

# A Complete, Reductive Depolymerization of Concentrated Sulfuric Acid Hydrolysis Lignin into a High Calorific Bio-oil using Supercritical Ethanol

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## Abstract

It is imperative to develop an effective pathway to depolymerize lignin into liquid fuel that can be used as a bioheavy oil. Lignin can be converted into liquid products either by a solvent-free thermal cracking in the absence air, or thermo-chemical degradation in the presence of suitable solvents and chemicals. Here we show that the solvent-assisted liquefaction has produced promising results in the presence of metal-based catalysts. The supercritical ethanol is an efficient liquefaction solvent, which not only provides better solubility to lignin, but also scavenges the intermediate species. The concentrated sulfuric acid hydrolysis lignin (CSAHL) was completely liquefied in the presence of solid catalysts (Ni, Pd and Ru) with no char formation. The effective deoxy-liquefaction nature associated with scEtOH with aid hydrodeoxygenation catalysts, resulted in significant reduction in oxygen-to-carbon (O/C) molar ratio up to 61%. The decrease in oxygen content and increase in carbon and hydrogen contents increased the calorific value bio-oil, with higher heating value (HHV) of 34.6 MJ·Kg<sup>-1</sup>. The overall process is energetically efficient with 129.8% energy recovery (ER) and 70.8% energy efficiency (EE). The GC-TOF/MS analysis of bio-oil shows that the bio-oil mainly consists of monomeric species such as phenols, esters, furans, alcohols, and traces of aliphatic hydrocarbons. The bio-oil produced has better flow properties, low molecular weight, and high aromaticity.

*Keywords: Concentrated sulfuric acid hydrolysis lignin, supercritical ethanol, hydrodeoxygenation, energy efficiency, energy recovery*

## I. INTRODUCTION

Growing energy demand and depleting fossil fuel resources has led the world to find new energy alternatives, which not only are renewable, but also environmentally friendly. Lignocellulosic biomass, the largest carbon source currently available, shows the great potency in this regard. It is composed of three main constituents: cellulose (30-50% of biomass), hemicellulose (20-35% of biomass), and lignin (15-30 % of biomass). Although cellulosic fraction has found the huge industrial applicability such as paper and bio-ethanol production, however, the lignin is still being used as low energy boiler fuel and low value chemical production. The conversion of technical lignin (organosolv lignin, kraft lignin, soda lignin, and liginosulfonate), into high energy density liquid fuels and/or value added chemicals has attracted huge attention in past few decades [1]-[5]. Lignin, the largest source of cross-linked, aromatic carbon, is responsible for water transport and structural integrity to the plants. The amorphous structure having variety of chemical bonds ( $\beta$ -O-4,  $\beta$ -5,  $\alpha$ -O-4, 5-5, 4-O-5,  $\beta$ -1,  $\beta$ - $\beta$ ), makes it difficult to depolymerize. The chemical structure is highly dependent on lignin source (softwood/hardwood) and pretreatment method (e.g., Kraft process, liginosulfonate process, organosolv process, strong acid hydrolysis, etc.) [2][6][7]. Therefore, it is crucial to develop an efficient lignin conversion method that is capable of breaking all stable bonding of lignin.

For lignin depolymerization, various thermochemical methods have been tested to date under oxygen, inert and hydrogen environments. These methods include oxidative degradation, ionic liquid assisted depolymerization, fast pyrolysis [8]-[12], sub-

