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Catalytic depolymerisation of isolated lignin to fine chemicals:

Depolymerisation of Kraft Lignin.

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Highlights

- Strategic depolymerisation of residual Kraft lignin yielded fine chemicals
- Selective generation of 2-methoxyphenol addressed by suitable catalyst and solvent
- Isotopic tests show distinct mechanisms for lignin solvolysis and hydrogenolysis

Abstract

Kraft lignin depolymerisation over Pt/alumina, Rh/alumina and solvolysis was studied under a range of solvent solutions (ethanol/water, isopropanol/water, acetone/water 25:75, 50:50, 75:25 v/v), high temperature (573 K) and pressure (20 barg). The reactions generated mainly non-alkylated phenolic monomers, especially 2-methoxyphenol. In terms of overall yield, solvolysis was shown to be as effective as the catalyzed reactions in some experiments. Nevertheless, it was found that for individual molecules a suitable combination of solvent mixture and catalyst resulted in the possibility of target compound generation. To contribute to an understanding of the mechanism of Kraft lignin depolymerisation, kinetic isotopic effects (KIE) were evaluated using fully deuterated and partially deuterated experiments. This revealed hydrogen exchange between the molecules and solvents. In addition, a variety of positive and inverse KIE showed the complexity of lignin depolymerisation and the direct involvement of solvents in those reactions.

Keywords

Kraft lignin; Phenols; Depolymerisation; Kinetic isotopic effect;

1. Introduction

The move from fossil fuels to biomass as the main carbon source requires the use of non-food material including waste streams. One such waste material is Kraft lignin. The paper and pulping industries produce Kraft lignin (KL) in a black liquor (Chen et al., 2014) that is used for heat and power generation in pulp mills (Dessbesell et al., 2017). The procedure results in a sulfur containing lignin with an estimated production of 100,000 tons p.a. (Institute T.I.L., 2000) Thus, an effective re-use of a waste product, such as KL, to produce fine chemicals could be a promising application in a biorefinery context.

Lignin, cellulose and hemicellulose are the three major components of lignocellulosic materials (Gillet et al., 2017). While cellulose and hemicellulose are the polysaccharide constituents, lignin is an amorphous polymer (Cheng et al., 2018). Due to its complexity and technical limitations, lignin's chemical structure is still not fully defined. However, it was found that most lignins are mainly composed of three building blocks classified as guaiacyl alcohol (G unit), syringyl alcohol (S unit) and *p*-coumaryl alcohol (H unit) (Sjöström, 1993). In the lignin framework, they are linked between each other by C-C or C-O bonds such as β -O-4, α -O-4, β - β , 5-5 and β -1 linkages. To produce fine chemicals, an efficient cleavage of these bonds in the biopolymer is essential (McVeigh et al., 2016).

Depolymerisation of lignin is still a challenge despite the fact that numerous thermochemical studies including pyrolysis (Caballero et al., 1997), acidolysis (Wang et al., 2013) and oxidation (Fang and Meier, 2018) have been explored. The use of solvents for lignin breakdown can be a strategic tool due to their ability to solvolytically cleave linkages and their hydrogen donor facilities (Cheng et al., 2018). The addition of heterogeneous catalysts in this type of reaction shows the possibility of selective cleavage of lignin bonds and the generation

of target molecules (McVeigh et al., 2016). Interestingly, simple changes in catalyst may result in considerable changes in product distribution and individual yields (McVeigh et al., 2016), revealing the complexity of lignin breakdown. A possibility for further understanding reaction pathways in lignin depolymerisation could involve the study of kinetic isotopic effects (KIE). These are based on the comparison of protiated solvent based experiments with their deuteriated solvent analogues. These effects can be observed if the deuterated species is involved in the rate determining step of the reaction (Seoud et al., 1997). The technique is becoming a valuable tool to aid mechanistic understanding.

In previous work (Bouxin et al., 2015), it was reported that the content of β -O-4 bonds was a key aspect in catalytic lignin depolymerisation. It was also revealed that a suitable solvent greatly contributes to this reaction and the presence of a heterogeneous catalyst can enhance product yields (McVeigh et al., 2016). In this work, we continue our study by exploring a sulfur containing technical lignin (Kraft Lignin, KL). It was possible to investigate the effects of solvents in various proportions with water and assess how the addition of heterogeneous catalysts affected the reactions. In addition, to obtaining mechanistic insights about lignin depolymerisation, kinetic isotopic effects were evaluated.

