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Extraction of phenolic compounds from crude pyrolysis oil

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Abstract
Due to serious environmental problem and strict regulations to control pollution, researchers across the globe are putting their effort to find clean, renewable, greener and cost effective method to produce biochemical from biomass. The aim of this article was to highlight the method to extract phenolic compounds from crude pyrolysis oil using switchable hydrophilicity solvents (SHS). The pyrolysis oil was produced from softwood Kraft lignin through novel microwave pyrolysis process. The extraction efficiency of the method discussed in this article was about 95%. However, it was applied to small batch of pyrolysis oil (10 g). The highlight also presents the advantage and disadvantage of phenolic compound extraction methods including the recent proposed by Fu et al., 2013.

Keywords: biomass, extraction, phenols, pyrolysis oil

Phenol is one of the important industrial organic aromatic chemical compounds. It is a starting raw material not only for the production of synthetic polymers and adhesives, but also in the preparation of numerous pharmaceutical drugs for medical applications. Currently, the most dominant route to produce phenol is the oxidation of petroleum-based materials such as cumene and benzene. This chemical step involves the production of by-products, which is challenging. The demand for phenol is rising at the global level. Additionally, the raw materials for phenol production, such as cumene and benzene, are non-renewable fossil fuel or petroleum-based feedstocks. There is increasing international pressure to limit the use of fossil fuels in order to curb environmental pollution, which has caused the serious issue of climate change. Hence, an alternative route is sought to produce phenol in a greener and renewable way.

In the past few decades, scientists have been researching new renewable starting materials to produce phenol, such as lignin-rich biomass grasses, softwoods and agricultural residues. One driving force behind the extraction of phenolic compounds from biomass is the potential value added to the raw material, as biomass is cheap, abundantly available, renewable and carbon neutral. One can convert this biomass waste into wealth by producing value added products. Phenolic compounds produced from a biomass source can either partially or wholly replace petroleum or non-renewable feedstock-based phenol. Lastly, it can be cost effective and, importantly, can reduce environmental impacts.

Naturally, lignin is made up of phenolic chemical building blocks. Moreover, the paper and pulp industries generate abundant amounts of lignin as a waste material. Therefore, processing biomass materials such as wood or lignin waste through the thermo-chemical route (pyrolysis) produces pyrolysis oil. This oil is a mixture of complex chemical compounds. Pyrolysis is a process carried out in the total absence of oxygen and at moderately high temperatures (400 to 500°C). Pyrolysis oil typically contains more than 100 different chemical compounds (Garcia et al., 2000). However, pure lignin can provide a phenol-rich pyrolysis oil. The by-products of the pyrolysis process, such as gases and charcoal, can be used as fuel for energy or heating applications, and this heat can be recycled back into the process in order to save energy and reduce costs. Several technologies are available to thermally degrade biomass into pyrolysis oil, including fluidized bed reactors, vacuum pyrolysis, ablative reactors, entrained flow reactors, fixed bed reactors, rotating cone, screw or auger reactors, and microwave-assisted pyrolysis (MAP). Among these, MAP is a new approach and still at an early stage. Researchers across the globe are working to develop MAP processes for various types of biomass and waste materials. Overall, scientists have been successful in proving the concept of MAP to produce value-added products at the lab scale.

Very recently, Fu et al. (2013) described a method to extract phenol from pyrolysis oil using switchable hydrophilicity solvents (SHS). In their study, softwood Kraft lignin was used as the raw material to produce pyrolysis oil via MAP. The pyrolysis oil was produced using a MAP system under different process conditions, and the pyrolysis oil sample with the most abundant phenolic content was selected for the extraction process. Even though the extraction of phenol from pyrolysis oil was carried out at a small scale of 10 g, they were able to extract about 95% of the phenolic compounds.

Table 1. Methods to extract phenol from pyrolysis oil.