and supercritical fluid assisted base-catalyzed depolymerization [13]-[17], two step base-catalyzed depolymerization followed by hydrodeoxygenation using metal-based catalysts and molecular hydrogen [18][19], heterogeneous catalyst-based reductive depolymerization [20]-[25], and sub- or super-critical fluid assisted depolymerization [26]-[34]. The extent of depolymerization, the composition and bio-oil properties strongly depend on the conversion technique. For example, oxidative degradation of lignin produces structurally preserved, complex platform aromatic chemicals such as aromatic aldehydes and carboxylic acids, such as vanillin, which is a major product of the oxidative cleavage of lignin [35][36]. The reaction protocols involve metal oxides or homogeneous acid/base catalysts in the presence of H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub> as oxidants. The thermal degradation of lignin in the absence of air at high temperature for very short reaction time of a few seconds, called fast pyrolysis, produces low yield of liquid (10-40 wt%), high char/tar formation (30-50 wt%). The line plugging, low quality oil and less conversion are the major drawbacks [8]. Sub- and supercritical fluids (water and alcohols) in the presence of alkali base (e.g., NaOH, KOH etc) is an effective media for hydrolysis of aryl-alkyl ether bonds (C-O-C linkage) to produce phenolic monomers [16]. Reductive depolymerization of lignin in the presence of hydrogen donating solvent such as formic acid was successfully used to produced deoxygenated bio-oil [27][37]. However, the lignin conversion is almost complete but it requires longer reaction time. Noble metal catalysts and Mo based catalysts are well- known catalytic hydrodeoxygenation of lignin [18][19]. High monomeric yield with low oxygen content has been reported.

Since the wood source and process conditions used for isolating lignin from lignocellulosic biomass have strong effect on the structure and reactivity of isolated lignin. The depolymerization strategy efficient for certain type of lignin may not be effective for other type, because the chemical structure and reactivity of lignin depends on the delignification process [6]. For example, most of the recent work available for Kraft and Organosolv lignin (relatively milder lignin) depolymerization may not be efficient for the very recalcitrant concentrated sulfuric acid hydrolysis lignin (CSAHL). However, there are only a few studies focused on the lignin conversion, extracted from the cellulosic ethanol plants. Some of the newly developed commercial-scale bio-ethanol production plants from cellulose are based on a strong acid delignification process (e.g., BlueFire Renewables). Therefore, it is imperative to develop an efficient depolymerization technique for lignin isolated from cellulosic ethanol plants. Moreover, non-stirred bomb reactor was commonly used which provided an additional disadvantage of diffusion and solubility.

Herein, we explored supercritical ethanol (scEtOH,  $T_c = 241$  °C,  $P_c = 6.3$  MPa) in the presence of noble and non-noble based metal catalysts for effective depolymerization of lignin. In this study, a stirred batch reactor was used to minimize diffusion constraints to have better solubility. Although ethanol is an expensive solvent, the in-house availability of ethanol from cellulosic ethanol plants, built locally, reduces its transportation cost. The effects of different catalysts on the lignin conversion, liquid and gas yield, bio-oil properties and energy efficiency of the process were examined in detail to have a better understanding of the lignin depolymerization behaviors under our proposed reaction conditions. By changing the catalyst under fixed process parameters, the scEtOH-based hydrogenolysis of lignin, resulted in complete lignin-to-liquid conversion with no char formation, low oxygen content (O/C ratio of 0.16), and high calorific content (HHV of  $34.6$  MJ·kg<sup>-1</sup>) of bio-oil produced using concentrated sulfuric acid hydrolysis lignin (CSAHL).

## II. MATERIALS AND METHODS

### A. Materials

The lignin used in this study was obtained in two-step, concentrated strong acid hydrolysis of oak wood. The oak wood (hardwood) sawdust (C: 46.5 wt%, H: 6.0 wt%, O: 45.4 wt%) was introduced from the top of a pilot-scale hydrolysis reactor. The reaction was consisted of two steps: pre-hydrolysis and post hydrolysis. In the first step, cellulose was decrystallized using a 70 wt% sulfuric acid solution at 40 °C for 30 min. The second main hydrolysis step was conducted under reduced concentration of 3 wt% sulfuric acid solution at 80 °C for 120 min. After reaction, the precipitated lignin was filtered and the filtrate, containing acid soluble cellulose, was discarded. The lignin was washed with double-distilled and deionized water to remove the hydrolyzed holocellulose compounds from the lignin. The thermogravimetric analysis (TGA) under inert and air conditions was performed to check the degradation behavior of raw lignin (Fig. 1). Ethanol (HPLC grade), and acetone (HPLC grade) were obtained from Sigma-Aldrich Co. High-purity N<sub>2</sub> (99.99%), and H<sub>2</sub> (99.99%) for purging the reactor and for catalytic reactions were obtained from JC Gas Company (South Korea). All catalysts were purchased from Sigma-Aldrich, and used after reduction.

