



# High-yield and high-calorific bio-oil production from concentrated sulfuric acid hydrolysis lignin in supercritical ethanol



Asim Riaz<sup>a</sup>, Chang Soo Kim<sup>b</sup>, Yunje Kim<sup>b,\*</sup>, Jaehoon Kim<sup>a,c,\*</sup>

<sup>a</sup> School of Mechanical Engineering, Sungkyunkwan University, 2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea

<sup>b</sup> Clean Energy Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

<sup>c</sup> SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, 2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea

## HIGHLIGHTS

- Lignin was liquefied in supercritical ethanol/formic acid mixture.
- Concentrated sulfuric acid hydrolysis lignin was more recalcitrant than Kraft lignin.
- 30 min reaction resulted high bio-oil yield of 85 wt% and HHV of 31.2 MJ kg<sup>-1</sup>.
- The process achieved a 44% reduction in O/C molar ratio.
- The bio-oil mainly consisted of phenols, esters, furans, and alcohols.

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## ABSTRACT

The aim of this work is to explore process parameters (pressure, time, formic acid content) for producing high-yield and high-calorific bio-oil from concentrated sulfuric acid hydrolysis lignin (CSAHL) with formic acid as an *in-situ* hydrogen source in supercritical ethanol (scEtOH). Even at short reaction time of 30 min, high conversion of 92% and high bio-oil yield of 85 wt% were observed at 350 °C and formic-acid-to-lignin mass ratio of 1.5 using a stirred reactor. The effective deoxy-liquefaction nature associated with scEtOH with aid of formic acid resulted in significant reduction in oxygen content of 44% and high higher heating value of 31.2 MJ kg<sup>-1</sup> of produced bio-oil. The overall process is energetically efficient with 112% energy recovery (ER) and 78% energy efficiency (EE). The results are compared with Kraft lignin (KL) under identical reaction conditions. The inherent recalcitrant nature of CSAHL resulted in lower conversion and lower bio-oil yield when compared to the liquefaction of Kraft lignin (KL, 99% conversion, 90 wt% bio-oil yield). Bio-oil with better flow properties, low molecular weight, and a high amount of monomeric phenol was produced after 60 min of reaction. The compounds in the bio-oil were mainly phenols, esters, furans, alcohols, and traces of aliphatic hydrocarbons.

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## 1. Introduction

Conversion of technical lignin (e.g., Kraft lignin (KL), organosolv lignin, alkali lignin, lignin from cellulosic ethanol plants, etc.) into transportation fuel and/or value-added chemicals has been in the limelight over the last few decades. With the growing demand for cellulosic bioethanol, developing effective lignin conversion techniques has become an alluring focus for economically viable integrated biorefineries. Lignocellulosic biomass typically consists

of up to 40% lignin on a dry-weight basis, which has a myriad of potential for producing renewable fuels and value-added chemicals [1–5]. The existence of various types of chemical bonding ( $\beta$ -O-4,  $\beta$ -5,  $\alpha$ -O-4, 5-5, 4-O-5,  $\beta$ -1,  $\beta$ - $\beta$ ) and functionalities (methoxy, hydroxyl, phenolic, and carbonyl groups), along with the inherent recalcitrant nature of lignin associated with the polymeric structure of aromatic rings, make efficient conversion to liquid fuels and monomeric aromatic chemicals difficult. In addition, the chemical reactivity and structure of lignin are highly dependent on the isolation process (e.g., Kraft process, lignosulfonate process, organosolv process, steam explosion, strong acid hydrolysis, etc.) [2,6,7]. Thus, a lignin conversion process effective for a certain type of lignin may not result in satisfactory conversion or liquid yield when other types of lignin are used. Therefore, to

\* Corresponding authors at: School of Mechanical Engineering, Sungkyunkwan University, 2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea (J. Kim). Tel.: +82 31 299 4843; fax: +82 31 290 5889.

E-mail addresses: [yjkim@kist.re.kr](mailto:yjkim@kist.re.kr) (Y. Kim), [jaehoonkim@skku.edu](mailto:jaehoonkim@skku.edu) (J. Kim).

produce high-yield, high-calorific liquid that can be used as transportation fuel and/or aromatic chemicals, it is crucial to develop an effective lignin conversion method that is not strongly dependent on the nature or delignification process of lignin.

To date, various types of thermochemical techniques have been explored for effective depolymerization of lignin. These include fast pyrolysis [8–12], base-catalyzed depolymerization under high-temperature water or alcohol conditions [13–17], base-catalyzed depolymerization followed by deoxygenation using sulfided Mo-based catalysts [18,19], oxidative degradation, heterogeneous catalyst-based conversion [20–25], and sub- or supercritical fluid-based liquefaction [26–34]. Each technique has its own unique strategy for depolymerizing lignin. The process conditions and the bio-oil properties are quite different depending on the conversion technique (see Table S1). For example, fast pyrolysis degrades the macromolecular lignin structure by a radical reaction over a very short period of a few seconds, but low liquid yield (10–40 wt%), high char/tar formation (30–50 wt%), and line plugging during continuous runs are the major drawbacks [8]. Subcritical water (subH<sub>2</sub>O) and supercritical water (scH<sub>2</sub>O) are effective media for hydrolysis of aryl-alkyl ether bonds (C–O–C linkage) to some extent [28,35], and the use of alkali base (e.g., NaOH, KOH, etc.) under sub- or scH<sub>2</sub>O conditions can enhance the cleavage of C–O–C linkage to produce different proportions of phenolic monomers [16]. Recently, formic acid in supercritical alcohols was successfully used as active hydrogen donor to depolymerize and deoxygenate lignin [27,36]. The reaction temperature was maintained at ~380 °C in a high-pressure, non-stirred microreactor for a prolonged period of up to 54 h. The oil product exhibited low oxygen content (O/C ratio less than 0.10) and high calorific value (higher heating value of ~38 MJ kg<sup>-1</sup>). The use of mild pre-treated lignin and the incomplete separation of solvent from the liquefied product was also one of the reasons of low oxygen content and high HHV [36]. However, prolonged reaction times and the use of expensive solvent-cum-reactant (e.g., isopropanol), which is consumed during the reaction, may not be suitable for cost-effective biofuel production. In summary, the current challenges of lignin depolymerization include low depolymerization yield/high char formation, high oxygen content and low calorific values of the liquid product, multi-step batchwise running mode, use of expensive noble metal catalysts (e.g., Pd, Pt, Ru, etc.)/chemicals (e.g., boric acid, phenol, etc.), use of excess molecular hydrogen, and long reaction times (12–24 h).

