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# **Influence of reaction conditions on the composition of liquid products from two-stage catalytic hydrothermal processing of lignin**

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## **Abstract**

The influence of reaction conditions on the composition of liquid products during two-stage hydrothermal conversion of alkali lignin has been investigated in a batch reactor. Reactions were carried out in the presence of formic acid (FA) and Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The two different sets of reaction conditions involved alternative reaction times of 1 h and 5 h at 265 °C and 350 °C respectively. These provided different contributions to reaction severity, which affected the compositions of liquid products. Yields of liquid products reached up to 40 wt% (on lignin feed basis) in the presence of FA under the less severe reaction condition. With 5 h reaction time at 350 °C, alkylphenols, alkylguaiacols and hydrocarbons were the dominant liquid products. However, with 5 h reaction time at 265 °C, phenol and methanol became dominant. The two-stage hydrothermal process led to improved lignin conversion, with the potential to manipulate the liquid product range.

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## 1.0 Introduction

Lignocellulosic biomass is a vastly abundant resource that has the potential to replace crude oil and coal as source of fuels and industrial chemicals. The world can sustainably produce around 220 billion tonnes of lignocellulosic biomass annually [1] in the form of agricultural wastes, forestry residues, municipal solid waste and other biowastes. Comprising of lignin, cellulose and hemicellulose, this type of biomass can be fractionally processed into useful products in a conceptual integrated biorefinery. Cellulose and hemicellulose can already be hydrolysed to produce sugars for bioethanol production via fermentation. These two biomass components are also sources of other platform chemicals and monomers such as lactic acid [2-3], levulinic acid [4-5], gamma-valerolactone (GVL) [6-8], 5-hydroxymethylfurfural (5-HMF) [9-11] and liquid alkanes for alternative transportation fuels [9, 12].

Lignin on the other hand is a by-product of biomass pulping, either removed by biomass pretreatment before fermentation or left as the major component of fermentation broth. The structure of pristine lignin within biomass is still a research topic of interest. However, the structure of extracted lignin shows that, like cellulose and hemicellulose it is a natural polymer but made up of phenylpropane units with numerous C-O (ether) and C-C linkages [13-14]. Many researchers have proposed lignin as the potential source of renewable aromatic chemicals and fuels [1, 15-16].

Liquid-phase and hydrothermal depolymerization of lignin is being investigated as a potential solution to the historical difficulty of lignin valorisation [16-18]. The presence of some organic co-solvents and capping agents has been found to minimize heat-induced polymerization of lignin and its primary degradation products to form char. For instance, the addition of formic acid (FA) has been shown to influence the degradation pathway of lignin

via hydrolysis of ether linkages, possible hydrogenolysis of C-C and C-O bonds, and hydrogenation of C=C bonds to produce a variety of compounds [19]. In recent work [19] carried out at 265 °C and 6.5MPa, lignin degraded to produce guaiacol as the dominant product in the absence of formic acid. However, in the presence of formic acid, the O-CH<sub>3</sub> bonds of the methoxy side groups were extensively hydrolysed, so that catechol became the dominant product. This result showed that the alkali lignin sample from Sigma-Aldrich was most probably a guaiacyl-type (G-type) lignin. The bonds with the strongest bond energies in this type of lignin are the β-O-4 and the 1 – α bonds with values of 574 and 513 kJ mol<sup>-1</sup>, respectively [20]. In addition, Forchheim et al. [21] found that the yields of catechol increased with increasing reaction temperature due to favourable reaction kinetics during non-catalytic lignin depolymerization in subcritical water. Onwudili and Williams [19] also reported significant formation of catechol and phenol from guaiacol.

Formic acid can react completely under hydrothermal conditions to produce carbon dioxide and hydrogen [19, 22 - 23]. However, formic acid is also a hydrolysis agent and could therefore be used to promote lignin depolymerization via hydrolysis and subsequently as a hydrogen source for hydrogenolysis and hydrodeoxygenation (HDO) of depolymerization products in the presence of a catalyst. The ability of formic acid to perform both roles could depend on its own reactivity under hydrothermal conditions and also on its concentration. It has been argued [19] that there might be a need to allow sufficient time for formic acid to act as a hydrolysing agent in order to achieve sufficient lignin depolymerization prior to acting a hydrogen-donor for hydrogenolysis or HDO of lignin products.

Yields of single-ring aromatic compounds from lignin depolymerization exceeding 20 wt% have been reported in literature [19, 24]. One of the proposed uses of lignin is to produce

fuel-range liquid products via HDO. As reported by Liu et al. [20], the major challenge in improving the yields of lignin hydrogenation products is the large bond enthalpies of the relevant bonds, thereby requiring high activation energies for HDO. Some researchers have carried out HDO of lignin and lignin model compounds with external hydrogen supply in a one-pot procedure, while others have envisaged a three-stage process involving depolymerization, followed by isolation of aromatic degradation products and finally HDO of the isolated compound. Yan et al. [16] obtained a total yield of 6 wt% of C<sub>9</sub>-C<sub>14</sub> cycloalkanes and methanol from the HDO of lignin depolymerization products.