### B. Reaction Protocol

The liquefaction experiments were performed using a custom-built, batch reactor made of SUS 316 having an inner volume of 140 mL. The reactor was equipped with a magnetic driven stirrer (HM-3200, Hnawoul Engineering Inc., South Korea). Prior to the reaction, the catalysts were activated under 2 MPa hydrogen pressure at 400 °C for 1 hr. In order to avoid catalyst deactivation, the exposure of catalyst to external air was minimized by injecting solvent into the reactor through inlet line without opening reactor. Once the catalyst was covered with solvent, the reactor was opened to inject the desired amount of oven-dried lignin. The ethanol-to-lignin-to-catalyst ratio was fixed to 20:1:0.1. The reactor was pressurized with H<sub>2</sub> to 2 MPa after purging with N<sub>2</sub> gas several times. The reaction temperature of 350 °C was achieved by heating it with an electrical furnace and cartridge heaters at an average heating rate of ~20 °C·min<sup>-1</sup>. After reaction, the reactor cooled to 100 °C by submerging it in a cold water bath, and then further cooled to room temperature by using an electric fan. Rapid quenching of the reactor was performed to avoid possible condensation and repolymerization reactions during cooling. The heating time (~21 min) and cooling time (~60 min) was not considered in the reaction time. The reaction pressure was recorded at each stage, such as when it reached the desired reaction temperature, and then after completion of reaction and finally after quenching. The change in the pressure served as an indication of the extent of depolymerization and amount of gas produced during the reaction. The gas was collected in a 0.5-L Tedler<sup>®</sup> bag after passing through a wet gas meter (W-NK-2 type, Shinagawa Corporation, Japan), and quantified using RGA-GC. The liquid products were collected by rinsing reactor with acetone. Then it was subjected to vacuum filtration with a Whatman filter paper # 2 to separate solid and liquid products. The solvents and low molecular weight by-products in filtrate were evaporated in a rotary evaporator under reduced pressure of -1MPa at 50 °C for 45 min. The resulting thick liquid was dried further in a vacuum oven at 70 °C for 24 hr. The dried liquid product (without any residual ethanol) was designated as bio-oil. The filter cake containing catalyst and solid residue was dried in vacuum oven at 70 °C for 24 hr. The weight of solid residue was calculated after subtracting the weight of catalyst initially taken. The average values of three replicates are reported.

The yields and conversion are calculated using the following equations:

$$\text{Yield of bio-oil (wt\%)} = \frac{\text{Weight of bio oil}}{\text{Weight of dry ash free lignin}} \times 100 \quad (1)$$

$$\text{Yield of solid residue (wt\%)} = \frac{\text{Weight of solid residue}}{\text{Weight of dry lignin}} \times 100 \quad (2)$$

$$\text{Yield of gas (wt\%)} = \frac{\text{Weight of produced gas}}{\text{Weight of dry ash free lignin}} \times 100 \quad (3)$$

$$\text{Conversion} = \frac{\text{Weight of dry ash free lignin} - \text{Weight of organics in solid residue}}{\text{Weight of dry ash free lignin}} \times 100 \quad (4)$$

The higher heating value (HHV) of bio-oil was calculated using the DIN 51900 standard:

$$\text{HHV (MJ}\cdot\text{kg}^{-1}) = (34\text{C} + 124.3\text{H} + 6.3\text{N} + 19.3\text{S} - 9.8\text{O})/100 \quad (5)$$

where carbon, hydrogen, nitrogen, sulfur, and oxygen weight percentages are denoted as C, H, N, S, and O respectively, which were obtained by elemental analysis.

