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## Review

# Production, separation and applications of phenolic-rich bio-oil – A review

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## HIGHLIGHTS

- This paper provides an overview of current research trend of phenolic-rich bio-oil.
- Various production methods for phenolic-rich bio-oil by pyrolysis are provided.
- Recent approaches for the separation of bio-oil are presented.
- Application of phenolic compounds in the synthesis of phenol resins is discussed.

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## ABSTRACT

This paper provides an overview of current research trends in the production and separation of phenolic-rich bio-oils, as well as their applications. The first part of this paper highlights the strong dependency of the phenolic content of bio-oil on the kinds of biomass feedstock, reaction system, reaction conditions, and the type of catalysts used in their production. More recent separation technologies are also discussed in the second part of the paper. The final part of the paper deals with recent experimental results from applications of phenolic-rich bio-oils in the synthesis of phenolic resins. The paper suggests that the microwave-assisted pyrolysis of palm residues is a promising route for phenolic-rich bio-oil production, and that the use of supercritical CO<sub>2</sub> and switchable hydrophilicity solvents during extraction, as well as molecular distillation techniques, can be applied to increase the recovery of phenolic compounds from bio-oils.

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## 1. Introduction

Pyrolysis is one of the principal conversion technologies which are used to extract bioenergy from biomass in an eco-friendly and cost-effective manner. Bio-oils derived from biomass pyrolysis can be used directly as fuel oils in boilers and furnaces without any upgrading. However, bio-oils contain a relatively high amount of oxygenates, which results in undesirable fuel properties, such as high viscosity and corrosiveness, low heating value, and instability. Due to the relatively low fuel values of bio-oils, they cannot directly replace high-grade fuels such as gasoline or diesel, and hence, cannot fuel transportation. In order to explore the feasibility of bio-oil as a high-grade fuel, there has been intensive research on the upgrading of bio-oils to higher fuel value hydrocarbons, mainly through the use of hydrodeoxygenation (HDO) and catalytic fast pyrolysis, which have been applied mainly since the mid-2000s. The current status of research on HDO and catalytic fast pyrolysis

is well represented by a small number of papers (Choudhary and Phillips, 2011; Liu et al., 2014; Ruddy et al., 2014). Although these intensive efforts to upgrade bio-oils have resulted in considerable progress, there are still a number of technical barriers to overcome, such as catalyst deactivation and increasing the yield of hydrocarbons for zeolites, short catalyst lifetime and the additional supply of hydrogen which is required for HDO (Mortensen et al., 2011). Meanwhile, it is not necessarily optimal to simply convert bio-oils to fuels, as bio-oils contain commodity and specialty chemicals. Hence, the isolation of these chemicals is an additional consideration of biomass pyrolysis. Accordingly, a number of studies have been performed either to investigate mechanism and kinetics for the formation of such chemicals, to optimize reaction conditions for chemical production, or to separate a specific chemical from bio-oils. (Ranzi et al., 2008; Teella et al., 2011; Oh et al., 2013). These studies have repeatedly shown that the recovery of chemicals by pyrolysis has a number of drawbacks, including low contents of such chemicals in bio-oil, and high costs of bio-oil separation, etc. Nevertheless, the application of various catalysts and the continuous development of separation technologies are

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stimulating the research area of the chemical recovery from the biomass pyrolysis. In particular, phenolic compounds of bio-oil have a wide range of use within industry, and can often be directly applied without any intensive separation procedures. A few previous studies have provided a good overview of the phenolic compounds arising from biomass pyrolysis (Amen-Chen et al., 2001; Effendi et al., 2008).

This review focuses on the more recent studies of phenolic compounds arising from biomass pyrolysis. In particular, this study provides an overview of the production, separation and application of phenolic compounds.

## 2. Bio-oil, chemicals, phenolic compounds and separation technologies

### 2.1. Chemicals in bio-oil and their quantification

#### 2.1.1. Chemicals in bio-oil

Bio-oil is a complex mixture of water (15–30 wt%), and organic compounds. The addition of water to bio-oil gives rise to an aqueous-organic phase separation. If a phase separation procedure involves the addition of drops of bio-oil to a large amount of water, followed by filtration and drying of the filtrate, and the resulting powder is commonly referred to as a pyrolytic lignin, containing lignin-derivative oligomers (Czernik and Bridgewater, 2004). Bio-oils contain a broad range of organic chemicals, including a range of high-value bio-chemicals, such as levoglucosan. Hence, there is potential for the extraction and use of a range of chemicals from bio-oils as renewable feedstocks for a broad range of chemical industries. The quantities of the various bio-oil components are strongly dependent on the feedstock composition, production method, and reaction conditions. Table 1 shows typical components of bio-oils produced from different biomass feedstocks.