In this present work, lignin conversion was investigated by allowing lignin and formic acid to react in two ways; namely at two different temperatures for different reaction times to investigate the influence of severity of the reaction conditions on lignin depolymerization products. Detailed analysis of reaction products obtained under these conditions would contribute to the understanding of the reaction mechanisms involved during hydrothermal depolymerization and conversion of lignin. In some experiments, Pt/Al<sub>2</sub>O<sub>3</sub> catalyst has been added to promote subsequent conversion of the depolymerization products. In addition, similar experiments were carried out with guaiacol, phenol and propylguaiacol, which are the main products of lignin depolymerization [22], to investigate their conversions.

## **2.0 Materials and Methods**

### **2.1. Materials**

Alkali lignin powder, 5 wt% platinum on alumina support, diethyl ether solvent (stabilized by butylated hydroxytoluene, BHT), formic acid and guaiacol (99 % purity) were purchased from Sigma Aldrich UK and used as received. The hydrothermal reaction system used has previously been described [19, 25]. Briefly, it was made of a non-stirred 75 ml Inconel

reactor fitted with a thermowell into which a thermocouple was inserted to measure the internal temperature. A pressure gauge was mounted on the head of the reactor to monitor pressure. The reactor was heated with a 1.5 kW ceramic knuckle heater fitted with a temperature controller.

## **2.2. Methods**

When required in this study, 0.50 g of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was loaded into the reactor with 1.00 g of lignin sample. For tests involving FA, 1.00 g (0.82 ml) of the acid was pre-mixed with 19.18 ml of deionized water and added to the reactor. In studies without catalyst, the lignin was reacted with 20 ml deionized water. After loading the reactor, it was sealed, purged with nitrogen for 10 min and heated to the designated reaction temperature. The heating rate was approximately 21 °C min<sup>-1</sup>, with the reactor reaching 265 °C in 12 min. The reactor pressure increased with time and stabilized within 5 - 10 min at the designated reaction temperatures. The maximum pressure reading of 6.5 MPa at 265 °C and 20.0 MPa at 350 °C were obtained during experiments. These values are higher than the vapour pressure of water in steam tables at these temperatures (5.14 MPa and 16.6 MPa, respectively) due to gas production during the reactions. At the end of the designated period, the reactor was withdrawn from the heater and rapidly cooled to ambient temperature under 1 h. The cooled gas pressure and temperature were noted prior to gas sampling for analysis.

Two sets of reaction conditions, each involving a two-stage process, were used to manipulate the reactions as shown in Table 1. In the first set of experiments (Condition#1), the loaded reactor was heated to 265 °C, held at this temperature for 1 h, raised to 350 °C in 5 minutes and finally held at 350 °C, 20MPa for 5 h. In a second procedure (Condition#2), lignin and formic acid were reacted at the lower temperature for 5 h, then raised to the higher

temperature of 350 °C (20 MPa) and held for 1 h. Each two-stage procedure involved conditions with the same total reaction times but with different reaction times at different temperatures, which influenced reaction severities. The severity factors (Log R<sub>o</sub>), which is dependent on reaction temperature and reaction times, have been calculated based on equation (1) [26];

$$\text{Log } R_o = \text{Log} \sum_{n=1}^n \left( t_i \exp \frac{T_i - T_b}{\varpi} \right) \text{-----} \quad (1)$$

where t<sub>i</sub> = reaction time; T<sub>b</sub> = base temperature, (200 °C in this work); T<sub>i</sub> = main reaction temperature (265 or 350 °C, respectively) and  $\varpi$  = fitted parameter (usually 14.75 for biomass pre-treatment) [26].

However, depending on reaction conditions  $\varpi$  can be estimated from equation (2), which shows its dependence on activated energy as follows [27-29];

$$\varpi = \frac{T_i^2 R}{E_a} \text{-----} \quad (2)$$

where T<sub>i</sub> = main reaction temperature (265 and 350 °C); R= Universal gas constant; E<sub>a</sub> = Activation energy

In this work, the activation energies of 58 kJ mol<sup>-1</sup> (lignin depolymerization to guaiacol) and 101 kJ mol<sup>-1</sup> (subsequent conversion of guaiacol to phenol/catechol) reported by Forchheim et al., [21] have been used. Hence, the calculated values of  $\varpi$  were 41.9 for reactions at 265 °C and 31.95 for reactions at 350 °C. Table 1 therefore shows that the sums of the severity factors for both conditions are exactly the same. However, the contributions of the reaction times and the respective reaction temperatures were different. For instance, under Condition#1, reactions at 350 °C contributed 65.1% to the severity factor, while under Condition#2, reactions at the same 350 °C provided 54.8 % severity contribution. Based on

these severity contributions, Condition#1 was designated as more severe while Condition#2 was the less severe condition in this study.

