Feature Article

Determination of Levoglucosan Compounds in Pyrolysis Oil of Empty Fruit Bunches and its Potential Application

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INTRODUCTION

Generally, pyrolysis is one of the most promising technologies for biomass utilisation. It is essential in the first stage thermochemical conversion of biomass into bio-oil, bio-char and gases dependent on process conditions in complete absence of oxygen. Usually, pyrolysis occurs at moderate temperature (400°C to 700°C) with rapid heating (Abnisa *et al.*, 2013). It is mainly used for optimising liquid products at high heating and heat-transfer rates using finely ground biomass. Nitrogen (N_2) - an inert gas - is commonly used to accelerate vapours sweeping from the hot zone (pyrolysis zone) through the cool zone (condenser). Condensation is an important step for liquid production during pyrolysis. Without this, only the biochar and gas products can be obtained from the process. Once the pyrolysis vapours are condensed, a dark brown liquid is formed, namely bio-oil or pyrolysis oil. The bio-oil yield can be up to 80% of the initial dry mass (Bridgwater and Peacocke, 2000).

Bio-oil is a free-flowing organic liquid, comprising highly oxygenated compounds. The oil is a complex mixture of many compounds such as water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid and other carboxylic acids. Others *e.g.* hydroxyaldehydes, hydroxyketones, sugars and phenolics are also present (Zhang *et al.*, 2007). This unique mixture has resulted in the oil having a relatively low energy density (16–18 MJ kg^{-1}, which is about 40%-45% less than that of hydrocarbon fuels), immiscibility with hydrocarbon fuels and storage instability (Wang *et al.*, 2018). Among the compounds present, sugar appearing in larger fraction is particularly of interest as a carbon building block for chemicals and fuels production.

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Sugars in bio-oil are originated from the celluloses of biomass. One main components of sugar *i.e.* levoglucosan (1,6-anhydro-β-D-glucopyranose) is commonly found from pyrolysis of biomass. Levoglucosan can be formed from cellulose during burning through glycosidic bond cleavage and depolymerazation (*Figure 1*). Pyrolysis of lignocellulosic biomass typically results in oils with ≈ 8 wt.% of levoglucosan (David *et al.*, 2018).

Sugars from bio-oil can be extracted using the total carbohydrate determination method developed by the Association of Analytical Communities (AOAC). The method 988.12 (44.1.30) is simple, fast, accurate and specific to carbohydrate extraction. The method was developed for food and agriculture applications. In principle, carbohydrates will be destroyed by strong acids at high temperatures. Under these circumstances, a series of reactions occur, starting with a dehydration reaction, followed by the production of various furan derivatives. This method detects soluble sugars as well as oligomeric or polymeric sugars which are hydrolysable into monomers under high acid condition (Rover *et al.*, 2013). These reducing groups give an orange-yellow color which absorbs light in the ultraviolet visible (UV) range. Nearly all classes of sugars (*i.e.* sugar derivatives, oligosaccharides, polysaccharides) can be determined. The color produced is permanent, thus, it is not necessary to pay special attention in controlling conditions during sugar extraction.

PYROLYSIS OF EMPTY FRUIT BUNCHES (EFB)

Pyrolysis of empty fruit bunches (EFB) was carried out using a fluidised-fixed bed reactor as shown in *Figure 2*. Firstly, 5 g of air-dried EFB were sieved to the desired particle size of 107-125 μm and then placed in the reactor. The pyrolysis commenced at different temperatures *i.e.* 400ºC, 500ºC and 600ºC, using parameters optimised previously (heating rate: 30ºC

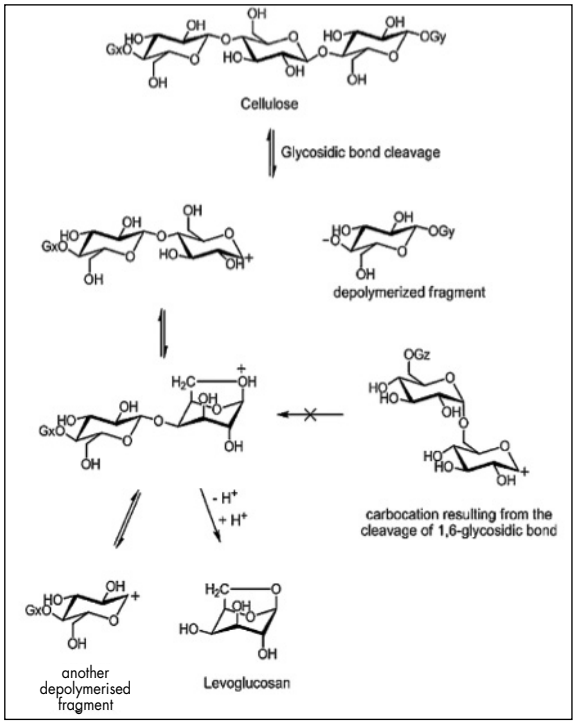
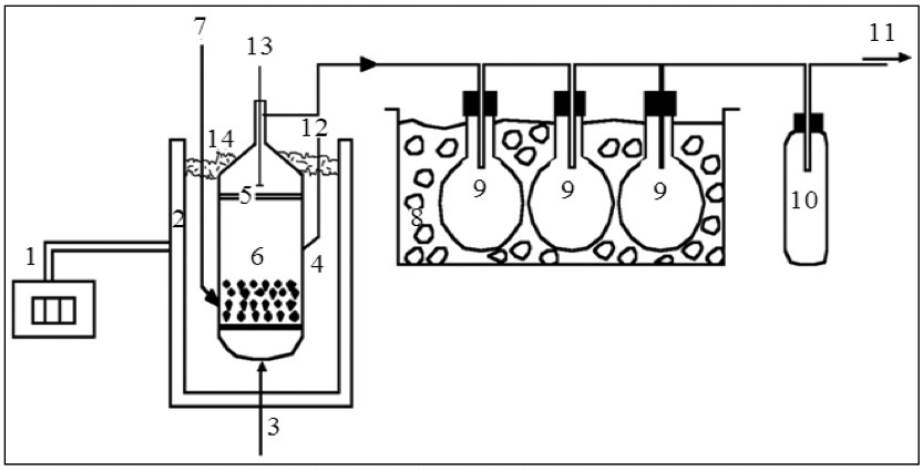