The overall energy balances are discussed in two ways. Energy recovery (ER), percentage of energy recovered in the process, which is a comparison of the total energy content of the bio-oil produced with the total energy content of the raw feedstock. It is calculated using Eq. 6 [38].

$$\text{ER} = \frac{\text{HHV of bio-oil} \times \text{mass of bio-oil}}{\text{HHV of lignin} \times \text{mass of dry ash-free lignin}} \times 100 \quad (6)$$

Energy efficiency (EE) was calculated using Eq. 7, to have an idea of process profitability. It compares the output energy obtained from the bio-oil with the input energy provided to the system (energy in raw lignin + energy consumed for the liquefaction reaction). Although there are some other factors as well, such as cost of harvesting, handling, transportation of raw materials, and revenue from gaseous and solid products, which must be included in the techno-economic evaluation.

$$\text{EE} = \frac{\text{HHV}_{\text{oil}} \times Y \times m_1}{[\text{HHV}_{\text{raw}} \times m_1] + [m_1 \times C_{\text{ps}} \times (T-20) + m_2 \times C_{\text{palc}} \times (T-20) + m_3]} \times 100 \quad (7)$$

where  $m_1$  and  $m_2$  are the masses of lignin (dry, ash free) and ethanol, respectively.  $C_{\text{ps}}$  and  $C_{\text{palc}}$  are the average specific heats of the dry solids ( $1.24 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ), and ethanol ( $2.44 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ), respectively.  $T$  is the reaction temperature and  $Y$  is the bio-oil yield.

### C. Analysis

The PerkinElmer Clarus 600 GC-Model Amel 1115PPC Refinery Gas Analyzer (RGA) (PerkinElmer, CT, USA) was used to analyze the gaseous products for quantification of all components ( $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{-C}_6$  compounds). The GC was composed of two detectors: a thermal conductivity detector (TCD) and a flame ionization detector (FID). The GC was composed of seven packed columns and two capillary columns. The bio-oil composition was analyzed using an Agilent Technologies 7890A GC, equipped with a time of flight mass spectrometer (TOF-MS). The 7683B series auto-sampler (Agilent Technologies) was used for sample injection. A non-polar column (Rxi-5ms) with specification of  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$  was used. He was used as the carrier gas at a flow rate of  $2.0 \text{ mL}\cdot\text{min}^{-1}$ . A  $1\text{-}\mu\text{L}$  acetone solution of bio-oil was injected into the column in a split mode of 50:1, after filtering through  $0.2 \mu\text{L}$  syringe filter. The temperature of injector was set at  $270 \text{ }^\circ\text{C}$ . The temperature ramping program was set at  $40 \text{ }^\circ\text{C}$  for 2 min, followed by a rate of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to  $300 \text{ }^\circ\text{C}$ , and then maintained at  $300 \text{ }^\circ\text{C}$  for 5 min. The chemical compounds in the bio-oils were identified using the National Institute of Standards and Technology (NIST) library. The elemental composition (C, H, N, and S) of the feedstock lignin and produced bio-oil was determined by using a Vario EL cube elemental analyzer that is equipped with a TCD detector (Elementar Analysensysteme GmbH, Germany). The temperature of the combustion tube was

maintained at  $1150 \text{ }^\circ\text{C}$  and the temperature in the reduction tube was kept at  $850 \text{ }^\circ\text{C}$ . The oxygen of the sample was analyzed in a pyrolysis tube using TCD detector in O-mode at a temperature of  $1,150 \text{ }^\circ\text{C}$ . The Q50 TGA (TA Instruments) was used to measure the total inorganic content in the samples. Sample was heated at the temperature range of  $30\text{-}800 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  and the gas flowrate was kept at  $60 \text{ mL}\cdot\text{min}^{-1}$ .

## III. RESULTS AND DISCUSSION

The structure and properties of lignin are dependent on the lignin source and delignification method [6]. The lignin obtained from strong acid hydrolysis conditions may undergo condensation reactions of intermediate species forming stable C-C bond which is hardest to break in lignin structure [39]. Herein, we used one of the most recalcitrant lignin to test the efficiency of our process. Table 1 shows the degradation behavior of lignin in the presence of air. The lignin contains around 2.1 wt% of moisture content, and under oxygen condition, the entire organic content was combusted with approximately 6.5 wt% of ash remaining in CSAHL. The volatile matter (VM), calculated under nitrogen conditions, was 62.8 wt%, whereas 30.9 wt% of fixed carbon (FM) was present. The elemental composition of the lignin is also given in the Table 1, and the O/C ratio is very high (0.49%) which is due to high oxygen and low carbon content. The lignin has very low calorific value of  $21.4 \text{ MJ}\cdot\text{kg}^{-1}$ .