### Gas analysis

The gas products obtained during the hydrothermal reactions were collected via a 50 ml gas-tight syringe and analysed immediately using a system of three gas chromatographs. The details and analytical procedures for the gases have been published earlier [25]. Briefly, the gas samples were analysed using three packed column gas chromatographs. The permanent gases, hydrogen, oxygen, nitrogen and carbon monoxide, were separated on a molecular sieve column and analysed using a Varian CP-3380 gas chromatograph with a Thermal Conductivity Detector (GC/TCD). Hydrocarbon gases, C<sub>1</sub> to C<sub>4</sub>, were separated on a Haysesp column and analysed using a second Varian CP-3380 gas chromatograph with a Flame Ionisation Detector (GC/FID). Carbon dioxide was analysed using a third gas chromatograph fitted with a TCD. The results obtained from the GCs were given as a volume percent and were converted into masses of each gas using the ideal gas equation.

### Solid and liquid sampling

After gas analysis, the remaining gas products were discharged and the reactor opened to sample the contents – solid and liquid. Diethyl ether was added to the mixture to extract the organic compounds into the organic phase. In addition, a known amount of an internal standard (2-hydroxyacetophenone) was added to the combined liquid samples before the next steps of the analytical procedure. The solid residues retained by the dry, pre-weighed filter paper were washed with additional diethyl ether to extract any remaining organic products. The liquid fractions were partitioned into an organic phase and aqueous phase by liquid-liquid extraction technique. The volume of the diethyl ether extract (organic phase) was kept

typically at 40 ml in a pre-weighed amber glass vial. Thereafter, the ether solvent was evaporated under very low nitrogen flow and the yields of oil products determined by weighing.

The solid residues were dried at 105 °C and weighed to determine their yields. The solid residues, where applicable, contained both the catalyst and char from lignin. The solid residues were homogenized and portions oxidized in a muffle furnace at 750 °C for 2 h to obtain the ash (mainly catalyst). The yield of char arising from lignin was calculated as the difference between the weight of the solid residue and the weight of ash. The amount of water-soluble high-molecular weight products in the homogeneous aqueous-phase were determined by placing a known volume of each in a crucible and evaporating to dryness on a waterbath. The yields of the water-soluble products (WSP) were calculated as the difference between the crucible containing the dried residue and the empty crucible. The total volume of the aqueous phase was used to obtain the total water-soluble products obtained from the reaction.

#### Analysis of the liquid fractions

The organic products in the diethyl ether extracts were analysed on a GC/MS/MS and quantified using the internal standard added during sample preparation. The procedure used for the instrumental analysis has been previously provided in detail [19]. The aqueous residuals from the hydrothermal reactions were also analysed for methanol using a Varian 430 GC fitted with a flame ionization detector (FID). The column used was a water-tolerant HP-FFAP Polyethylene Glycol TP with dimensions 50 m x 200 µm x 0.3 µm, obtained from Agilent UK. The column's maximum operating temperature was 240 °C. In the procedure, 2 µL of aqueous residual sample was introduced into the injector operated at a split ratio of

1:20. The injector was held at 240 °C while the FID was at 280 °C. The oven temperature programme was as follows; 100 °C for 4 min, then ramped at 3.5 °C min<sup>-1</sup> to 140 °C held for 1 min and finally ramped at 5 °C min<sup>-1</sup> to 200 °C for 1.57 min; giving a total analysis time of 30 min. Methanol concentration in the sample was quantified using external standard method.

### **3.0 Results and Discussion**

#### **3.1. Product yields**

Figure 1a and Figure 1b present the yields of products from the reaction of lignin with or without formic acid and the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, under Condition#1 and Condition#2, respectively. The products have been categorized into liquid (methanol and ether extract), gas, solid and water-soluble products (WSP). The product yields have been presented on the basis of the combined weight of lignin and formic acid in the feed, where applicable, in order to make it easier to compare. As previously shown [22] gas yields were greatly influenced by the presence of formic acid. Mass balances were more than 93% in every case; and in cases where formic acid had been used, gas products dominated the mass balances, with >50 wt% yields.

In all cases, the less severe reaction condition gave higher liquid product yields than Condition#1, indicating that there was clear a benefit of allowing an extended reaction time for formic acid and lignin at the lower temperature, possibly to achieve higher depolymerization. The yields of liquid and gas suggest that the Pt/Al<sub>2</sub>O<sub>3</sub> was active in catalysing the formation of gas rather than liquid with extended reactions at 265 °C. The results show that under Condition#1 liquid yield decreased by about 7.7 % in the presence of Pt/Al<sub>2</sub>O<sub>3</sub> compared to liquid yields from the reactions involving lignin and formic acid without added metal catalyst. Similarly, under Condition#2 liquid yields decreased by nearly

