure of the lignocellulosic biomass such as its surface area and there by makes cellulose and hemicellulose more accessible to hydrolysis (Wyman *et al.*, 2007; Centi, 2009; Shi *et al.*, 2009). Pre-treatment methods can be categorized into three major groups, namely (i) mechanical processes, i.e. physical such as grinding or milling, (ii) chemical means (iii) and biological means (Centi, 2009). Dilute sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) pre-treatment gives high yields, and is the preferred option because of its extensive development (Wyman *et al.*, 2007; Joshi *et al.*, 2011). According to Centi (2009), pre-treatment was the most expensive step in the conversion of lignocellulosic biomass into biofuel. It accounted for 22% of the global ethanol production cost in 2009. Fungal pre-treatment has also been proposed for bioethanol production using lignocellulosic biomass (Sanchez, 2009; Salvachúa *et al.*, 2011). Generally, it is a slow process, which is carried out under mild conditions (Sanchez, 2009).

Hydrolysis is carried out using acids, enzymatic processes and biological processes. Dilute acid hydrolysis, for example, which is a fast process, is carried out at 120 oC. However, it yields high amounts of waste products, which are required to be disposed of (Centi, 2009; Sanchez, 2009). Cellulose hydrolysis yields sugars, which are mainly hexoses.

A major challenge with the fermentation of sugars derived from cellulose and hemicelluloses is to ferment all the hexoses and pentoses at high rates and yields. The fermentation of pentose, however, gives lower rates (0.29 g /g/h) and yields (10–40 wt.%) than those of hexose (> 0.3 0 g /g/h ; 30–50 wt%) (Jarvis, 2005; Dien *et al.*, 2006; Centi, 2009).

### **Thermochemical conversion of biomass**

Thermochemical processes for the conversion of lignocellulosic biomass into biofuels include combustion, torrefaction, pyrolysis and gasification (Zanzi *et al.*, 2002). They are rapidly becoming an alternative source for renewable energy production globally. However, the sustainability of the processes requires the availability of sufficient biomass as feedstock to satisfy the demand of emerging bio-energy industries. Combustion, which is the easiest and

oldest means of producing heat energy from biomass, converts solid biomass in the presence of air to heat in boilers, burners or turbines. Depending on the type of combustion equipment, some types of biomass require pre-treatment, which is associated with high operating and financial costs (McKendry, 2002).

Torrefaction, a process which is carried out at low temperatures (200–300 °C) in the absence of oxygen and long residence time, is used to upgrade biomass. It completely dries the biomass and makes it easy to grind. The process partially removes hemicellulose, dehydrates cellulose and increases the calorific value of the biomass (Garcia-Perez, 2010). Biomass, which has been torrefied is similar to char and can be used as feedstock in various thermochemical applications for heat and power generation, and also for liquid fuel production

Gasification, a partial oxidation of biomass, is carried out under pressure at high temperatures, which range between 650–900 °C. The primary products are syngas, bio-oil and char as the main products. Syngas, which consists mainly of carbon monoxide (CO), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) and traces of ethane, ethene, water, char particles, ash and tar, can be fed into turbine power plants for energy production (FWPA, 2007; Trifirò, 2007).

Pyrolysis, the decomposition of biomass by heating either in the absence or in a limited supply of oxygen, is carried out at 400–800 °C with bio-oil, non-condensable gases and char as the main products. Based on the heating rate, it can be grouped into three main categories, namely: slow pyrolysis (<283 °C/min), intermediate pyrolysis (373 °C/min) and fast Pyrolysis (>1273 °C/min) (Bridgwater, 2007; Papadikis *et al.*, 2009; Zhang *et al.*, 2009; Duku *et al.*, 2011). These categories produce different product yields, each of which has a potential economic use (Yoder, 2009; Mullen *et al.*, 2010).

Slow pyrolysis of biomass, which is carried out under a slow heating rate, results in higher yields of char and lower yields of bio-oil than fast pyrolysis due to enhanced dehydration and condensation reactions. Therefore, it has often been employed in industry for charcoal production (Ganesh and Banerjee, 2001; Papadikis *et al.*, 2009; Yoder *et al.*, 2009).

Fast pyrolysis, however, is carried out between 400 and 550 °C with bio-oil, char and non-condensable gas as the main products. It gives high yields of bio-oil. Its major steps include (i) biomass drying, (ii) reduction of the biomass to small particle-sized (0.5–1 mm), (iii) fast pyrolysis, (iv) bio-char separation and (v) liquid recovery or collection after condensation of the vapours (Bridgwater, 2007). Its key characteristics are very fast heating rate (376 °C/s) at a controlled temperature and a short vapour residence time (< 2s) (Aho *et al.*, 2008; Papadikis *et al.*, 2009). Rapid heating and cooling rate of the vapours reduce the extent of secondary reactions, which result in high yields of bio-oil (Antal and Grønli, 2003; Asadullah *et al.*, 2008; Zhang *et al.*).

During fast pyrolysis, the main components of lignocellulosic biomass contribute differently to product yields. Cellulose fast pyrolysis yields bio-oil, which contains many oxygenated organic compounds such as levoglucosan, alcohols and esters (Antal and Gronli, 2003). Fast pyrolysis of hemicellulose also yields similar products (Zhu *et al.*, 2006). Fast pyrolysis of lignin, however, gives higher yields of char but lower bio-oil yields than either that of cellulose or hemicellulose (Antal and Gronli, 2003). The extractives volatilise to yield mainly liquid and gas (Antal and Grønli, 2003). Minerals, particularly alkaline metals, catalyze secondary decomposition reactions of cellulose and hemicellulose, which result in high char yields but low bio-oil yields (Bain, 2009).

Many types of pyrolyzers such as fluidized-bed, transported, circulating fluidized-bed, fixed bed, ablative and vacuum have been developed and applied in biomass fast Pyrolysis (Asadullah *et al.*). Fluidized-bed is proposed for this study because it is a well developed technology. Moreover, it can provide a high heating rate of more than 1000 °C/s. It uses small-sized biomass particles with diameters below 2 mm to ensure rapid heat transfer (Yoder *et al.*, 2009).

Bio-oils are generally dark-brown organic liquids, acidic, unstable and immiscible with diesel oil. They have a high viscosity and an unpleasant odour. They are also chemically complex due to the presence of many oxygenated organic compounds. Compared with petroleum diesel oil, they have higher oxygen and water content. These characteristics limit their direct application as fuels for transportation (Trifirò, 2007; Zhang *et al.*, 2009). They can, however, be upgraded through processes such as hydrogenation and catalytic cracking into bio-gasoline and bio-ethanol, and used as alternative sources to fossil fuels for transportation (Yoder *et al.*, 2009).

## CONCLUSION

Biofuel presents itself as a suitable option and has received considerable attention in recent years. Fast pyrolysis is a viable option since it uses a non-food renewable resource, which is low cost and globally available unlike fossil fuels, which are finite and located in just a few regions in the world. Bio-oil production as replacement or supplement would reduce the dependence on fossil fuels for transportation and consequently contribute to the national economy through foreign earning savings, job creation and rural development. The use of bio-oils would result in reduced GHG emissions compared to conventional fossil fuels.

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