2. Materials and Methods

2.1 Catalyst Preparation

The main catalyst used in this study was a Pt/alumina catalyst supplied by Johnson Matthey (reference number 1074). A Rh/alumina catalyst was prepared by incipient wetness impregnation as previously reported (McVeigh et al., 2016) using the same support as Pt/alumina. Prior to reaction, the catalysts were reduced in a flow microreactor. The procedure

consisted of heating to a reduction temperature of 523 K for Pt/alumina and 573 K for Rh/alumina in 2% H₂/N₂ at a ramp rate of 10 K min⁻¹, with a dwell time at reduction temperature of 2 h for Pt/Al₂O₃ and 1 h for Rh/Al₂O₃. Afterwards, the catalysts were cooled to room temperature in flowing argon.

2.2 Hydrogenolysis of Kraft lignin

The Kraft lignin used in this study was purchased from Sigma Aldrich. Lignin depolymerisation reactions were conducted using a 300 cm³, 316 stainless steel, Parr batch autoclave reactor, which was equipped with a digital temperature controller (± 1 K). Typically, lignin (0.5 g), catalyst (0.1 g) and solvent mixture (100 cm³) were added to the reactor. The solvents used were ethanol (VWR chemicals, purity 99.96 %), isopropanol (Honeywell, purity 99.5 %), acetone (Fisher scientific, purity 99.88 %) and distilled water. The mixtures used contained EtOH/H₂O, IPA/H₂O or acetone/H₂O in different volumetric ratios (25:75, 50:50, 75:25, 100 v/v). Subsequently, the reactor was sealed, purged three times with hydrogen, pressurised to 20 barg and heated to 573 K under mechanical stirring (1000 rpm). When the reactor temperature was achieved, it was kept constant for 3h. The method developed by Bouxin *et. al* was used to obtain the phenolic compounds from the reaction mixture. The post reaction mix was filtered using a sintered glass (porosity 3) in order to recover the catalyst and remove insoluble products. Subsequently, it was centrifuged and the recovered fraction was mixed with 200 cm³ of the same solvent/water mix used in the reaction, named Fraction 1. All the residues containing lignin fragments of higher molecular weight were solubilised in acetone (Fraction 2). A known amount of internal standard (0.2 cm³, 1 g.L⁻¹) was added to a 15 cm³ aliquot of Fraction 1 and the mixture acidified to pH 2. A mixture of 8/2 v/v of dichloromethane/dioxane was used three times for extraction of phenolic compounds. After the removal of solvents, the mixture was solubilised in 2 cm³ of dichloromethane (DCM) to be analysed by gas chromatography – mass spectrometry (GC-MS).

2.3 Product Analysis by GC-MS

To identify and semi-quantify the products a GC-MS-QP2010S coupled to a Shimadzu GC-2010 GC equipped with a ZB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) was used. 10 μL of this samples was mixed with 70 μL of pyridine and 30 μL of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and after 2 hours the sample was analysed. The sample was measured on the TIC using four authentic reference compounds originated from a G unit or S unit of lignin (2-methoxyphenol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxyphenol and 4-methyl-2,6-dimethoxyphenol) in concentration of .0.01, 0.05, 0.1, 0.5 and 1 g.L⁻¹, and hexadecane as internal standard (1 g.L⁻¹) while the BSTFA was used to derivatise the hydroxyl groups present in the compounds. This resulted in a graph of concentration versus intensity where the gradient was the response factor (RF) for each molecule. The RF values revealed a trend for molecules, which originated from G and S lignin units. This allowed the semi-quantification of the unknown compounds by rearranging equation 1

$$\alpha = \frac{\text{Intensity of reference}}{\text{Intensity of internal standard}} \times \frac{\text{Mass of internal standard}}{\text{Mass of reference}} \quad (1)$$

and by taking in account the volumes used to prepare the samples. In terms of the identification of monomers by mass spectroscopy eight molecules were successfully identified according to the literature, based mainly on alkyl phenolics with different functional groups.