16% in the presence of Pt/Al<sub>2</sub>O<sub>3</sub>. Yields of liquid products were at least 3 times higher when lignin reacted with formic acid compared to reactions without the acid. As shown in Figure 1, the yields of liquid products increased dramatically in the presence of FA under both conditions. The reduction in liquid product yields in the presence of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst may be related to the high yields of char as well as the increase in gas yields. However, results show that the reduction in liquid yields in the presence Pt/Al<sub>2</sub>O<sub>3</sub> was much more dependent on increased char formation than on the increase in gas yields. For instance, under Condition#1, with the use of Pt/Al<sub>2</sub>O<sub>3</sub>, gas yields increased by 5.74%, while char yield increased by 150%. Similarly, under Condition#2, the metal catalyst also increased gas yields by 16% but char yield increased by 246%. While, on the one hand liquid yields were significantly higher in the presence of FA compared to reactions without it, on the other hand, yields of chars and water-soluble products were higher when no formic acid was used. This showed that the formic acid was able to suppress the repolymerization of lignin and its degradation products to form char. The presence of the Pt/Al<sub>2</sub>O<sub>3</sub> produced more char and a closer look at the product yields in the presence of Pt/Al<sub>2</sub>O<sub>3</sub> suggests that the char could have arisen from both the liquid and the water soluble products, since yields of these products were lower with the Pt/Al<sub>2</sub>O<sub>3</sub> when compared with reactions in which FA was the only additive.

The char products were quite visible in the solid residues (catalysts). EDX (Energy-Dispersive X-ray Spectroscopy) characterization of the fresh and used Pt/Al<sub>2</sub>O<sub>3</sub> catalyst shows the presence of carbon, accounting semi-quantitatively for more than 55% of the catalyst surface (Please see Supplementary Information SI1). In the used catalyst, other elements such as sulphur (from lignin) and nickel, chromium, silicon and iron (from reactor) can be seen. Comparison between the two sets of results showed that the reactions with longer reaction times at 265 °C produced more water-soluble products and less char than

those kept longer at 350 °C. This suggests increased overall conversion of lignin at extended reaction times at the lower temperature of 265 °C.

### **3.2. Gas yields**

As mentioned earlier, gas products dominated the reaction products for reactions conducted in the presence of formic acid. Formic acid has been shown to hydrothermally react to produce CO<sub>2</sub> and hydrogen. In this work, reaction of formic acid in the presence of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst gave 99.6% conversion to CO<sub>2</sub> and hydrogen at 265 °C after 1 h. This confirmed the total conversion of formic acid under the reaction conditions used in this work. This agreed with our earlier work [19] using Pd/C as catalyst under similar conditions. Table 2 presents the compositional yields of the components gas products from the depolymerization of lignin, which clearly demonstrates that carbon dioxide was the dominant gas when lignin was reacted without formic acid. Although, carbon dioxide still remained the dominant gas during the reactions involving the acid, its yields increased over 3-fold. In addition, the yields of hydrogen also increased but fell below the expected yield (4.34 wt%) from formic acid, which indicated its consumption during the reactions. The consumption of formic acid-hydrogen, could be either as gas (during hydrogenolysis or hydrogenation) or as proton (during hydrolysis). Of interest is the yield of CO in the presence of Pt/Al<sub>2</sub>O<sub>3</sub> during extended reaction times at 265 °C, which may indicate a change in the activity of the catalyst in relation to reaction conditions.

Based on the carbon contents of the gas products it could be possible to determine the yield of gaseous carbon from lignin. This was done by calculating the carbon mass yields from the gas products as follows;

$$\text{Lignin-carbon gasification (\%)} = \frac{C_{total} - C_{FA}}{C_{total}} \times 100 \quad \text{-----} \quad (3)$$

$C_{total}$  = total carbon mass yield in gas products

$C_{FA}$  = carbon mass yields from formic acid (total conversion)

Table 3 shows clearly that the presence of formic acid led to more of the lignin-carbon in the gas phase compared to when lignin was reacted without the acid. Moreover, what is clearer is that the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst caused slightly less gasification of the lignin-carbon than when formic acid alone was present, possibly due to increased char formation under the more severe Condition#1.

### 3.3. Yields and compositions of liquid products

The yields of components in the liquid products (ether soluble and aqueous phase compounds) have been reported here on the basis of the lignin feed, since most of the detected compounds could apparently be formed from lignin. Figure 2a and Figure 2b show the yields of major components in the liquid products, under Condition#1 and Condition#2, respectively. These components accounted for ≥80% of the liquid products from GC analysis. These have been grouped into eight categories as methanol, phenol, alkyl phenols, guaiacol, alkyl guaiacol, catechol, hydrocarbons and others. In this study, liquid product yield under Condition#1 was 5.96 wt% (11.9 wt% if based only on lignin feed) when lignin was reacted in the absence of formic acid and the metal catalyst. This liquid product contained 33.6 % methanol (wood alcohol) and 36% alkylphenols. However, under Condition#2 the liquid yields using the same reactants was 7.0 wt% (14.0 wt% if based only on lignin feed). Total liquid product yields increased up by a factor of about 3 when lignin was reacted with formic acid compared to reactions without the acid.

