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Production of bio-based phenolic resin and activated carbon from bio-oil and biochar derived from fast pyrolysis of palm kernel shells



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HIGHLIGHTS

• Bio-oil from palm kernel shells were used for the production of phenolic resin.

• Biochar was activated using CO₂ to produce activated carbon.

• The maximum phenol content in the bio-oils was 8.1 wt.%.

• Bio-oil appeared to substitute for fossil phenol in phenolic resin synthesis.

• Activated carbon was microporous with a maximum surface area of 807 m²/g.

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1. Introduction

The use of biomass for energy has recently become of great interest around the world, because biomass is a clean, renewable energy source, and its global balance of CO_2 is neutral. In particular, lignocellulosic biomass, composed mainly of cellulose, hemicelluloses, and lignin, is considered an economical and eco-friendly energy source, because it is available in large quantities, and does not compete with the food chain. Several conversion technologies for lignocellulosic biomass have been used to extract bioenergy in cost-effective ways. Fast pyrolysis is one of such conversion technologies, primarily to produce bio-oil, which is a complex mixture of organic compounds such as anhydro-sugars, alcohols, ketones, aldehydes, carboxylic acids, and phenols. Bio-oil itself can be used directly as a fuel oil for boilers or furnaces. Recently, however, there have been many trials to upgrade bio-oil by several methods,

ABSTRACT

A fraction of palm kernel shells (PKS) was pyrolyzed in a fluidized bed reactor. The experiments were performed in a temperature range of 479–555 °C to produce bio-oil, biochar, and gas. All the bio-oils were analyzed quantitatively and qualitatively by GC-FID and GC–MS. The maximum content of phenolic compounds in the bio-oil was 24.8 wt.% at ~500 °C. The maximum phenol content in the bio-oil, as determined by the external standard method, was 8.1 wt.%. A bio-oil derived from the pyrolysis of PKS was used in the synthesis of phenolic resin, showing that the bio-oil could substitute for fossil phenol up to 25 wt.%. The biochar was activated using CO₂ at a final activation temperature of 900 °C with different activation time (1–3 h) to produce activated carbons produced was 807 m²/g.

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such as catalytic upgrading and hydrodeoxygenation (HDO) to enhance its fuel properties (Lu et al., 2013; Zhang et al., 2013). However, it may seem undesirable to simply convert bio-oil into fuels, because bio-oils contain many value-added chemicals too. Thus, many studies have been performed with the goal of producing such chemicals by pyrolysis and their separation from bio-oil (Rout et al., 2009; Oudenhoven et al., 2012; Oh et al., 2013). Among the valuable chemicals in bio-oils, phenolic compounds, which are degradation products of lignin, have attracted the attention of many researchers (Bu et al., 2013; Salema and Ani, 2013). In particular, studies on the application of phenolic-rich bio-oil (or pyrolytic lignin) in the synthesis of phenolic resins has been conducted since the early 2000s (Amen-Chen et al., 2002; Sukhbaatar et al., 2009). Another valuable product from the pyrolysis of lignocellulosic biomass is carbonaceous biochar, which can be used as a solid fuel in power plants, as a soil amendment material, and as an effective adsorbent for uses in environmental remediation (Mukherjee et al., 2014). The applicability of biochar as an adsorbent can be improved by its physical activation, which



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produces a high-surface-area material, known as activated carbon. In physical activation, air, carbon dioxide, and steam are used as activating agents.

Recently, the pyrolysis of palm kernel shells (PKS) was widely examined. PKS is an attractive biomass residue for the production of a phenolic-rich bio-oil, because of its high lignin content (over 45 wt.%) (Kim et al., 2010).

