

Catalytic pyrolysis of larch sawdust for phenol-rich bio-oil using different catalysts



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ABSTRACT

Different kinds of catalysts have a great influence on the characteristics and products of the biomass catalytic pyrolysis. Catalysts of Cu/C, Pd/C, Pd–Ag and H-Zeolites socony mobil #5 (HZSM-5) were selected and characterized by the X-ray diffraction (XRD) and field-emission scanning electron microscope (FE-SEM). Decomposition behaviors of the larch catalytic pyrolysis were studied by the thermogravimetric analyzer (TG). The total carboxylic acids (TCAs) and total phenolic compounds (TPCs) in bio-oil were determined using the non-aqueous potentiometric titration method. The chemical distribution of bio-oil was investigated by the gas chromatography/mass spectrometry (GC/MS). Results showed that the temperature of the maximum weight loss rate of larch was decreased by adding these four catalysts. The carbon residue rate was increased by using HZSM-5. The content of GC-detected phenols increased from 25.28% to 35.11% (area) by adding Pd/C. However, TCAs in bio-oil were decreased sharply with Pd–Ag and Pd/C. HZSM-5 promoted the formation of phenols and enhanced TPCs in bio-oils (26.56 wt%), which increased by approximately 35% compared to that from the non-catalytic pyrolysis process. This phenol-rich bio-oil can be used to replace the traditional phenol for the manufacturing of high-value biomaterials.

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1. Introduction

Fast pyrolysis is an attractive way to convert woody biomass into liquid products called bio-oil, which is achieved by the rapid heating (heating rates of over 1000 °C/s), short residence times (could be less than 2 s), and temperatures of 400–650 °C in the absence of oxygen. Bio-oil is a mixture of degraded products of cellulose, hemicellulose and lignin. It contains hundreds of reactive, oxygenated species such as organic acids, (dehydrated) carbohydrates, aldehydes, ketones, (depolymerized) lignin fragments, etc. [1–3]. The concentration of valuable compounds in the bio-oil like phenols and the efficient utilization become the focus of attention for researchers. Derived from the lignin decomposition, phenolic compounds in the bio-oil are high-valued chemicals and show a great potential to replace fossil phenols. They are composed of both monophenols consisting of a singly substituted phenolic ring with

different groups and oligomeric polyphenols having multiples of phenol structural units [4]. The monophenols in bio-oil (<10 wt%) are valuable chemicals, which are suitable for a broad range of application such as in the phenolic resin synthesis. However, the oligomeric polyphenols (pyrolysis lignin) existed in bio-oil (25–30 wt%) are non-volatile and viscous, making them more difficult to be converted into useful products [5]. Therefore, the conversion of lignin to monomers instead of oligomers is highly desired in order to enrich the content of total phenolic compounds in the bio-oil and improve the reactivity.

Catalytic pyrolysis, such as the catalytic fast pyrolysis using the fixed bed or fluidized bed reactors and catalytic microwave pyrolysis [1,2,6–9], is a thermochemical conversion process by using catalysts to enhance reactions including cracking, decarbonylation, decarboxylation, deoxygenation, etc., resulting in improving the bio-oil quality in situ by enhancing the content of valuable compounds. To acquire high-performance bio-oil, it is critical to effectively use catalysts. Recently, some researchers reported the catalytic pyrolysis of biomass converting into phenol-rich bio-oil using different catalysts. Zhang et al. [10] prepared a magnetic solid

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base catalyst (potassium phosphate/ferroferric oxide) and used it for catalytic fast pyrolysis of poplar wood to selectively produce phenolic-rich bio-oil. It was found that the maximal total actual yield of major phenolic compounds was 43.9 mg/g, compared with the value of 29.0 mg/g in the non-catalytic process. The mechanism of the phenols formation during catalytic upgrading over HZSM-5 of vapors from fast pyrolysis of biomass was reported by Mukarakate et al. [11]. It was suggested that the phenols did not only arise from phenolic products formed during the pyrolysis of the lignin component of biomass, phenols were also formed by the reaction of water molecules with aromatic intermediates formed during the transformation of all pyrolysis products. Some researchers [12] focused on using the activated carbon as catalyst and investigated its capability on catalytic microwave pyrolysis of palm kernel shell for the phenol production. Results showed that total phenolics concentration in bio-oil reached 71.24% (area) at 500 °C using the activated carbon.

However, the yield of phenolic compounds in bio-oil is usually very low due to the majority of lignin-derivatives being phenolic oligomers and char. Most previous studies focused on understanding the catalytic pyrolysis of biomass to obtain the value-added bio-oil, but they did not provide a good account for the different catalysis of catalytic pyrolysis process for phenols in bio-oil with typical catalysts such as metal catalysts and zeolite catalysts. In this study, four typical catalysts of Cu/C, Pd/C, Pd–Ag and HZSM-5 were used for the catalytic pyrolysis of larch sawdust, and the pyrolysis characteristics and products distribution were investigated. The GC-detected phenols and total phenolic compounds, including volatile and non-volatile phenols, in the bio-oil were also discussed prominently.