These observed liquid yields showed that formic acid was able to suppress char formation via repolymerization reactions and possibly by promoting the depolymerization of lignin into liquid products as well as preventing char formation. Even raising the temperature did not adversely influence char formation from lignin in the presence of the acid. In addition, liquid yields were higher under Condition#2 compared to Condition#1, indicating the ability of formic acid to depolymerize lignin when allowed sufficient time as a hydrolysis agent.

Compared to an earlier work [19] where guaiacol and catechol were the dominant liquid components after reacting lignin and formic acid at 265 °C for 6 h, results in this present study indicated that raising the temperature to 350 °C for reaction times between 1 h and 5 h, dramatically changed liquid products' compositions. Indeed, in all cases, phenol, alkylphenols, alkylguaiacols and hydrocarbons were the dominant reaction products in this study. The yields of guaiacol and catechol were considerably low, except in the presence of the Pt catalyst. Interestingly, phenol was the dominant compound in the liquid under Condition#2, which involved longer reaction times at the lower temperature of 265 °C. However, under Condition#1 with longer reaction times at 350 °C, the yields of alkylphenols increased. In fact, the yields of phenol and alkylphenols were respectively highest, when lignin was reacted in the presence of formic alone.

The structure of isolated lignin samples often shows a preponderance of methoxy groups on the aromatic rings. Hence, the formation of phenols from lignin would indicate the formation of methanol via hydrolysis of the O-CH<sub>3</sub> groups. In general, methanol yields were lower under the severe Condition#1 than under Condition#2. The liquid product obtained from lignin alone under Condition#1 contained 34% methanol and 36% alkylphenols. Similarly,

under the less severe condition, methanol yield was 43% of the liquid product followed by phenol at 30%. This may indicate that reaction between phenol and methanol were accelerated under the more severe Condition#1 to produce alkylphenols, as discussed in later in this Section. Significant methanol formation during hydrothermal processing of biomass model compound mixtures has been recently reported in literature [23]. Ideally, the yield of methanol could be estimated from the yield of catechol, (and also on the yield of phenol, where phenol had formed directly from guaiacol). However, observed yields of methanol were lower, especially in the presence of formic acid, indicating possible methanol conversion during lignin depolymerization. For example, the reforming of methanol to hydrogen can be represented by;



Equation (4) presents the two-stage reaction including methanol decomposition ( $\Delta\text{H} = + 92 \text{ kJ mol}^{-1}$ ) to CO and hydrogen; followed by water-gas shift reaction ( $\Delta\text{H} = - 41 \text{ kJ mol}^{-1}$ ) of the CO to more hydrogen and CO<sub>2</sub>. The overall methanol reforming reaction is endothermic and so favoured at higher temperatures. From Equation (4), 1.00 g of methanol would yield 0.1875 g of hydrogen and 1.375 g of carbon dioxide. The hydrothermal reaction of methanol was tested by reacting 1.00 g of methanol under Condition#1 with the presence of Pt/Al<sub>2</sub>O<sub>3</sub>. Experimental yields of hydrogen and carbon dioxide were only 0.0095 g (0.95 wt%) and 0.0297 g (2.97 wt%) respectively, in the presence of Pt/Al<sub>2</sub>O<sub>3</sub>. In addition, 2.72 wt% total yields of C<sub>1</sub> to C<sub>4</sub> hydrocarbon alkane gases were obtained. The formation of hydrocarbon gases, CO<sub>2</sub> and hydrogen suggested the possibility of cracking of methanol indicating that methanol reforming to hydrogen was not favoured under these conditions. The presence of longer chain hydrocarbon gases of up to C<sub>4</sub> (as detected in the gas product), indicated the

methanol formed reactive alkyl species. Gadhe and Gupta [29] reported that significant methanol reforming to hydrogen occurred in supercritical water in a tubular reactor at 700 °C and 27.6 MPa. They achieved the highest hydrogen yield of 1.23 mole H<sub>2</sub> per mole of CH<sub>3</sub>OH, just 41% of the stoichiometric yield. In this present work, the presence of formic acid did not improve methanol conversion, producing a total of 0.054 g of hydrogen, which is slightly higher than the maximum hydrogen yield (0.0435 g) obtainable from formic acid alone. Hence, hydrogen yield from methanol was 0.0105 g (1.05 wt %), so that formic acid did not actually influence methanol reforming.



The equation (5) is a combination of methanol reforming reaction ( $\Delta\text{H} = + 49.3 \text{ kJ mol}^{-1}$ ) and formic acid decomposition ( $\Delta\text{H} = + 32 \text{ kJ mol}^{-1}$ ). Clearly, the energy requirement for formic acid decomposition is clearly lower than that required for methanol reforming. It was possible that the rate of formic acid decomposition could have been fast enough for it to avoid some reaction with methanol according to equation (5). However, hydrogen production from formic acid could lead to the exothermic hydrogenolysis of methanol to form methane;



Hence, Equations (4) to (6) show that the reactions of molecular methanol to produce hydrogen were at least thermodynamically hindered under the reaction conditions, especially by the highly positive enthalpy change for methanol decomposition step of reforming reaction in Equation (4), indicating that molecular methanol was resistant to conversion.