The idea of a polyaromatic chemical structure of lignin indicates a range of products that can be formed from its depolymerisation in either gas, liquid, or solid phases. The specific products selected to be discussed in this work were those in the liquid-organic phase and with higher concentration. Mass balance closure was not possible mainly due to technical limitations including detection limit of the GC-MS system, formation of char, gas and compounds soluble into the water which could not be recovered. The overall yield discussed consisted of the sum

of all alkyl phenolics identified per g/100 g of lignin and selectivity $S = (\text{the specified molecule}/\text{total amount of detected molecules}) \times 100$.

2.4 Isotopic labelling studies

The methodology used in these experiments was the same as that used in the protiated experiment. In order to carry out these studies fully deuterated catalysed (FDC), partially deuterated catalysed (PDC) and fully deuterated non-catalysed (FDNC) reactions were performed. In an FDC reaction, the experiment was altered by replacing acetone, water and hydrogen by their deuterated forms: deuterated acetone ($(\text{CD}_3)_2\text{CO}$), deuterium oxide (D_2O) and deuterium ($\text{D}_2(\text{g})$). In the PDC reaction, solvents were deuterated while hydrogen remained as $\text{H}_2(\text{g})$. In the FDNC reaction the system was fully deuterated but in the absence of catalyst. For FDC, PDC and FDNC reactions the ratio of acetone:water was 50:50 v/v, all other reaction parameters remained the same. A kinetic isotopic effect for individual molecules was obtained according to equation 2, where r_{H} and r_{D} are the rate of the protiated and deuterated reactions, respectively. The rate of reactions was obtained according to equation 3.

$$\text{KIE} = \frac{r_{\text{H}}}{r_{\text{D}}} \quad (2)$$

$$\text{Rate of reaction (r)} = \frac{\text{Individual product yield}}{\text{Time (minutes)}} \quad (3)$$

2.5 Gel Permeation Chromatography (GPC)

Gel permeation chromatography was performed in order to obtain information about the molecular number (M_n), molecular weight (M_w) and polydispersity (I_p) of the lignin. Reaction products were also analysed to compare with the initial lignin by mixing 1 cm^3 of Fraction 1 and Fraction 2. The procedure was conducted according to the methodology developed by McVeigh (2016) as previously described (McVeigh, 2016). A calibration (McVeigh, 2016)

experiment was performed using polystyrene standards (PS) in the range of 474 to 28 000 g mol⁻¹, resulting in a line equation of $y = -0.031x^3 + 1.2581x^2 - 17.264x + 83.146$. A Gilson pump system equipped with a UV detector (280 nm), a set of PS/DVB columns (5 m, 300x7.5 mm, 50 and 500 Å, Polymer Lab) set at 303 K was used with an injection volume of 100 µL and a tetrahydrofuran (THF) eluent flow rate of 1 ml.min⁻¹. Samples were prepared by mixing equal volumes of Fraction 1 and Fraction 2. Subsequently, the solvent was evaporated, the remaining material acetylated and solubilised in THF and filtered ready for injection.

2.6 Thermogravimetric analysis and elemental analysis

Thermogravimetric analysis was performed using a combined TGA/DSC SDT Q600 thermal analyser coupled to an ESS mass spectrometer (TGA). Typically 0.01-0.015 g of catalyst was used and the samples were heated from room temperature to 1273 K with a thermal ramp of 10 K.min⁻¹ under O₂/Ar. Elemental analysis for carbon, hydrogen and nitrogen (CHN) were carried out using a CE-440 elemental analyser.

2.7 Surface area and pore volume determination

Surface area and pore volume was determined using a Micrometrics Gemini III 2375 Surface Area analyser. Approximately 0.04 g of catalyst sample was weighed in a glass tube and left overnight at 383 K under nitrogen. Prior to analysis the samples were reweighed.

2.8 Raman spectroscopy analysis

Raman spectra were obtained using a Horiba Jobin Yvon LabRAM High resolution spectrometer. Helium Cadmium IK3201 and R-F 325 nm UV lasers were used. The laser light was directed to the sample for 10 seconds using a 15x UV objective lens with 1200 cm⁻¹ grating. A range of 500 to 3000 cm⁻¹ was analysed. Back scattering configuration collected the scattered light and was detected by a nitrogen cooled charge-coupled detector CCD.

2.9 X-ray diffraction analysis

A Siemens D500 X-ray diffractometer (40 Kv, 40mA, monochromatised) with a CuK α source (1.5418 Å) was used over a range of 5-85° 2 θ with a scanning rate of 2 s/step with step size of 0.02°.