#### 2.1.2. Quantification of bio-oil components

Bio-oils produced by the pyrolysis of lignocellulosic biomass contain over 400 different chemical compounds. These compounds can be classified into the primary categories of organic acids, aldehydes, ketones, furans, sugar based components, and phenolic

**Table 1**  
Typical bio-oil components derived from different biomass at different reaction conditions.

Components	Poplar wood (500 °C), wt% mf feed (Scott et al., 2000)	Hardwood chip (550 °C), area% (Dobele et al., 2007)	Maize stalk (445 °C), wt% (Zheng, 2008)
Sugars			
Levoglucosan	3.0	1.6	
Other sugars	5.7		
Alcohols, aldehydes		9.3	
Hydroxyacetaldehyde	10.0		
Glyoxal	2.2		
Acids, ester		20.2	
Acetic acid	5.4		2.7
Butyric acid			1.5
Ketones			
Dihydroxyacetone			3.9
Ethers			
Pyrans		1.5	
Furans		6.6	2.4 (acetyl furan)
Phenolic compounds			
Phenol			1.4
Guaiacol			2.5
Pyrolytic lignin	16.2		

mf: moisture free.

compounds. The diversity and complexity of bio-oils make the accurate analysis of their specific chemical composition a very complicated task. Such analysis of bio-oil typically utilizes gas chromatography–mass spectroscopy (GC–MS), chromatography–flame ionization detector (GC–FID), high-performance liquid chromatography, ion-exchange chromatography, and/or nuclear magnetic resonance (NMR) spectroscopy. In particular, hyphenated techniques, such as GC–MS are considered to be the more appropriate methods for the analysis of more complex mixtures. However, limited chemical information can be obtained from conventional GC–MS analysis of bio-oils due to the large number of compounds and co-elutions contained therein (Tessarolo et al., 2013). Recent advances in the analysis of bio-oils, such as comprehensive two-dimensional gas chromatography, have led to the enhancement of their qualitative analysis. In particular, the use of a time-of-flight mass spectrometer has led to a dramatic improvement in the separation and identification of complex mixtures. However, the quantitative determination of bio-oil components remains a tedious and expensive analytical procedure, largely due to the requirement for multiple-calibrations of a plethora of chemicals, and the individual expenses associated with their supply, management and maintenance. Therefore, the absence of an all-encompassing quantitative method for the chemical analysis of bio-oils remains. As with most other complex materials, the vast majority of papers focus on semi-quantitative analysis of bio-oil, or on the more detailed analysis of a single component/group of components.

### 2.2. Phenolic compounds

Phenolic compounds found in bio-oils are composed of both simple phenols consisting chiefly of a singly substituted phenolic ring with alcohol, aldehyde or carboxylic acid groups and oligomeric polyphenols having multiples of phenol structural units, each of which being products of lignin decomposition. Lignin is one of the primary components of dry wood, accounting for 18–40 wt% of the total mass, depending on the species of wood (Amen-Chen et al., 2001). Lignin is a very complex macromolecular compound, and is composed of monomeric phenylpropanoid units known as syringyl-, guaiacyl-, and p-hydroxyphenyl, originating from three monolignol monomers which differ in their degree of methoxylation; p-coumaryl, coniferyl, and sinapyl alcohols. In softwood lignin, coniferyl alcohol is the predominant building unit, while in hardwoods the ratio of coniferyl/sinapyl shows considerable variation. Therefore, the pyrolysis of softwood lignins yields mainly guaiacols, whereas hardwood lignins give both guaiacols and syringols (Brebú and Vasile, 2010). Lignin thermally decomposes over a broad temperature range, covering the 160–900 °C region (Yang et al., 2007). Evans et al. proposed a possible free radical mechanism for the pyrolysis of lignin. According to this mechanism, alkyl hydroxyl groups in the  $\alpha$ -position are first eliminated from the propane side chain, followed by a  $\beta$ -ether cleavage (Evans et al., 1986). Liu et al. confirmed the readiness of  $\beta$ -ether cleavage by a quantum chemistry calculation in their study on the guaiacyl type lignin model compound, drawing a comparison with the  $C_{\alpha} - C_{\beta}$  cleavage of the propane side chain (Liu et al., 2011). After  $\beta$ -ether cleavage, monolignol monomers are produced, which may be further degraded at different positions of the propane side chain, yielding a variety of simple phenols. Hydrogen transfer at the  $\gamma$ -position to free radical species can produce formaldehyde, dimers and methoxyphenols. Recently, Shen et al. investigated the formation of a number of common products from the pyrolysis of kraft lignin. They found that guaiacols and syringols were mostly produced by the cracking of the side-chain of the lignin monomeric units in parallel to the cleavage of the  $\alpha$ - or  $\beta$ -4-aryl ether linkage. They also acted as precursors for the formation of phenol-

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