The liquid products from lignin depolymerization contained a high yield of alkylated compounds including alkylguaiacols, alkylphenols and alkylbenzenes. Literature shows that methanol can be used to alkylate aromatic rings in non-hydrothermal environments. In a recent study, Wang et al. [30] showed that methanol could be used to methylate aromatic hydrocarbons and olefins in the presence of HZSM-5 catalyst. It is generally accepted that such reactions proceed via the meth-oxonium ion and/or the methyl carbenium ion pathways to produce methyl-substituted aromatics and methyl alkanes [30-31]. While, alkylation of aromatic rings usually follows the electrophilic substitution (ionic) mechanism resulting from  $\text{CH}_3^+$ , the formation of hydrocarbon gases with more than one carbon atom from methanol also suggests the presence of radical  $\text{CH}_3^\bullet$  species or methyl carbenium ( $\text{CH}_3^-$ ) ions. However, the stability of molecular methanol under the conditions of this study indicated that it was hardly responsible for the formation of alkylated aromatics. However, it may be the case that the cleavage of methoxy groups in guaiacols may generate reactive species than can directly act as alkylating agents.

In addition, the predominance of guaiacol as the main product from an earlier study [19] showed that its formation from lignin was due to the cleavage of aryl-C bonds, to release the propanoid units, which may be responsible for alkylation of aromatic rings and formation of gas products. The identified alkylguaiacols in this study were mainly methylguaiacol, ethylguaiacol and propylguaiacol; and interestingly, these alkyl groups were all at the para-positions. This indicated that their formation were possibly via the original phenylpropane units of lignin. This was supported by the evidence that propylguaiacol gave the highest yields of alkylguaiacols in nearly all cases.

The degradation of the propanoid units, especially the multi-hydroxylated propanoids, could lead to the formation of reactive hydrocarbon species, responsible for alkylation reactions

under the hydrothermal conditions used in this study. These species could influence the composition of liquid products; for example, they may be capable of reacting with phenol to produce various multi-alkylated phenols. The alkyl phenols identified in this study were mainly methyphenols, dimethylphenols, ethylphenols, trimethylphenols and propylphenol. However, the presence of methanol in all the aqueous residuals obtained from this study showed that most of the arylO-CH<sub>3</sub> bond cleavages produced methanol which remained stable under reaction conditions.

The hydrocarbon compounds were mainly heavily alkylated benzenes (e.g. 1-methyl-4-(2-propenyl)-benzene and 1, 2-dicyclopropyl-2-phenylethyl) benzene), alkylated indene and dihydro-indenes, (e.g. 2, 3-dihydro-4-propenyl-1H-indene), naphthalene, alkylnaphthalenes including alkylated dihydro- and tetrahydro-naphthalenes (e.g. 5-ethyl-1, 2, 3, 4- tetrahydro-naphthalene), biphenyl and bibenzyl. The yields of some products including the dihydro- and tetrahydro- compounds shows evidence of HDO of the lignin depolymerization products. Results showed that the yields of the hydrocarbon compounds under both sets of conditions were largely dependent on the presence of formic acid rather than on the presence of the metal catalyst. Infact, the reaction of lignin with formic acid yielded more hydrocarbons than in the presence of the metal catalyst under both sets of reaction conditions. Thus, the formation of hydrocarbons might have resulted from the deoxygenation/condensation of phenolic compounds rather than hydrogenation of aromatic rings. Moreover, hydrocarbon yields were considerably higher when reactions were held for 5 h 350 °C than when they were held for the same period at 265 °C, even though overall liquid product yields decreased due to char formation. It therefore shows that longer residence times at higher temperatures favour formation of hydrocarbons from bio-based feedstock, which often involves deoxygenation/condensation of phenolic compounds, requiring higher activation energy. It

should also be pointed out that some of these hydrocarbon compounds were also present but in much lower yields in oils from reactions not involving formic acid. For example, under Condition#2, the hydrocarbon yield was 0.78 wt% from the reaction of lignin alone but increased to approximately 4.0 wt% in reactions involving the use of formic acid. In the same vein, under Condition#1 hydrocarbon yields were below 1 wt% in the oil from lignin alone but increased dramatically to up to 14 wt% in the presence of formic acid.

A mixture of compounds identified as 'others' in Figure 2 are those with yields  $\geq 0.1$  wt% and included compounds obtained from phenolic compounds via reduction, oxidation and ring-opening reactions such as cyclohexanone, 2-hexenal, 2-methylcyclohexanone, 1, 3-cyclohexadiene, 1-cyclohexene-1-carboxaldehyde, methylcyclopentanones and 3-methyl-3-hexene. Other compounds identified in this group included compounds which retained the aromatic functionality such as compounds trimethylbenzofuran-1-ol, dimethoxytoluene, dimethoxybenzene, alpha-methyl benzenemethanol, trimethylbenzeneacetic acid and 2-methyl-3-phenylpropanal. The yields of these compounds varied considerably with the different reaction conditions and additives. In general, there were more yields of these types of compounds under Conditions#2 than under Condition#1.