3. Results and Discussion

3.1 Catalysts Characterisation

Powder XRD of the Pt/Al₂O₃ catalyst showed that the support was principally θ -alumina. Carbon monoxide chemisorption gave a platinum dispersion of 56 % (McVeigh et al., 2016) and a particle size of ~ 2 nm (McVeigh et al., 2016). BET analysis gave a surface area of 124 m².g⁻¹, a pore volume of 0.6 cm³.g⁻¹ and a pore diameter of 14.6 nm. For Rh/alumina, BET analysis confirmed a surface area of 102 m².g⁻¹, a pore volume of 0.5 cm³.g⁻¹ and a pore diameter of 14.5 nm, whilst CO chemisorption showed a dispersion of 121 % (McVeigh et al., 2016).

3.2 Elemental analysis and bond patterns in Kraft lignin

Bouxin et al., 2015 reported earlier that lignins richer in β -O-4 bonds were more able to generate monomers from depolymerisation and that the removal of lignin from wood resulted in changes in structure dependent upon the process used (Bouxin et al., 2015). Kraft lignin is a waste product that is known to be highly condensed and thioacidolysis has indicated a low level of β -O-4 linkages (~5 %) with only guaiacol (G-unit) linkages. Elemental analysis (CHN) gave a chemical formula of C₆H₈O₂ which is also consistent with a G-unit structure. The structure was further examined using HSQC-NMR analysis. Using this methodology, the β -O-4 linkage was detected in Kraft lignin at a level ~11 % compared to 4.5 % for β - β and 4.4 % for β -5 bonds. These values for β -O-4 linkages are low, for example, ammonia lignin had a value (Bouxin et al., 2015) of ~29 % and would suggest low reactivity may be expected.

Nevertheless we were interested to determine whether process conditions optimised in earlier studies (McVeigh et al., 2016), would be suitable for conversion of KL into monomers. It should be remembered that as a large tonnage waste product even relatively small yields of specific chemicals may be commercially advantageous as the residual material can still be used as fuel. Therefore we examined the effect of solvents alone and in conjunction with various catalysts to see whether they influenced specific monomer yields.

3.3 Solvolysis of Kraft lignin

A preliminary study on the influence of solvents on the depolymerisation of Kraft lignin was carried out. Reactions using only solvent/water and hydrogen at 573 K and 20 barg were conducted, and eight monomeric compounds were identified, as listed in Table 2. These compounds followed the basic monomeric motif in Fig. 1 having various functional groups attached to the ring (for a G-unit $R_1 = H$ and $R_2 = OCH_3$). As described in Section 2.3, a trend between the monomer type (S or G unit) and the response factor (RF) was found. For guaiacyl, 2-methoxyphenol and 4-ethyl-2-methoxyphenol (all G unit molecules) an RF value of 0.23 was obtained. Syringyl, 2,6-dimethoxyphenol and 2,6-dimethoxy-4-methylphenol (all S unit compounds) gave RF values of 0.19, 0.19 and 0.18, respectively. Hence, the response factors assumed for a molecule originated from a G or S unit was assumed as 0.23 and 0.19, respectively

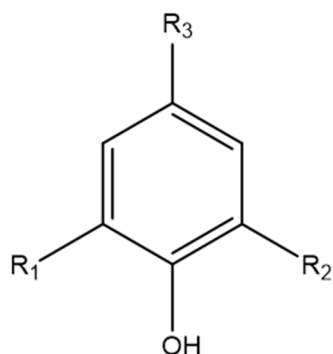


Fig. 1. Basic lignin monomeric motif (for a G-unit $R_1 = H$ and $R_2 = OCH_3$).

Standard deviations for individual molecules were obtained to show the limitations of the quantitative method used. The values were not high, being below 0.1, which was deemed acceptable. The reaction over Pt/Al₂O₃ catalyst and acetone water 50:50 v/v was chosen as representative for the method and carried out in triplicate, results are presented in Table 1.