Method	Quality product	Advantages	Disadvantages	Reference
Steam distillation	Syringol purity - 92.3%	Low temperature, Steam-distilled fractions were found to be chemically and thermally stable	Thermo-sensitive to pyrolysis oil, further separation is needed because of low concentration of phenol in distillate	Murwanashyaka et al. 2001
Molecular distillation	N/A	Technically suitable for separation and purification	Expensive equipment and high vacuum requirement	Guo et al., 2010
Supercritical CO2 extraction	Phenol selectivity - ~ 42 %	Low temperature process, Non-toxic, non-flammable method	Low selectivity	Wang et al., 2010
Aqueous extraction and Hydrophobic-polar solvent	N/A		Produced large amount of salts	Fele Žilnik and Jazbinšek, 2011
Liquid-liquid extraction	Phenol yield – 80%	Full extraction of phenols from the aqueous phase	Incomplete extraction of the selected Compounds, highly depended on pH	Amen-Chen et al., 1997

Several methods are available in the literature to extract phenols from pyrolysis oil. Table 1 describes these methods with their merits and demerits. The method of extracting phenols from pyrolysis oil using SHS is different from the other methods listed in Table 1. Accordingly, the SHS process offers some inherent benefits. The most important is that SHS can be removed from the product without a distillation process. It can be easily separated without heating the mixture, thereby reducing energy consumption and the release of undesired by-products. Therefore, this method can be beneficial in terms of economic and environmental impacts. Details on types and properties of different kind of switchable solvents can be found in a recent review paper

(Jessop et al., 2012). Most SHS compounds are tertiary amines. The suitability of SHS for extracting phenol from pyrolysis oil is due to the following reasons:

- SHS has a basic nature to attract weakly acidic phenols
- SHS is switchable between hydrophobic (excluding water) and hydrophilic (including water) compounds
- SHS can be recovered after the extraction process

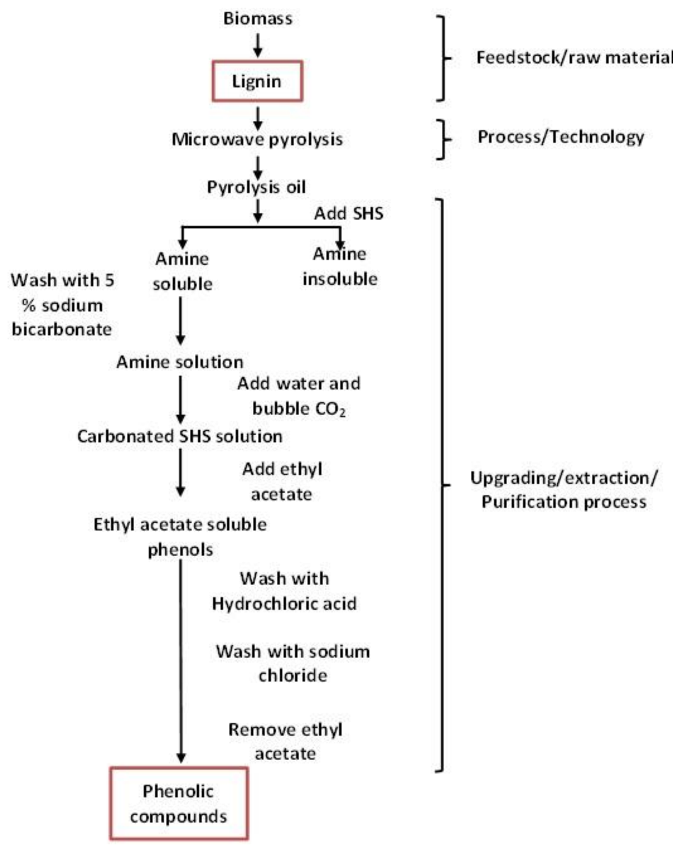

Figure 1. Flow path for extracting phenol from pyrolysis oil

The flow process to extract phenol from pyrolysis oil using SHS is illustrated in Fig. 1. The extraction efficiency of the phenolic compounds is in the range of 69% to 95%, and about 91% of the SHS is recovered from the process. The ratio of SHS to water plays a critical role in the extraction of phenols.

Even though the extraction efficiency of phenol was higher in the case of Fu et al. (2013), the research work was applied to a small batch (10 g) of pyrolysis oil. However, the method needs to be refined at a larger scale. Furthermore, pure lignin-based pyrolysis oil contains a high amount of phenolic compounds. Therefore, the extraction efficiency of phenolic compounds might be higher. However, typical pyrolysis oils contain more than 100 different types of chemical compounds which are not produced from pure lignin-based biomass/waste. The extraction process proposed by Fu et al. (2013), as illustrated in Fig. 1, is extensive and involves several steps. Although the authors successfully demonstrated the extraction of phenolic compounds from pyrolysis oil, it remains a daunting task to extract pure phenol from pyrolysis oil.

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