### **3.4. Other tests**

To investigate some of the observed results from the catalytic conversions of lignin, a series of aligned experiments were conducted. These included the reactions of guaiacol and propylguaiacol under both sets of conditions. The tests with guaiacol were carried out in the presence of formic acid and Pt/Al<sub>2</sub>O<sub>3</sub>, while experiments with propylguaiacol involved only formic acid. In these tests, results of product yields and detailed results of the yields of liquid products have been presented.

### 3.4.1. Hydrothermal reactions of guaiacol

To further understand the formation of products from lignin depolymerization, guaiacol a major depolymerization product of lignin [19], was reacted under the two sets of reaction conditions with the formic acid. Figure 3 shows the yields of products from the hydrothermal reactions of guaiacol. The formic acid and Pt/Al<sub>2</sub>O<sub>3</sub> showed different activities on guaiacol conversion under the different conditions. Certainly, the Pt/Al<sub>2</sub>O<sub>3</sub> produced more char compared to reactions without it, which is consistent with the results of char formation during lignin depolymerization. This may indicate the presence of stronger acidic sites on the Pt catalyst. In the presence of the catalyst, the yield of liquid products was slightly less under Condition#1 than Condition#2, possibly due to the higher severity factor in the former.

The yields of components in the liquid products shown in Figure 4 indicate that the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was active in overall guaiacol conversion, leading to higher yields of catechol under both conditions. Under Condition#1, Pt/Al<sub>2</sub>O<sub>3</sub> gave phenol and catechol yields of 7.0 wt% and 22 wt% based on guaiacol feed, respectively. However, with extended reaction times at 265 °C, the yield of phenol increased nearly 3-times to 19 wt% while that of catechol increased much slower to 27 wt%. This may suggest that Condition#2 was more applicable to phenol production from guaiacol via the hydrogenolysis of the aryl-O ether bond. This is also consistent with the improved yield of phenol during lignin depolymerization in the presence Pt/Al<sub>2</sub>O<sub>3</sub> and formic acid under identical reaction conditions.

The formation of guaiacol as the main product from the depolymerization of the alkali lignin sample indicates the cleavage of the aryl-C bonds thereby releasing the propanoid groups. Therefore, the formation of other compounds such as phenols and catechol would depend on

the further reactions of guaiacol. The reaction schemes shown below demonstrate the various possible routes of deriving catechol and phenol from the hydrothermal reactions of guaiacol;

1. Guaiacol + H<sub>2</sub>O → Catechol + Methanol (Hydrolysis of arylO-CH<sub>3</sub>/aryl-OCH<sub>3</sub> bonds)
2. Guaiacol + H<sub>2</sub> → Catechol +Methane (Hydrogenolysis of arylO-CH<sub>3</sub> bond)
3. Guaiacol + H<sub>2</sub> → Phenol + Methanol (Hydrogenolysis of aryl-OCH<sub>3</sub> bond)

Hydrolyses of aryl methyl ethers, like guaiacol, would yield catechol and methanol. In addition, hydrogenolysis of the aryl-OCH<sub>3</sub> bond in guaiacol would result in phenol and methanol, while hydrogenolysis of the arylO-CH<sub>3</sub> bond would also give catechol and methane. These reaction schemes therefore suggest that catechol was twice as likely to be produced from guaiacol as phenol by a combination of hydrolysis and hydrogenolysis under the hydrothermal conditions of this study. Hence, the relative yields of catechol and phenol in the reaction products could be used to determine the dominant mechanisms during lignin/guaiacol conversion. Onwudili and Williams [19] reported lower yields of phenol compared to catechol indicating that hydrolysis, rather than hydrogenolysis, was the dominant mechanism for hydrothermal guaiacol conversion in the presence of formic acid. As shown in Figure 2, reactions carried out with extended reaction times at 350 °C produced more aromatic hydrocarbons including naphthalene, bibenzyl and biphenyl compared to reactions with extended times at 265 °C. This may indicate that the formation of these compounds may originate from products of guaiacol conversion rather than from guaiacol directly.

