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Characterization and separation of corn stover bio-oil by fractional distillation

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HIGHLIGHTS

- Corn stover bio-oil was distilled under atmospheric and reduced pressure conditions.
- High yield of heavy fraction boiling at 180–250 °C was obtained.
- There were significant reduction in moisture and acidity in the heavy fraction.
- Aromatic and oxygenated compounds were distributed in the light and middle fraction.
- Phenolic compounds were concentrated in the heavy fraction.

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ABSTRACT

Fractional distillation of bio-oil derived from pyrolysis of corn stover was investigated under atmospheric and reduced pressure/vacuum conditions. Characterization of the fractions in terms of moisture, total acid number (TAN), energy content, elemental and chemical compositions was performed to evaluate the effectiveness of the distillation process in separating the components and rendering improved product properties. Results showed high yields (wt.%) of the heavy fractions (b.p. 180–250 °C at 1 bar; 160–230 °C at 0.5 bar) and significant reduction in moisture and TAN content. Water was obtained as a separate layer in the first (light) fraction (b.p.⩽100 °C at 1 bar; ⩽80 °C at 0.5 bar). The heating values increased, especially for the light distillates in both atmospheric and vacuum distillation and the heavy distillates in atmospheric distillation. Analysis of the chemical composition showed that aromatic and oxygenated compounds were distributed in the light and middle fractions (~15–20%) while phenolic compounds were concentrated in the heavy fraction (~53%). The distillation process was effective in separating the components and yielding a product (heavy fraction) with improved properties and composition and which can be further utilized as feedstock for future upgrading procedures or as a blending material with other liquid fuels.

1. Introduction

Biomass has been widely investigated as a potential energy source in recent years mainly due to the need for fuels that are relatively clean as compared to conventional fossil fuels and can be produced on a sustainable basis [1–4]. Different types of biomass have been utilized as energy source, ranging from woods, agricultural residues, biomass-processing wastes, oilseeds and their residues, and even pure chemicals [5]. Among the agricultural residues, corn stover tops the list in terms of abundance. According to the USDA data in 2002, corn is the most widely planted crop and its residue, termed as the stover, which consists of the aboveground portion of the corn plant such as the stalk, leaves, cob and husk [6], is the most abundant agricultural residue [7]. Estimates of corn stover availability by Nielsen [8] suggests a value of 217 Mt y^{-1} (dry basis), which approximates the 243 Mt y^{-1} (dry basis) data by USDA (2002). From these values, assuming only 40% removal of the stover on a sustainable basis, approximately 82 Mt y^{-1} (dry basis) of corn stover is available [7,9]. Thus, development of technologies that would effectively convert this crop residue into potentially valuable energy sources should be undertaken to take advantage of its availability and abundance.

Thermochemical conversion, particularly pyrolysis, is one method by which fuels and other chemicals can be produced from biomass materials. Pyrolysis is an old-age technology which involves thermal decomposition of biomass in the absence of oxygen to produce solid, liquid and gaseous products [10–12]. The yields and properties of the product formed are strongly affected by such process parameters as pyrolysis reactor design, reaction parameters (temperature, heating rate, residence time, pressure, and

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catalyst) and biomass type and characteristics (particle size, shape, and structure) [13–15]. Various pyrolysis processes have been employed for the conversion of corn stover into fuels and chemicals, using different reactor configurations and reaction conditions. Table 1 lists the various pyrolysis technologies reported by different investigators, specifically utilizing corn residues as feedstock.

Among the pyrolysis products, bio-oil or pyrolytic oil has been identified as a potential petroleum fuel substitute. It is a complex mixture of oxygenates produced from the thermal decomposition of the biopolymers in the biomass [21] and contains a wide variety of functional groups and molecular weights including acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers due to the complexity of the pyrolysis reactions [22]. Some of these compounds may indirectly render some undesirable properties in the bio-oil such as high moisture, high acidity and lower heating value as oxygen, which limit its use as direct liquid transportation fuel substitute [23]. Hence, further processing of the bio-oil is necessary to make it suitable either as a direct liquid transportation fuel substitute or as a bio-refinery feedstock.