Supercritical ethanol is known as an efficient media for lignin depolymerization because it is not only a good media to solubilize lignin but it also scavenges the active intermediate species, whereas other solvents such as water and methanol do not produce such results. In a typical experiment, without the use of catalyst, the only 73.6 % of lignin conversion was achieved. A very thick bio-oil, with total yield of 51 wt% was produced. The high yield of solid residue (28 wt%) is due to either incomplete conversion or repolymerization of intermediate species. Lignin structure has variety of chemical bonds such as  $\beta\text{-O-4}$ ,  $\beta\text{-5}$ ,  $\alpha\text{-O-4}$ ,  $5\text{-5}$ ,  $4\text{-O-5}$ ,  $\beta\text{-1}$ ,  $\beta\text{-}\beta$ . The bond energy of these linkages is different, and highest bond energy is associated with C-C bond such as  $\beta\text{-1}$  and  $\beta\text{-}\beta$ . The higher percentage of these linkages is present in concentrated sulfuric acid hydrolysis lignin (CSAHL). The concentrated sulfuric acid causes dehydration of intermolecular lignin functional groups, hence forming C-C condensed bonds at the expense of  $\beta\text{-O-4}$  bonds such as benzylic hydroxyl and/or ether bonds [40][41]. Therefore, it requires either harsh reaction condition or a catalyst which enables selective cleavage of these linkages in the presence of molecular hydrogen. When the reaction was conducted in the presence of hydrogenating catalyst, such as 5% Pd/  $\text{Al}_2\text{O}_3$ , the conversion increased to 95.3% as shown in Table 2. Fig. 1. shows that the bio-oil yield increased quite considerably to 75.2 wt%. This increase in the yield is due to selective hydrogenolysis of lignin in the presence of catalyst. Although, the blank experiment was also conducted in hydrogen environment, but due to lack of catalyst, hydrogen was not active to hydrogenolyse the lignin structure, resulting in low bio-oil yield. The low yield of solid residue is also an evident of effective depolymerization and less repolymerization in the presence of catalyst. The Ni/ $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_3$  has shown promising results and a complete conversion with high bio-oil yield of 84.1 wt% was achieved in this case. This shows Ni catalyst is very effective for the hydrogenolysis of lignin structure. The lignin conversion

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

|       | Proximate analysis (wt%, d.b) <sup>a</sup>  |                 |     |          |     |      |      |                               |
|-------|---|-----------------|-----|----------|-----|------|------|-------------------------------|
|       | VM <sup>c</sup>                             | FC <sup>d</sup> | ash | Moisture |     |      |      |                               |
| CSAHL | 62.8  | 30.9            | 6.5 | 2.1      |     |      |      |                               |
|       | Ultimate analysis (wt%, d.a.f) <sup>b</sup> |                 |     |          |     |      |      | HHV<br>(MJ·kg <sup>-1</sup> ) |
|       | C   | H               | O   | N        | S   | O/C  | H/C  |                               |
| CSAHL | 54.6  | 4.98            | 36  | 0.79     | 1.0 | 0.49 | 1.09 | 21.5                          |

<sup>a</sup> On a dry basis.<sup>b</sup> On a dry, ash free basis.<sup>c</sup> VM: volatile matter.<sup>d</sup> FC: fixed carbon.<sup>e</sup> VM and FC were determined using TGA in N<sub>2</sub> at 10 °C·min<sup>-1</sup> to 800 °C.

Table 2. The mmol of gas produced under different catalytic conditions. All reactions were conducted at 350 °C, for 5 hr.

|   | mmol of gas produced |      |                 |                 |  |                                |
|---|----------------------|------|-----------------|-----------------|--|--------------------------------|
|   | H <sub>2</sub>       | CO   | CO <sub>2</sub> | CH <sub>4</sub> | C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> | C <sub>3</sub> -C <sub>4</sub> |
| Blank   | 75.6                 | 9.7  | 1.8             | 9.8             | 6.9  | 0                              |
| 5% Pd / Al <sub>2</sub> O <sub>3</sub>                    | 16.9                 | 13.0 | 8.3             | 25.4            | 44.7   | 2.0                            |
| 5% Ni / Al <sub>2</sub> O <sub>3</sub> , SiO <sub>3</sub> | 16.4                 | 32.7 | 3.1             | 41.2            | 28.3   | 2.2                            |
| 5% Ru / Al <sub>2</sub> O <sub>3</sub>                    | 31.3                 | 21.4 | 2.9             | 20.3            | 15.3   | 0.6                            |