### 3.4.2. Liquid products from hydrothermal reactions of propylguaiacol

The hydrothermal reactions of propylguaiacol were investigated in the presence of formic acid and Pt/Al<sub>2</sub>O<sub>3</sub> under Condition#1 and Condition#2, respectively. Results show that propylguaiacol certainly produced many more liquid products during its reaction than phenol. Under both conditions more than half of the propylguaiacol feed was converted, showing more reactivity than phenol but comparable to guaiacol. Figure 5 shows the yields of liquid products from the reaction of propylguaiacol. The major new compounds observed included phenol, propylphenol, eugenol (1-propenyl guaiacol) and propylcatechol. The yield of propylcatechol as a product was the highest under both conditions; however, Condition#1 produced slightly less propylcatechol and phenol than Condition#2. The formation of propylcatechol suggests that propylguaiacol reacted in a similar way to guaiacol, mainly hydrolysis of the ether bond. The formation of propylphenol showed that hydrogenolysis of the aryl-O bond occurred, while formation of phenol indicated a combination of hydrogenolysis of aryl-O bond and dealkylation of the propane side group. The C-C linkages in lignin are often the most difficult to break [32], which explains why the major compounds from the reaction of propylguaiacol were those that retained the propyl group. In addition, the presence of eugenol showed possible hydroxylation of the propane side group followed by dehydration. However, in lignin most of the propanoid groups are highly hydroxylated and not pure hydrocarbons as in propyl guaiacol and may therefore react differently. Therefore, under certain hydrothermal conditions guaiacol and not propylguaiacol was the major compound formed from lignin depolymerization, indicating the potential cleavage of aryl-C bonds. The minor products detected at low concentrations (<1 wt%), which could have arisen from the reactions of the propanoid groups of lignin included 2-methylphenol, guaiacol, 3-methyl-6-propylphenol, 4-ethylguaiacol, 1,2-dimethoxy-4-n-propylbenzene and 1-methoxy-4-(1-methylpropyl)benzene. The formation of some of these products may be related to the reactive (alkyl and alkoxy) species obtained from the cleavage of aryl-C bonds, possibly after

hydroxylation of side groups in alkylguaiacols. Direct methylation of aromatic rings from alkyl species from the HDO of guaiacol have been reported in non-aqueous conditions [33-34].

### **3.5. Plausible reaction mechanisms for lignin conversion**

The possible overall mechanism for the hydrothermal conversion of alkali lignin appeared to include depolymerization and subsequent conversion to fuel range (Please see Supplementary Information, SI2). However, it is important to note that the yields of final hydrogenation products in this present study were low, possibly due to the quantity of hydrogen gas available from formic acid. Although, significant yields of hydrocarbons were obtained under Condition#1 in this present study, most were alkylbenzenes and PAHs, indicating insufficient hydrogen production for their HDO. Literature shows that conversion of compounds with alcohol and ether functional groups to hydrocarbons often involves a dehydration step followed by a hydrogenation step [34-35]. Therefore, HDO of phenolics involves sequential hydrogenation-dehydration-hydrogenation steps and the conversion of aryl alcohols and ethers to hydrocarbons follow this mechanism. For instance, the conversion of phenol to cyclohexane would involve initial hydrogenation of the aromatic ring to produce cyclohexanol/cyclohexanone followed by dehydration to cyclohexene and then hydrogenation to cyclohexane/methylcyclopentane. However, phenol can also be converted to benzene via hydrogenolysis of C-O  $\alpha$  bond and then to cyclohexane by hydrogenation.

Echeandia et al. [34] found that during the HDO of phenol using Ni-based catalysts, the hydrogenation route through cyclohexanol was predominant over the route involving hydrogenolysis of C-O  $\alpha$  bonds. The preference for the hydrogenation route over hydrogenolysis may involve many factors including favourable reaction kinetics. Although,

the total enthalpy change for the conversion of phenol to cyclohexane will be the same irrespective of the route taken, the kinetics and enthalpy changes associated with the individual steps could determine the route in relation to the reaction conditions. For instance, hydrogenolysis of C-O bonds is more endothermic with a standard enthalpy change of +39.3 kJ mol<sup>-1</sup> [34], than the overall standard enthalpy of HDO of phenol, which is +7.83 kJ mol<sup>-1</sup> [16]. The lower enthalpy change for HDO of phenol arises from the combination of enthalpies of hydrogenation (exothermic), dehydration (endothermic) and destabilization of aromatic structure (endothermic). Future work would involve using higher loadings of formic acid to generate sufficient hydrogen gas for in-situ HDO of lignin depolymerization products.

#### **4.0 Conclusion**

The influence of different reaction conditions on the two-stage catalytic hydrothermal conversion of alkali lignin has been investigated in the presence of formic acid and Pt/Al<sub>2</sub>O<sub>3</sub>, to understand the mechanisms of liquid products' formation. Overall yields of liquid products demonstrated successful lignin depolymerization, but their compositions depended on reaction conditions. Investigations on the separate reactions of guaiacol and propylguaiacol indicate that guaiacol was the main source of catechol and phenol. Guaiacol and propylguaiacol yielded their corresponding catechols and phenols as the major products of their hydrothermal reactions. Future work would involve using increased concentrations of the hydrogen-producing formic acid.

## 5.0. References

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## **Figure Captions**

Figure 1: Product yields and mass balances during lignin conversion (a) Condition#1, (b) Condition#2

Figure 2: Detailed compositions of the liquid products from lignin conversion (a) Condition#1; (b) Condition#2

Figure 3: Product yields from hydrothermal conversion of guaiacol under Condition#1 and Condition#2

Figure 4: Composition of liquid products from hydrothermal conversion of guaiacol under Condition#1 and Condition#2

Figure 5: Composition of liquid products during hydrothermal reactions of propylguaiacol under Condition#2