Figure 1. Mechanism of levoglucosan formation from cellulose (Patwardhan et al.*, 2009).*

min^{-1} and residence: 30 min) (Sukiran *et al.*, 2016). The connection tubes between the reactor and the cooling system were heated using heating tape to avoid condensation of vapors during pyrolysis The whole process must be held for either a minimum of 20 min or until no further significant release of gas is observed. The highest bio-oil yields obtained was 47 wt.% at 500ºC (*Table 1*) indicated a maximum collection of condensable liquid products; which then decreased as temperature increased further. The bio-oil collected was used to determine the total soluble sugars concentration in bio-oil. Extraction of sugars from bio-oil was also conducted.

TABLE 1. PRODUCTION OF BIO-OILS AT DIFFERENT PYROLYSIS TEMPERATURE

Sample	Temperature (°C)	Bio-oil yield (wt.%)
Bio-oil-1	400	32.1 ± 1.4
Bio-oil-2	500	47.4 ± 1.8
Bio-oil-3	600	34.9 ± 2.1



(1) Temperature recorder; (2) Furnace; (3) Fluidising gas; (4) Reactor; (5) Quartz fritz; (6) Sand bed; (7) Feedstock inlet; (8) Water-ice bath; (9) Bio-oil collector; (10) Gas dryer; (11) Gas exit; (12) Sand feeder; (13) Thermocouple; (14) Glass wool.

Figure 2. Schematic diagram of the pyrolysis system.

DETERMINATION OF LEVOGLUCOSAN IN BIO-OIL

The concentration of levoglucosan in bio-oils was determined using high performance liquid chromatography (HPLC) (Waters, 2707) as follows: Waters XBridge C18 column (4.6 mm x 250 mm) with internal diameter, 5 mm; mobile phase, methanol: water (9:1, v/v); column temperature, 30°C; flow rate, 1 ml min^{-1}; and injector volume, 10 µl. Prior to this, the standard calibration curve of levoglucosan was established through measuring the concentrations of diluted levoglucosan standard solutions (0.1%, 0.3%, 0.5%, 0.7%, 1.0% and 1.5%) and plotting them. Based on the calibration curve, the levoglucosan concentrations in bio-oil samples collected were determined. The results (*Table 2*) indicated that 6.4 wt.% maximum levoglucosan concentration is attainable at 500°C.

TABLE 2. LEVOGLUCOSAN CONCENTRATION IN THE PRODUCED BIO-OIL

Sample	Concentration (wt.%)
Bio-oil-1	4.82 ± 0.8
Bio-oil-2	6.36± 0.5
Bio-oil-3	4.35± 0.3

EXTRACTION OF SUGAR COMPOUNDS IN BIO-OILS

Sugar compounds in bio-oil were extracted by total carbohydrate determination method (AOAC method 988.12). About 10 ml of each bio-oil sample was treated with 3.26 ml of concentrated sulfuric acid, followed by 0.65 ml of 5% phenol solution. The mixture was heated for 5 min in a 90°C static water bath. The solution was cooled and then the extracted sugar compounds were analysed using a UV-visible spectrophotometer. Since each sugar has a unique absorption maximum at specific wavelength, absorption curves were obtained by plotting absorbance versus wavelength for each respective positive control (sugar). The absorption maximum for levoglucosan, the most prominent sugar in bio-oil, was at 490 nm. Other sugars detected were D-xylose and D-glucose (*Table 3*). The extracted levoglucosan yield using this method was 1.8 wt.% at extraction rate from 29% to 41%. In addition, the purity of levoglucosan was determined using HPLC. The obtained levoglucosan was washed three times using 95% alcohol (10 ml-15 ml) with continued stirring for 15 min, then centrifuged at 5000 rpm for 15 min and the centrifuged residue was dissolved in 10 ml of water. A purity of levoglucosan up to 91% was obtained from bio-oil-2 (*Table 4*).

