



Production of renewable alkyl-phenols from catalytic pyrolysis of Douglas fir sawdust over biomass-derived activated carbons



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HIGHLIGHTS

- Highly porous ACs were produced from low-cost corn stover via chemical activation.
- Operation conditions during AC preparation were optimized.
- High selectivity towards simple phenols and furfurals in bio-oil products.
- Corn stover derived ACs exhibited mesoporosity and acidic surface functionality.

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ABSTRACT

The catalytic conversion of Douglas fir sawdust into bio-phenols on activated carbons (AC) obtained by chemical activation of corn stover with H₃PO₄ was investigated. Taguchi experimental design was used to optimize the preparation of AC using microwave assisted pyrolysis. Based on an overall consideration of AC yield, bio-oil yield, and phenols content, the optimized conditions were phosphoric acid to biomass ratio of 0.8, microwave power of 600 W and reaction time of 20 min. The bio-oils were rich in phenolic compounds (up to 90 area %) that mainly comprised phenol, methyl and ethyl phenol. During the catalytic pyrolysis of biomass with AC, phenolic compounds could either be derived from decomposition of lignin, followed by deoxygenation, or derived from furfurals, which were degradation products of carbohydrates. The catalytic activities of ACs were mainly owing to the well-developed porosity and abundant acidic surface functional groups. The porous structures of ACs were characterized by N₂ isotherms, showing a strong dependence on the acid impregnation ratio and microwave irradiation power. The presence of acidic phosphoric-containing surface functional groups was confirmed by SEM/EDX, FTIR and NH₃-TPD.

1. Introduction

Due to the depleting of fossil fuel reserves and serious environmental issues associated with their utilization, more attention has been paid to produce chemicals and fuels from renewable resources. Biomass is a matrix of cellulose, hemicellulose and lignin, which are valuable and renewable carbon sources that can substitute fossil-based feedstock for synthesis of value-added products and transportation fuels in the near-to-midterm. Of all these biopolymers, cellulose and hemicellulose have been largely used to produce cellulosic ethanol fuels via hydrolysis and fermentation process [1], while leaving recalcitrant lignin as a residue. Additionally, 50 million tons of lignin-containing residues are

discharged as black liquor from the pulp and paper industry every year [2]. Currently, lignin is mainly utilized as a low-value fuel for process heat generation and pulping chemicals recovery. Thus, more high-value applications of lignin for chemicals and transportation fuels are of particular interest to boost the bioeconomy and the sustainability of the chemical industries. Lignin constitutes approximately 10–35% of plant matter by weight and 40% by energy, and is the most abundant aromatic biopolymer in nature [3]. Lignin's polymer is a complex network of alkylated phenols, namely *p*-hydroxyphenyl (H), guaiacyl (4-hydroxy-3-methoxyphenyl, G), and syringyl (4-hydroxy-3,5-dimethoxyphenyl, S), which connected by ether (C-O) or carbon (C-C) linkages. Phenolic compounds, such as phenol, alkyl phenols, alkoxy phenols,

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and catechol can be obtained directly via thermal cracking of lignin polymers under noncatalytic/catalytic reaction conditions [4]. These biomass-derived phenolic compounds are of high energy density, thus can provide important feedstocks for the sustainable production of phenol-containing, high-octane-oxygenated gasoline additive via hydrodeoxygenation (HDO), alleviating the current dependency on limited petroleum resources [5,6]. In addition, lignin-derived phenolics have the potential to substitute traditional petroleum-based phenolics in manufacturing of important chemical products, such as phenolic resins. Attempts have been made to substitute phenol with lignin or bio-oil for phenolic resin. However, due to steric hindrance effects, lignin has low reactivity with formaldehyde [7]. Bio-oil from conventional fast pyrolysis of biomass can only serve as a partial (~25%) phenol replacement due to its abundant methoxy-substituted phenolic compounds, which have fewer available positions for polymerization than pure phenol [8]. Based on these facts, various high-value chemicals, especially monomeric phenolics can be potentially produced from lignin-rich biomass in a cost-effective manner [9].