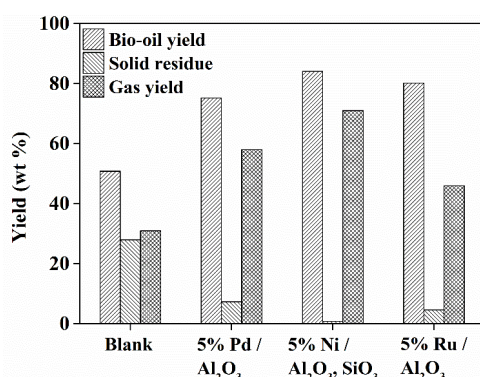


Fig. 1. Effect of catalyst on product yields. All reactions were conducted at 350 °C, for 5 hr.

slightly decreased in the presence of 5% Ru / Al<sub>2</sub>O<sub>3</sub> to 98.1% and the bio-oil yield was 80.2 wt%.

The high amount of gas was produced in the presence of catalysts as shown in Fig. 1. In the absence of catalysts, the gas yield was only 31 wt%, which increased to 58 wt%, 71 wt% and 46 wt% in the presence of Pd, Ni and Ru catalysts respectively. The gas was mainly composed of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>. The presence of higher amount of C1-C4 hydrocarbons in the presence of catalysts suggests that it might have produced from the liberation of alkyl chain connected to lignin. The less amount of C1-C4 in the absence of catalysts also suggests that the presence of catalyst may also enhance the decomposition of ethanol, which as a result produce high amount of gas. The high number of moles of hydrogen in the blank experiment (75.6 mmol) suggests that the molecular hydrogen is non-reactive in the absence of catalysts, which resulted in lower lignin conversion. The hydrogen in the presence of solid catalysts, consumes to hydrogenolyse the lignin structure, as shown in Table 2. The catalysts also promote the decarboxylation and decarbonylation reactions of lignin hence releasing higher amount of CO and CO<sub>2</sub> as shown in Table 2.

#### A. Bio-oil Properties

The elemental composition (C, H, N, S, O) of bio-oil is

reported in Table 3. The lignin has highly oxygenated structure and it is very tedious to remove its oxygen. The oxygen present in lignin structure is mostly attached in the phenolic species, which has very stable chemical bond. The depolymerization in ethanol has resulted in a significant decrease in the oxygen content of lignin that is from 36 wt% to 21.9 wt% and increase in the carbon content from 54.6 wt% to 68.6 wt% as shown in Table 1 and 3. The oxygen content keeps on decreasing in the presence of catalysts and it is the least (16.1 wt%) in the presence of 5% Ru / Al<sub>2</sub>O<sub>3</sub> catalyst. Similarly, the presence of higher amount of hydrogen in catalytic experiments also confirms the effective hydrogenolysis of lignin. The hydrogen not only assisted in depolymerizing the lignin structure but it also acted as a capping agent for reactive intermediate species. Therefore, it not only decreased the char formation but also increased the hydrogen content in bio-oil. The sulfur and nitrogen remained unchanged in all conditions.