Since the process conditions and chemicals used for isolating lignin from lignocellulosic biomass are quite different depending on the lignin delignification process, the properties of lignin, such as chemical structure and reactivity, depend on the isolation technique [6]. Thus, lignin depolymerization behaviors of a given conversion technique for producing liquid bio-oil could be different when different lignin sources are used. Most of the previous studies have used commercially available or custom-made organosolv lignin (produced by the Alcell process), KL (produced from paper and pulp industries), lignosulfonate lignin, and soda lignin (see Table S1) [10,21,22,27]. However, to the best of our knowledge, there are only a few studies focused on the conversion of lignin

extracted from the cellulosic ethanol process, and these studies used lignin that were isolated using weak acid saccharification and steam explosion [27]. Some of the currently developed commercial-scale cellulosic ethanol plants are based on a strong acid hydrolysis process to isolate lignin (e.g., BlueFire Renewables). Thus, it is crucial to develop an effective conversion process for lignin isolated from cellulosic ethanol plants.

Herein, supercritical ethanol (scEtOH,  $T_c = 241$  °C,  $P_c = 6.3$  MPa)-based deoxy-liquefaction with the aid of formic acid was explored for effective depolymerization of lignin. The lignin used in this study was isolated from oak wood using pilot-scale, concentrated sulfuric acid hydrolysis equipment for developing a cellulosic ethanol plant. To the best of our knowledge, there has been no study for converting lignin obtained from the strong acid hydrolysis process. In this study, efforts were made to minimize the reaction time through efficient stirring to counter diffusion constraints that may exist in a reactor. Ethanol is a natural choice as the liquefaction solvent because of the abundance of cellulosic ethanol plants to be built locally, thereby reducing the transportation costs required for other solvents (e.g. isopropanol). The effects of reaction pressure, time, and formic-acid-to-lignin (FL) mass ratio on the liquid and gas yield and their composition was examined in detail to understand the lignin depolymerization behaviors under the proposed reaction conditions. By controlling the process parameters, the scEtOH-based deoxy-liquefaction can result in high lignin-to-liquid conversion (92%), low char/tar formation (14 wt%), low oxygen content (O/C ratio of 0.21), low molecular weight (390 g mol<sup>-1</sup>), and high calorific content (HHV of 31.2 MJ kg<sup>-1</sup>) in the produced liquid using concentrated sulfuric acid hydrolysis lignin (CSAHL). A comparison of the liquefaction results using CSAHL and KL is also presented.

## 2. Materials and methods

### 2.1. Materials

The CSAHL used in this study was obtained from oak wood using a two-step, concentrated strong acid hydrolysis process. A pilot-scale hydrolysis reactor was filled from the top with oak wood (*Quercus acuta*, hardwood) sawdust (C: 46.5 wt%, H: 6.0 wt%, O: 45.4 wt%). In the pre-hydrolysis step, cellulose was decrystallized, while hemicelluloses were depolymerized at 40 °C for 30 min using a 70 wt% sulfuric acid solution. In the second main hydrolysis step, the acid concentration was reduced to 30% with water, and the reaction time was set to 120 min at 80 °C. After the hydrolysis reaction was complete, the precipitated lignin at the bottom of the reactor was separated from the liquid product by filtration. The filter cake was washed several times with double-distilled and deionized water to separate most of the hydrolyzed holocellulose compounds from the lignin. The obtained lignin was dried overnight at room temperature for several days. For comparison, KL from Norway spruce wood (*Picea abies*, softwood) was purchased from Sigma–Aldrich Co (St. Louis, MO, USA). Table 1 lists the proximate and ultimate analysis results of CSAHL and KL. The decomposition behavior of raw lignin was tested using thermogravimetric

**Table 1**  
Proximate and ultimate analysis of the lignin feedstocks used in this study.

	Proximate analysis (wt%, d.b) <sup>a</sup>				Ultimate analysis (wt%, d.a.f) <sup>b</sup>							
	VM <sup>c</sup>	FC <sup>d</sup>	Ash	Moisture	C	H	O	N	S	O/C	H/C	
CSAHL	62.8	30.9	6.5	2.1	58.0	5.35	29.3	0.45	0.30	0.38	1.11	
KL	54.2	43.6	2.3	2.9	63.7	5.11	30.0	0.26	1.74	0.35	0.96	

<sup>a</sup> On a dry basis.

<sup>b</sup> On a dry, ash free basis.

<sup>c</sup> VM: volatile matter – determined using TGA in N<sub>2</sub> at 10 °C min<sup>-1</sup> to 800 °C.

<sup>d</sup> FC: fixed carbon – determined using TGA in N<sub>2</sub> at 10 °C min<sup>-1</sup> to 800 °C.

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