Traditional conversion pathways for phenol production from biomass are focused on conventional fast pyrolysis and solvolysis technologies [6]. However, the phenol content in bio-oil obtained from conventional fast pyrolysis is highly dependent on the types of feedstock and pyrolysis conditions, which brings more challenges to the downstream separation process. Solvolysis can simultaneously depolymerize and hydrogenate lignin with the assist of hydrogen donating solvent such as tetralin, formic acid and 9,10-dihydroanthracene (AnH₂) [6]. However, the process usually requires long residence time (~16 h) and high temperature (~380 °C) in a closed reactor system with considerable pressure built-up [10]. These harsh operation conditions make the process implausible. Moreover, the large quantities of solvent consumption and low recovery efficiency cannot be ignored as well. With this context, more research attention has been paid to selectively produce phenol-rich bio-oil directly from biomass via catalytic pyrolysis. Typically, catalysts with impressive deoxygenation performance loaded on porous support materials, such as silica, zeolite or activated carbons are evaluated for direct conversion of biomass into phenolic compounds. Activated carbon (AC) is extensively used as catalysts or catalyst supports due to its distinguished physiochemical properties, such as high specific surface area, highly developed pore structure, tunable surface functional groups, and superior chemical inertness [11]. Solid carbon materials, like ACs are also superior microwave absorber. An interesting feature when ACs are exposed in microwave energy is that it generates “hot spots” which appear as small sparks and electric arcs [12]. These hot spots usually have much higher temperature than the surrounding bulk material, thus alternate the transient temperature distribution of the reactant and promote heterogeneous reactions [13,14]. Inspired by this unique phenomenon, we have evaluated the performance of commercial ACs in production of phenolics via microwave-assisted pyrolysis. According to our previous studies, AC proved to be an effective catalyst to selectively produce phenols via microwave-assisted pyrolysis of Douglas fir sawdust pellets [13,15–19]. High phenolic selectivity (up to 78 area %) was obtained by using commercial ACs such as DARCO MRX and DARCO 830 under a catalyst/biomass ratio of 3 and reaction temperature of 400 °C [17]. AC was believed to behave as a superior microwave absorber and created micro-plasmas or “hot spots” which can promote the deoxygenation of lignin-derived monomers [16,17]. Using the same method, the research group at University of Newcastle successfully produced phenol-rich bio-oil from palm kernel shell [20], peanut shell and pine sawdust [21]. Catalytic pyrolysis of palm kernel shell over AC was performed in a fixed-bed reactor and a microwave reactor. The results indicated that catalytic microwave pyrolysis (35.17–64.58%) resulted in a higher phenol selectivity than traditional fixed-bed pyrolysis (20.81–29.79%) under same operation conditions [20]. The highest phenol selectivity (64.58%) in bio-oil was obtained at 500 °C and a biomass to AC ratio of 10:2 [20]. AC was also effective for production of 4-ethyl phenol from

bagasse with high selectivity (28.8%) [22]. Apart from AC, mineral salts, especially solid base such as alkaline additive (e.g. KOH, NaOH, K₂CO₃ and Na₂CO₃) [23,24] and phosphates (e.g. K₃PO₄, K₂HPO₄, and KH₂PO₄) [25–27] also showed excellent performance in selective production of phenol-rich bio-oils. Peng et al [23] investigated the catalytic effects of alkaline additives on pyrolysis of lignin for phenolic products, which were mainly consisted of phenol, alkyl-phenols, methoxy-phenols and vanillin. They concluded that the addition of hydroxide alkalis, including KOH and NaOH enhanced deoxygenation and decarbonylation of methoxy-phenols and vanillin, therefore promoted the production of phenol and alkyl-phenols; while the carbonates, such as K₂CO₃ and Na₂CO₃ favored the production of methoxy-phenols [23]. Similar results were also reported in a study on catalytic pyrolysis of peanut shell by Mamaeva et al [24]. Catalytic pyrolysis of phosphates-impregnated biomass for phenol-rich bio-oil production was investigated by Lu et al [26]. As the K₃PO₄ content increased from 0.5 to 50 wt%, the selectivity of lignin-derived phenolics in the bio-oil obtained from catalytic pyrolysis of poplar wood increased steadily from 24.2 to 64.2%, compared with a benchmark of 20.4% in non-catalytic pyrolysis [26]. As a comparison, the selectivity of compounds that originated from carbohydrates fraction, including anhydrous sugars, furans, acids and aldehydes decreased significantly as the K₃PO₄ content increased. Based on these observations, they concluded that the addition of K₃PO₄ significantly inhibited the formation of carbohydrates-derived compounds while promoted decomposition of lignin to form phenolic compounds [26]. A comparative study on catalytic effects of different types of phosphates (K₃PO₄, K₂HPO₄, and KH₂PO₄) revealed that the capability of enhancing phenolics selectivity during catalytic pyrolysis followed the order of K₃PO₄ > K₂HPO₄ > KH₂PO₄, which matches the order of basicity of these compounds [25]. To improve the catalyst recyclability, K₃PO₄ was impregnated on Fe₃O₄ to form a magnetic solid base catalyst so that it can be simply separated from pyrolysis solids using magnet [27]. The supported catalyst demonstrated promising catalytic activity in selectively produce phenol-rich bio-oil. Catalysts reusability tests indicated that the catalytic activity did not show significant decrease after two regenerations [27]. To sum up, selective catalytic pyrolysis of biomass over AC and mineral salts are both promising techniques for biomass-to-phenols process.

As mentioned earlier, our previous studies showed that ACs are effective in selectively producing phenols from microwave-assisted catalytic pyrolysis. However, the existing commercial AC mainly utilizes coal and other high-cost agroforestry resources such as bamboo, wood and coconut as the feedstock. Thus, the high cost of AC production will adversely affect the economic feasibility of subsequent biomass-to-phenol process. In this study, the AC produced from a low-cost and abundant agricultural waste, corn stover will be used as an alternative catalyst for biomass-to-phenol process. The ACs were prepared using chemical activation method, and their catalytic performance and physiochemical properties were also analyzed. The objective of this study was to investigate the effects of operational parameters during preparation of ACs on their catalytic performance for phenols production.

2. Material and methods

2.1. Preparation of ACs from corn stover

Corn stover (collected from Brookings, South Dakota, USA) was selected as the AC precursor in this study. The as-received corn stover was milled and sieved to a particle size of less than 2 mm prior to use. The proximate analysis of corn stover was given elsewhere [28]. Phosphoric acid (85 wt%, Alfa Aesar, USA) was used as the activation agent. Approximately 50 g of corn stover were impregnated with H₃PO₄ at different acid (dry basis) to biomass ratios (0.3–1.8) for 24 h at room temperature. To insure proper contact of activation agent and biomass, distilled water was added to the acid/biomass mixture until the biomass

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