The van Krevelen plot shown in Fig. 2 indicates that even in the absence of catalysts, it exhibits 51% reduction of the O/C molar ratio. The presence of catalyst further decreased the O/C ratio to 0.19 in case of 5% Pd / Al<sub>2</sub>O<sub>3</sub>, and 5% Ni / Al<sub>2</sub>O<sub>3</sub>, SiO<sub>3</sub>. The presence of 5% Ru / Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest degree of deoxygenation with the lowest O/C molar ratio of 0.16. The degree of deoxygenation achieved in this study is much better than the recently reported in literature. For example, the deoxygenation organosolv lignin (obtained from switchgrass) in an ethanol-formic acid mixture over metal catalyst (Pt/C) resulted in the O/C molar ratio of 0.27 [21]. In another case, longer reaction times of 4-8 hr for depolymerization of an organosolv lignin reduced the O/C ratio to 0.17-0.25 in scEtOH over Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 260-300 °C [20]. The bio-oil with the O/C ratio of 0.25 was produced from Kraft lignin in an ethanol-water mixture at 300 °C when treated for 1 hr [26]. In these studies, the lignin used was easy to degrade as compared to the one we used in this study. Moreover, the lignin used in these studies has lower oxygen content as compared to our lignin. The decrease in oxygen content and increase in carbon and hydrogen contents also increased the calorific values of bio-oil. For example, the higher heating value of lignin feedstock was only 21.4 MJ·kg<sup>-1</sup> as shown in Table 1. It increased to 28.8 MJ·kg<sup>-1</sup> when lignin was treated in supercritical ethanol for 5 h. Among the catalysts, Ru was most effective which increased this value to 34.6 MJ·kg<sup>-1</sup>, which shows that the bio-oil has a great potential to be used as a fuel additive. The production of high calorific value bio-oil is due to the enhanced deoxygenation through decarboxylation, decarbonylation and hydrodeoxygenation.

The total energy content of bio-oil produced was compared with the total energy content possessed by the feedstock, called energy recovery (ER) as reported in Table 3. The ER increased from 68.6% to 129.8% whereas, EE increased from 39.2 to 70.8 % by changing catalysts. Although the HHV of bio-oil obtained by using 5% Pd / Al<sub>2</sub>O<sub>3</sub> was higher than the bio-oil obtained by using 5% Ni / Al<sub>2</sub>O<sub>3</sub>, SiO<sub>3</sub>, but ER and EE was lower. This is because high bio-oil yield obtained by using Ni catalyst, which enhanced the ER and EE values. The high value of energy recovery (129.8%) indicates that almost all energy content of raw lignin was recovered. Similarly, high EE (70.8%) shows that the process is energetically efficient.

#### B. Composition of bio-oil

The chemical composition of bio-oil produced under

Table 3. Properties of bio-oils obtained from CSAHL, ER, and EE of the liquefaction process for different catalysts. All reactions were conducted at 350 °C, for 5 hr.

|   | Pressure<br>MPa | Conversion (%) | Elemental analysis of bio-oil (wt%) |      |      |      |      | HHV<br>(MJ·kg <sup>-1</sup> ) | ER<br>(%) | EE<br>(%) |
|---|-----------------|----------------|-------------------------------------|------|------|------|------|-------------------------------|-----------|-----------|
|   |                 |                | C                                   | H    | O    | S    | N    |                               |           |           |
| Blank   | 2.5 - 29        | 73.6           | 68.6                                | 5.80 | 21.9 | 0.9  | 0.23 | 28.8                          | 68.6      | 39.2      |
| 5% Pd / Al <sub>2</sub> O <sub>3</sub>                    | 40 - 43.5       | 95.3           | 70.6                                | 7.33 | 18.3 | 0.6  | 0.31 | 32.6                          | 115.0     | 62.7      |
| 5% Ni / Al <sub>2</sub> O <sub>3</sub> , SiO <sub>3</sub> | 45.5 - 47       | 100            | 70.8                                | 8.22 | 18.3 | 0.98 | 0.19 | 31.8                          | 125.5     | 68.5      |
| 5% Ru / Al <sub>2</sub> O <sub>3</sub>                    | 40 - 43.8       | 98.1           | 73.6                                | 8.76 | 16.1 | 0.7  | 0.35 | 34.6                          | 129.8     | 70.8      |