One of the main aims of the present study was to produce a phenolic-rich bio-oil from the fast pyrolysis of PKS and to examine the content of phenolic compounds, especially phenol, in bio-oil. For the purpose, the fast pyrolysis of PKS was conducted in a fluidized bed reactor at different reaction temperatures (479–555 °C). Characteristics of the pyrolysis products were examined using various analytical tools. In particular, this study reports the content of each component of bio-oil obtained using relative response factor (RRF), calculated with the effective carbon number (ECN) and the content of phenol in bio-oil, obtained using an external standard method. Another goal of the work was to investigate the applicability of the resulting bio-oil. Because the bio-oil derived from PKS was reported to have a high content of phenol which has a high reactivity towards aldehydes (Kim et al., 2010), it was expected to replace fossil phenol in the synthesis of phenolic resins. For the purpose, three plywoods were manufactured using three phenolic resins that contained the whole bio-oil derived from PKS up to 50 wt.%, and the mechanical properties of plywood panels bonded with different resin formulations were examined. Finally, this work aimed to produce a value-added product, activated carbon, from biochar obtained from the fast pyrolysis of PKS. For the purpose, activation of biochar was conducted using CO₂ as an oxidizing gas in a fixed-bed reactor. The textural properties of the resulting activated carbons were also examined in this study.

2. Methods

2.1. Feed material

PKS was first crushed in a knife crusher, sieved to 1-2 mm and then dried in an oven at 105 °C for 24 h before use. Characteristics of the feed material are summarized in Table 1. The proximate

Table 1

Main characteristics of the palm kernel shells (PKS).

Proximate analysis ^a	wt.%	Chemical composition ^b	wt.%
Volatile matter Fixed carbon Ash	77.4±1.8 20.1±1.1 2.5±1.1	Cellulose Hemicelluloses Lignin Extractives	30.1±1.8 21.4±1.3 47.3±0.3 6.0±1.2
Alkali and alkali earth metal concentration	ppm	Ultimate analysis ^b	wt.%
Na	352	ſ	43.6+2.0
K	1971	н	4.9±0.2
Mg	975	N	0.5±0.0
Ca	9999	0 ^c	51.0±2.3
Al	3090		

^a Dry basis.

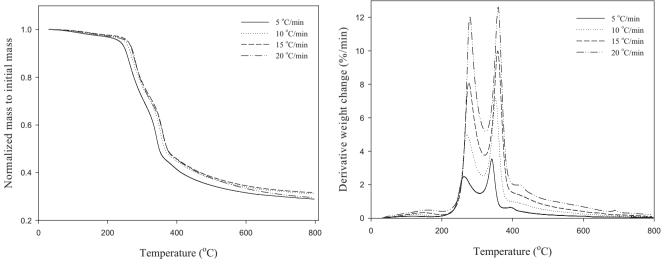
^b Ash free. ^c By difference.

by unterence.

analysis conducted following ASTM D3172 showed that the PKS had high contents of volatile matter and fixed carbon. The ash (2.6 wt.%) contained high amounts of alkali and alkali earth metals. To find out the contents of cellulose, hemicelluloses and lignin, the van Soest method was applied. As the result of the analysis, it was found that the PKS contained a high lignin content (\sim 47 wt.%).

To investigate the thermal degradation behavior of the feed material and to determine the reaction temperature in the pyrolysis plant, thermogravimetric analysis (TGA) was conducted with a thermogravimetric analyzer (TGA Q50, TA Instruments). The amount of PKS for the analysis was \sim 10–20 mg. The temperature range was 30–800 °C, and heating rates were 5, 10, 15, and 20 °C/min. The flow rate of nitrogen purge gas was 100 mL/min. TGA and differential thermogravimetric experiments (DTG) curves of the PKS are shown in Fig. 1.

The TGA and DTG curves showed that the thermal degradation took place within the wide range of 100–800 °C, and that the sample had three distinct decomposition regions. Comparing the degradation trend of lignocellulosic biomass reported by Yang et al. (Yang et al., 2007), the weight loss at 200–400 °C was likely due to the degradation of hemicelluloses (250–300 °C) and cellulose



(a) TG curves of PKS

(b) DTG curves of PKS

Fig. 1. TG (a) and DTG (b) curves of the PKS. (This figures show the thermal degradation behaviors of palm kernel shells.)

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