Table 1. Standard deviation values of individual molecules from Kraft lignin depolymerisation. Compounds: (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol

Compound							
1	2	3	4	5	6	7	8
Standard Deviation							
0.1	0.05	0.01	0.04	0.01	0.08	0.01	0.03

Regarding the experimental conditions, when the sealed reactor achieved the temperature (573 K) the pressure varied from 120 barg to 150 barg depending on the solvent used, therefore, except for water, all solvents could reach their critical points. Studies have shown that lignin can depolymerise in the presence of subcritical or supercritical solvents at various temperatures (553–673 K) and pressures (200–250 bar) (Joffres et al., 2013). In these conditions, vapour and liquid phases coexist and the supercritical fluid has a constant density. As an advantageous aspect, these circumstances can enhance hydrogen diffusion in the reaction medium. Similarly, water close to or at its supercritical conditions can also show favourable characteristics, such as the ability to solubilise organic compounds due to variations in its dielectric constant (Biswas and Bagchi, 1999) and presence of H⁺ and OH⁻ (McVeigh et al., 2016). In the context of a technical lignin depolymerization, such as Kraft, these conditions could favour the cleavage of the recalcitrant C-C bonds.

There have been reports of attempts to degrade lignin using solvent mixtures. McVeigh *et al.* revealed that by increasing the content of methanol in the depolymerisation of ammonia lignin,

the yield of monomeric products rose (McVeigh et al., 2016), while research (Saisu et al., 2003) using only water led to cleavage of lignin and monomer production but also considerable char formation. However, the addition of phenol in the reaction decreased re-polymerisation (Saisu et al., 2003). Likewise, studies with Organosolv lignins in supercritical acetone, ethanol and methanol brought advantages to depolymerization (Erdocia et al., 2016) leading to a range of monomers, mostly syringol and guaiacol. In the present work, solvent mixtures were used and it was found that phenolic compounds were generated from all reactions. There were more variations in the total monomers yield from ethanolic solutions compared to acetone and IPA. As detailed in Fig. 2 (a), the individual yields varied depending on the type of solution used.

Table 2. Identified compounds from the depolymerisation of Kraft lignin

Compound Code	R ₁ /R ₂ /R ₃ group	Compound Name
(1)	R ₁ =R ₃ =H; R ₂ =OCH ₃	2-methoxyphenol (guaiacol)
(2)	R ₁ =H; R ₃ =CH ₃ ; R ₂ =OCH ₃	4-methyl-2-methoxyphenol
(3)	R ₁ =H; R ₃ =CH ₂ CH ₃ ; R ₂ =OCH ₃	4-ethyl-2-methoxyphenol
(4)	R ₁ =H; R ₃ =CH ₂ CH ₂ CH ₃ ; R ₂ =OCH ₃	4-propyl-2-methoxyphenol
(5)	R ₁ =R ₃ =H; R ₂ =OH	1,2-dihydroxybenzene (catechol)
(6)	R ₁ =H; R ₂ =OH; R ₃ =CH ₂ CH ₃	4-ethylbenzene-1,2-diol
(7)	R ₁ =H; R ₂ =OCH ₃ ; R ₃ =CH ₂ CH ₂ CH ₂ OH	4-(3-hydroxypropyl)-2-methoxyphenol
(8)	R ₁ =H; R ₂ =OCH ₃ ; R ₃ =CH ₂ CH ₂ CH ₂ OCH ₃	4-(3-methoxypropyl)-2-methoxyphenol

According to Fig. 2 (a), the highest overall yield was obtained with 75/25 ethanol/water and the lowest with 50/50 IPA/water. Huang and co-workers (Huang et al., 2014) showed the advantage of ethanol usage in this type of reactions as it can stabilise intermediates, acting as a capping agent so decreasing lignin condensation (Huang et al., 2014). It was also reported that a catalysed reaction in ethanol at high temperature produced high yields of alkylated monoaromatics (Huang et al., 2015). In accordance with these reports, ethanol showed to be more involved in reaction than the other solvents. For example, using 50/50 ethanol/water, 2-methoxyphenol was the main product followed by 1,2-dihydroxybenzene (catechol) with selectivity of ~ 50 % and ~ 28 %, respectively. The molecular structure of these compounds suggested that ethanol favoured dealkylation and demethylation of lignin fragments. This may also be related to the action of ethanol as a formaldehyde scavenger, minimizing intermediate recombination (Huang et al., 2015) thereby enhancing product formation.