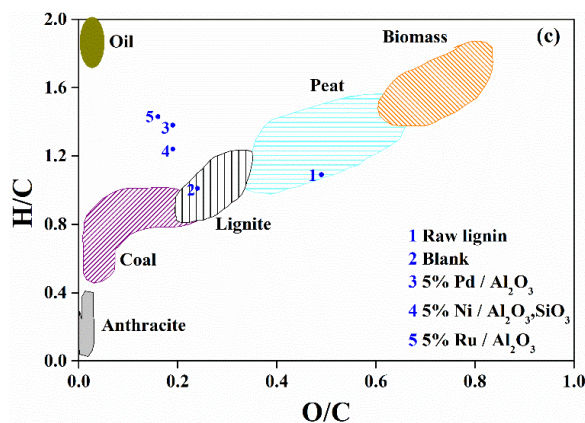
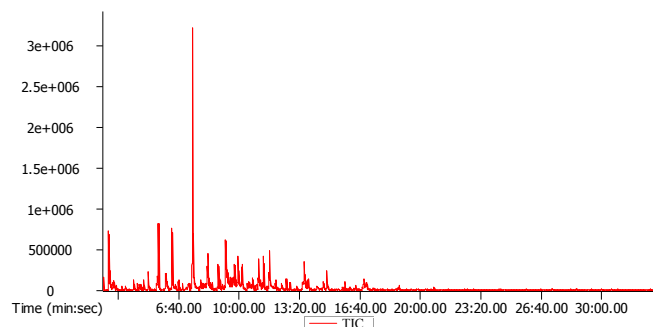


Fig. 2. Catalyst effect on H/C and O/C molar ratio of bio-oil. All reactions were conducted at 350 °C, for 5 hr.

different conditions was analyzed using GC-TOFMS. The GC chromatogram obtained in the reaction, when 5% Ru / Al<sub>2</sub>O<sub>3</sub> was used, is shown in Fig. 3, and indicates that the bio-oil consists of variety of chemicals including phenols, furans, esters, alcohols, oxygenated and traces of hydrocarbons. The chemical compositions of the bio-oils were categorized according to their structure and chemical functionalities. The compounds with phenolic functional groups are one of the major products in the bio-oil, which is expected because phenol is the basic building block of the lignin structure. Among the phenolic compounds, guaiacol, 2,6 dimethoxyphenol, 4-ethylphenol, 4-propylphenol, 2-methoxy-6-methylphenol, and creosol were dominant. In addition to the phenolic compounds, a considerable amount of furan-derived compounds was also observed. These compounds are generally originated from the carbohydrates (hollocellulose) fraction that was not completely separated from the lignin in delignification process [22]. Among the furanic compounds, dihydro-5-methyl-2(3H)-furanone, dihydro-3,5-dimethyl-2(3H)-furanone, dihydro-5-propyl-2(3H)-furanone, are the dominant species. Higher alcohols were also produced, especially in the presence of catalysts, and 1-butanol, 2-buten-1-ol, and 2-Hexanol are dominant among them. Esters were also detected in the bio-oil which might be produced by esterification of cellulose derived species. Butanedioic acid, diethyl ester, pentanoic acid, 4-oxo-, ethyl ester, acetic acid, ethoxy-, and ethyl ester are the main ester compounds.

#### IV. CONCLUSION

A supercritical ethanol (scEtOH)-based reductive depolymerization route was examined to obtain high yield and high calorific bio-oil using concentrated sulfuric acid hydrolysis lignin (CSAHL). The lignin used in this study was one of the recalcitrant lignin due to its harsher pretreatment method. The presence of solid catalysts increased the bio-oil conversion and almost 100% conversion was achieved in the presence of 5% Ni / Al<sub>2</sub>O<sub>3</sub>, SiO<sub>3</sub> catalyst. Other noble metal catalysts were also tested which produced significant results in terms of lignin

Fig. 3. GC-MS chromatogram of bio-oil produced in the reaction when 5% Ru / Al<sub>2</sub>O<sub>3</sub> was used. All reactions were conducted at 350 °C, for 5 hr.

conversion (above 95%). The presence of these catalysts enhanced the hydrogenolysis of lignin, which enabled to break refractive C–C bonds. The bio-oil produced possesses good quality in terms of low oxygen and high carbon and hydrogen content. This in turn, resulted in 61% of the O/C ratio as compared to the lignin feedstock, therefore, the oil produced has high calorific value of 34.6 MJ·kg<sup>-1</sup> in the presence of Ru-based catalyst. The production of high calorific bio-oil led to the energetically efficient liquefaction process with energy efficiency (EE) of 70.8% and energy recovery (ER) of 129.8%. These results suggest that this process has great potential of commercialization, which enable to convert a very low energy solid-waste lignin into very high calorific value liquid fuel.

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