2. Material and methods

2.1. Materials

Larch wood (*Larix gmelinii* (Rupr.) Kuzen.) was collected from the Xiao Hinggan Mountains in China, which is usually used for producing lumber and a large amount of larch sawdust is produced in the sawmilling process. The larch sawdust was regarded as the biomass wastes and usually just burnt in China. The traditional usage of the larch sawdust was contributing to the air pollution and presented low application value. In this study, the average size of 0.25–0.43 mm of larch sawdust particles were sorted out and dried to bone dry. The ultimate analysis of larch sawdust was conducted and the C, H, O and N were 53.40 wt%, 4.64 wt%, 41.85 wt% (by difference) and 0.11 wt%, respectively. The proximate analysis of

larch sawdust was 0.56w% of ash, 82.31w% of volatile, and 17.13w% of fixed carbon. The chemical composition was 42.26w% of nitric acid-ethanol cellulose, 66.66w% of holocellulose, and 26.63w% of klason lignin.

Purchased from Liaoning province in China, four catalysts, including Cu/C, Pd/C, Pd–Ag and HZSM-5, were calcined at 600 °C for 4 h under N₂ atmosphere in muffle furnace prior to use. The catalyst of Cu/C used activated carbon as carrier and prepared with the steps of immersion and vulcanization. The shape of Cu/C was black column and the active phase was CuO with 5 wt% content. Using also activated carbon as catalyst support, the catalytic active component of Pd/C was Pd (≥5.0 wt%). The catalyst carrier of Pd–Ag was Al₂O₃ and prepared using the coprecipitation method. Pd–Ag catalyst showed like Loess gray ball and its BET surface area was 220 m²/g. The catalyst of HZSM-5 (Si/Al = 20) presented as a cylinder, and its pore volume and BET surface area were 0.20 mL/g and 280 m²/g.

2.2. Experimental methods

A laboratory-made fluidized bed reactor combined with a fixed bed catalytic reactor was used for the larch pyrolysis (see Fig. 1). Prior to the experiment, the catalysts were filled in the fixed bed with the loading height of 100 mm ± 5 mm. Under a N₂ condition, 5 g larch sawdust was fed into the fluidized bed reactor with quartz sands as bed media material that was pre-heated at 550 °C. The gas residence time was 1.2 s. The initiation of primary pyrolysis reactions at this temperature released pyrolysis vapor and formed char. The char was collected by a tourbillion separator. The flow of pyrolysis vapor went toward to the fixed bed with different catalysts and then catalytic cracking occurred at 450 °C. The catalytic pyrolysis vapor was absorbed by the first-stage methanol absorber (200 g) followed by the second-stage water absorber (200 g) in an ice-water bath. The bio-oil was collected by the first-stage absorber. The second-stage absorber was to collect the methanol which was carried by the non-condensable gas in order to calculate the bio-oil yield.

The X-ray diffraction (XRD) pattern of catalysts was examined by the Bruker D8 Advance and collected from 10 to 80° at a scanning rate of 3°·min⁻¹. The surface morphology of the catalysts was investigated by a Hitachi SU 8010 field-emission scanning electron microscope (FE-SEM).

The NETZSCH STA449F3 (Germany) thermo-gravimetric analyzer was used for the thermal behavior analysis of the larch sawdust. Before the experiment, the larch sawdust and catalyst were mixed with the blending ratio of 5:1 (w/w) and ground

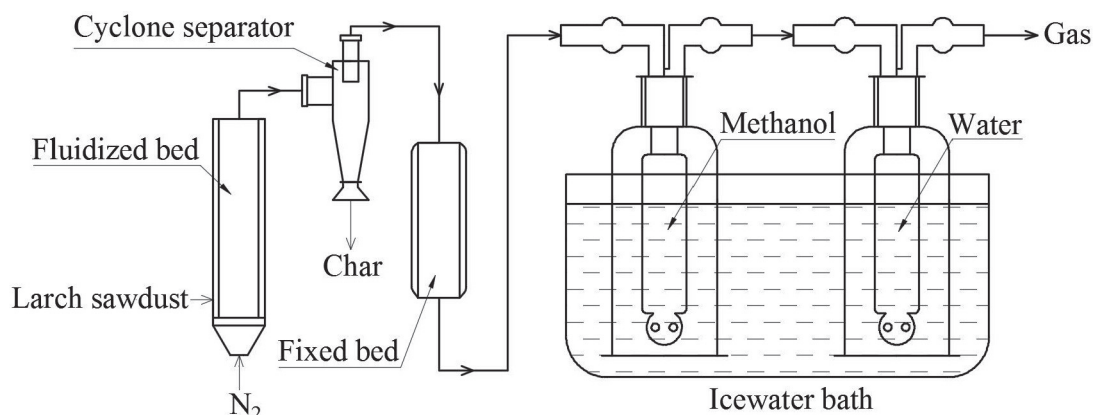


Fig. 1. The scheme of catalytic Pyrolysis process of Larch Sawdust.

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