In Fig. 2, IPA and acetone solvents did not have a considerable influence on the overall yield, but product distribution (Fig. 2c-2d) was affected. When the solution contained isopropanol (Fig. 2c), all compounds were maximised with the IPA/H₂O 25:75 v/v mix. The main products were 2-methoxyphenol (guaiacol), 4-methyl-2-methoxyphenol (4-methylguaiacol) and 4-propyl-2-methoxyphenol (4-propylguaiacol) with selectivity of ~ 42 %, ~ 28 % and ~ 11 %, respectively. Therefore, IPA favoured different mechanistic pathways compared to EtOH, giving more monomers with alkyl chains. This was also observed when ammonia lignin was used with isopropanol, giving high selectivity to alkyl-chain monomers (McVeigh et al., 2016) indicating that not only for KL the formation of alkylated molecules could be influenced by isopropanol. Despite no evidence of hydrogenation, isopropanol has a hydrogen donor capability, which has been explored in reactions such as coal liquefaction (Vasilakos and Austgen, 1985) and thermochemical transformation of lignin with formic acid and IPA (Kalabova et al., 2014). This characteristic of isopropanol and its less polar nature could

enhance lignin intermediate solubility, as a consequence re-condensation may have been depressed.

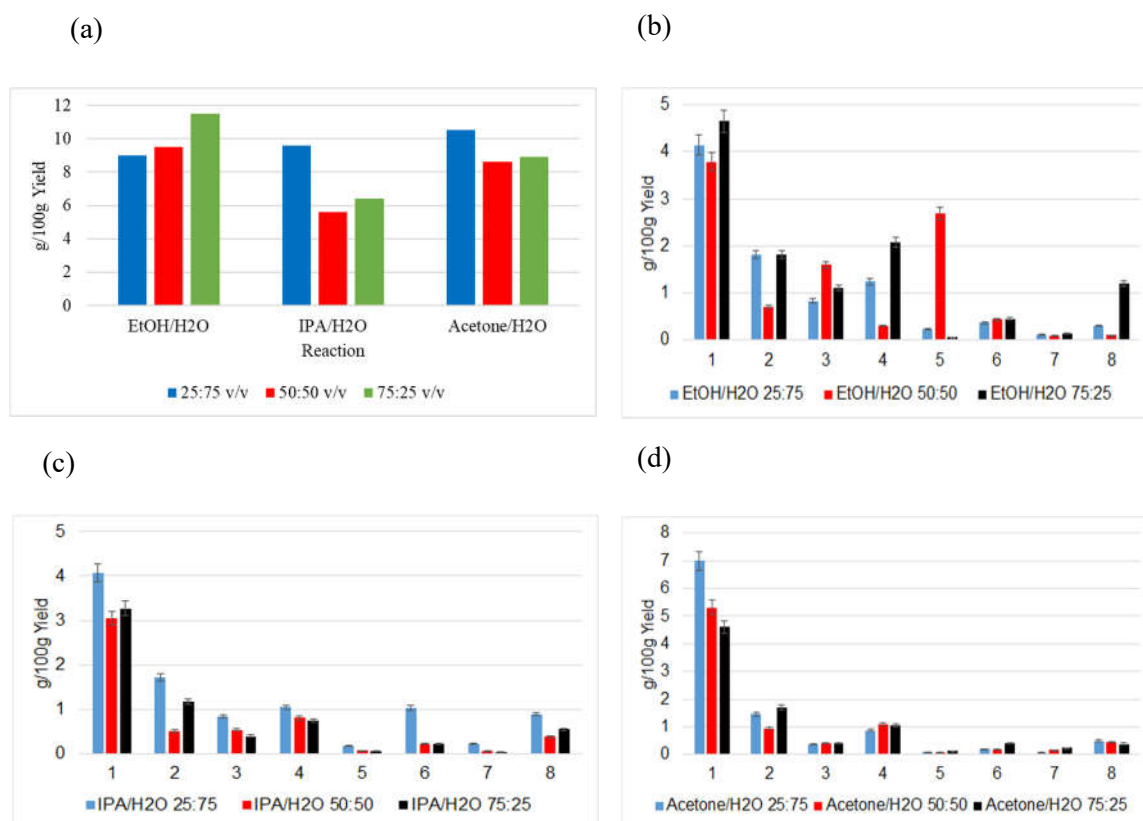


Fig. 2. (a) Overall yield of aromatic monomers from non-catalysed hydrogenolysis of Kraft lignin with different solvent mixtures. Product distribution in the presence of: (b) Ethanol/water v:v solutions; (c) IPA/water v:v solutions; (d) Acetone/water v:v solutions. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol.