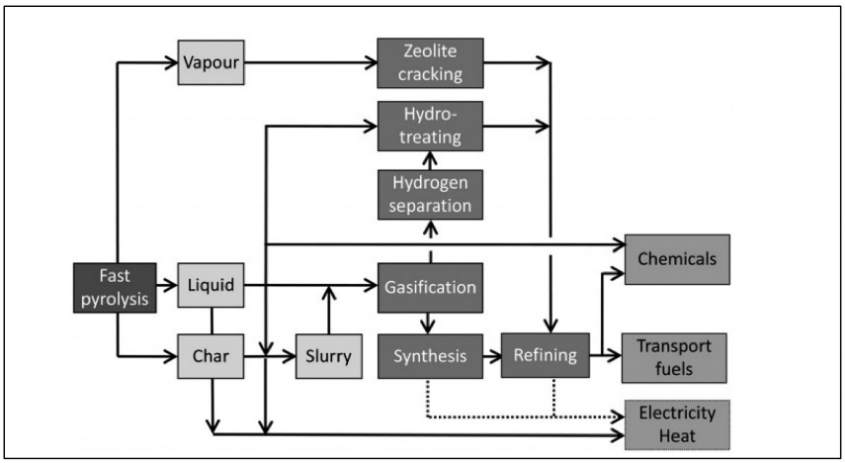


Figure 3. Bio-refinery concept for pyrolysis plant (Bridgwater, 2012).

TABLE 3. COMPARISON OF SUGAR YIELDS EXTRACTED FROM THE BIO-OIL BY TOTAL CARBOHYDRATE DETERMINATION METHOD

Type of extracted sugar	Wavelength maximum (nm)	Concentration (wt.%)		
		Bio-oil 1	Bio-oil 2	Bio-oil 3
Levoglucosan	490	1.84 ± 0.02	1.83 ± 0.02	1.80 ± 0.02
D-glucose	485	1.04 ± 0.03	1.35 ± 0.03	1.31 ± 0.03
D-xylose	480	0.38 ± 0.08	0.38 ± 0.07	0.37 ± 0.06

TABLE 4. EXTRACTION RATE AND PURITY OF LEVOGLUCOSAN

Sample	Extraction rate (%)	Purity (%)
Bio-oil-1	38.2	89.8
Bio-oil-2	28.8	91.4
Bio-oil-3	41.4	87.1

APPLICATION OF LEVOGLUCOSAN

Levoglucosan can be upgraded into transportation fuels via fermentation and catalytic synthesis to produce alcohols and hydrocarbons, and chemicals via dehydration and aqueous-phase re-forming to produce heterocyclic aldehydes (furfurals), aromatics (furans) and alkanes as building blocks of gasoline (Wang *et al.*, 2018). In addition, levoglucosan is also potentially used for biodegradable plastics production and as ligand for synthesis of high value specialty chemicals such as pharmaceutical compounds assisted by chiral catalysts.

BIO-REFINERY CONCEPT FOR PYROLYSIS PLANT

A bio-refinery features optimum performance and utilisation of biomass for materials, chemicals and fuels relating to cost, economics, market, yield, environmental impact, carbon balance and social aspects. In other words, it must incorporate an optimised use of resources to maximise profitability and benefits besides minimising wastes. *Figure 3* shows a pyrolysis bio-refinery plant. Its key feature is co-production. As explained earlier, three types of products can be obtained from pyrolysis *i.e.* liquid, char and gas/vapor and these products can undergo different routes (*e.g.* gasification, hydrotreating, cracking, *etc.*) to finally produce not just fuels but chemicals and power (electricity). However, the route to produce fuels is energy intensive as much of the energy content of the biomass is lost during processing so electricity generation may seem to be the final destination for efficient use of biomass.

MARKET ANALYSIS OF LEVOGLUCOSAN RECOVERY FROM PYROLYSIS

In a 200-dry t day^{-1} biomass pyrolysis facility, the levoglucosan recovery could reach 70 t day^{-1}. To improve its economic feasibility, other co-products obtained such as hydrogen and gasoline should be harnessed. The total installed equipment and capital costs are estimated to be USD 21 million and USD 32.6 million, respectively. The calculated internal rate of return (IRR) for pyrolysis facility is approximately 15% based on market prices of USD 3.33 kg^{-1} hydrogen, USD 2.92 gal^{-1} gasoline and diesel and USD1495 kg^{-1} levoglucosan (Wang *et al*., 2016).

CONCLUSION

In this study, levoglucosan in pyrolysis oil was extracted using total carbohydrate determination method. The maximum extracted levoglucosan was 1.8 wt.% at 38% extraction rate which was considered low but with 90% high purity. Other extraction method should be explored to increase levoglucosan recovery. To make pyrolysis profitable, optimisation of multiple processes and products is crucial and this will require in-depth economic assessment and development of feasible component processes for a holistic integration eventually. At least, provision of heat and power should be prioritised for energy use self-sufficiency.

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