Improvement in the properties of bio-oil can be done physically or chemically, depending upon the desired improvement in the bio-oil. Ash removal can be done by filtration techniques [24] while solvent addition can be employed to homogenize and reduce the viscosity of the bio-oil [25]. Upgrading can also be done by emulsifying the bio-oil with diesel oil to make either a transport fuel or engine fuel for power generation [26]. Since the bio-oil contains a wide range of compounds with different boiling ranges, separation of the components by distillation has been employed by a few researchers to improve the properties of the bio-oil. Molecular distillation at a pressure of 60 Pa and temperature of 130 °C was employed by Wang et al. [27] to fractionate sawdust bio-oil into three parts: light, middle & heavy fractions, with a total yield of 85%. Improved properties were observed for the middle fraction, which had less mobility and lower water content while the heavy fraction was void of volatile substances and had a relatively high heating value. Molecular distillation was also employed by Guo et al. [28] to separate carboxylic acids from pine bio-oil at operating conditions of 60 Pa and 50 °C. They were able to improve the properties of the bio-oil by reducing the acid content in the crude bio-oil from around 14.85% to as low as 0.96% and 2.2% in the two fractions they obtained after distillation. The energy and moisture content reduced to only 1% while the heating value increased from 15.6 to above 23 MJ kg^{-1} in the distilled fractions. On the other hand, Zheng and Wei [29] performed reduced pressure distillation of rice husk bio-oil at 2 kPa and 80 °C, resulting in a water phase yield was 29% and a distillate yield of 61%, which has lower oxygen content, higher heating value (34.2 MJ/kg), about twice that of the fast pyrolysis bio-oil), lower corrosivity and better stability than the original bio-oil, making it more suitable for fuel oil use or as chemical source. Atmospheric distillation of softwood bark bio-oil was performed by Boucher et al. [30] at temperatures up to 140 °C to determine the true boiling point distribution of the light fraction of the bio-oil. The distillation was stopped at 140 °C due to the onset of bio-oil cracking and polymerization. Rectification at normal and reduced pressures of sawdust bio-oil was performed by Xu and Lu [31] up to 145 °C temperatures which produced around 61% of coke. Flash distillation of wood tar was carried out by Carazza et al. [32] at 9.3 kPa and a maximum temperature of 300 °C on a bench scale process. Additionally, Zhang et al. [33] investigated the atmospheric distillation of bio-oil obtained from rice husk up to temperatures of 240 °C and recycled the distillation residue as a feedstock for co-pyrolysis to produce renewable chemicals. The distillate contained dozens of separable organic components, with acetic acid, propanoic acid and furfural recovery efficiencies being higher than 80 wt.%.

The above studies suggest the effectiveness of distillation in improving the properties of the bio-oil by separation of the components. However, advanced distillation equipment is necessary for molecular distillation. In addition, these studies were done using bio-oil derived from biomass such as rice husk, saw dust and soft wood, which may have different composition as compared to corn stover bio-oil, and therefore different distillation characteristics. Also, as to the authors' knowledge, there has been, if not none at all, limited studies published describing the fractional distillation of bio-oil specifically derived from corn stover at different temperature ranges up to 250 °C.

Hence, the overall goal of this study is to conduct fractional distillation of corn stover bio-oil at atmospheric and reduced pressure conditions to gain insights on the potential improvement in the characteristics of this bio-oil.

The specific objectives are as follows:

(a) evaluate product yields at different distillation conditions (reduced and atmospheric pressures);

Table 1
Various technologies for the pyrolysis of corn residues.

Feedstock	Pyrolysis process/equipment	Results	Researchers
Corn cobs	200-mL tube-type reactor	Solid (23.6–31.6 wt.%) and liquid yields (34–40.96 wt.%) decreased with temperature in contrast with the increase in gaseous yield (27–40.96 wt.%). Yields of hydrogen and methane gradually increased with an increase in temperature while the liquid product was analyzed by GC–MS to contain phenols, 2-furanmethanol, among others	Cao et al. [16]
Corn residues	Non-catalytic slow pyrolysis and catalytic pyrolysis in a fixed-bed reactor	Liquid was the major product from catalytic pyrolysis (about 40–44 wt.% on biomass)	Ioannidou et al. [10]
Corn stover	Microwave pyrolysis	The effect of reaction temperature (515–685 °C), time (4–22 min) and particle size (0.5–4 mm) of corn stover on the result of the microwave pyrolysis process was investigated. Results showed that the particle size did not significantly affect the results of the microwave pyrolysis process	Lei et al. [17]
Corn cobs/stover	Fluidized bed reactor	Bio-oil yield was 60% while that of char was of around 18.9% and 17% from corn cobs and corn stover, respectively. The bio-oil was found to have a heating value of ~20 MJ/kg	Mullen et al. [18]
Corn stalks	Laboratory captive sample reactor	Liquid yield is relatively low (maximum of 28% at 550 °C) while gas yield reached 60.8% at 710 °C and char yield 36.48% at 470 °C.	Zabaniotou and Ioannidou [19]
Corn stover	Batch pressurized reactor	Maximum bio-char yield of 37.3 wt.% and liquid product yield of 31.4% were obtained at 400 °C while the gas yield was maximum at 600 °C (21.2 wt.%).	Capunitan and Capareda [20]