With acetone solutions, dealkylation was also preferred due to the higher yields for 2-methoxyphenol as shown in Fig. 2d. The advantage of acetone may be related to its capacity of dissolving lignin fragments, contributing to the stabilization of reaction intermediates. However, without many variations in individual products yield, it is suggested that acetone has little direct role in linkage rupture, but more in stabilization of fragments. It is interesting to note that these solutions presented similar overall yields but differences in product distribution

related to individual monomer yield. Therefore, the type of solvent mixtures used affected the final product distribution, revealing that lignin deconstruction was not the same for each solvent mix or only by thermolysis. This can be related to the structure of KL. A recent paper on the structure of KL highlights at least two different structures separable on the basis of acetone solubility (Crestini et al., 2017). Hence, if different components of the bulk lignin were soluble in different solvents a variation in product yield and distribution would be expected.

3.4 Effect of alumina support

To investigate whether the alumina support had catalytic activity in the depolymerisation of Kraft lignin, experiments were conducted using only the support and solvent/water 50:50 v/v while maintaining all other reactions parameters constant. Table 3 summarises the overall yield of non-catalysed and Al₂O₃ experiments. It can be seen that the overall yield increased in the presence of Al₂O₃ only with IPA/water solution. Reactions using other solutions did not show a significant increase. However even when the yield was similar between the solvent and solvent/alumina, there was a change in selectivity revealing support activity. Fig. 3 shows that Al₂O₃ increased the yield of individual compounds, specifically 4-(3-hydroxypropyl)-2-methoxyphenol (compound 7), being the major product for this experiment in contrast to all the other reactions, where 2-methoxyphenol was the main compound. It has been reported that alumina can affect lignin depolymerisation (McVeigh, 2016) and it is possible that the acidic sites present in the alumina support contributed to cleavage of the lignin linkages.

Table 3. Overall yield of reference and Al₂O₃ experiments in the presence of EtOH/H₂O, IPA/H₂O and acetone/H₂O 50:50 v/v.

Reaction Type	Overall yield (g/100 g)	
	Solvolysis	Al ₂ O ₃
Kraft lignin EtOH/H ₂ O	9.5	9.7
Kraft lignin IPA/H ₂ O	5.6	6.9
Kraft lignin Acetone/H ₂ O	8.6	8.7

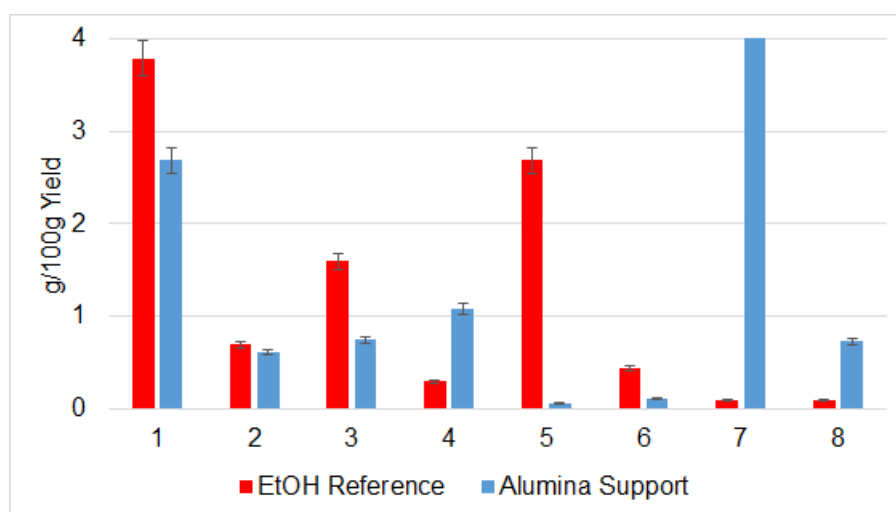


Fig. 3. Effect of Al₂O₃ in the depolymerisation of Kraft lignin in the presence of EtOH/H₂O 50:50 v/v. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol

3.5 Effect of Rh/alumina and Pt/alumina on the depolymerisation of Kraft lignin

A strategy to facilitate lignin deconstruction combining depolymerisation-stabilisation was conducted using solvent mixtures and catalysts (Rh/Al₂O₃ and Pt/Al₂O₃). It should be

mentioned that this particular process aimed mainly to achieve selective rupture of C-C and C-O-C linkages in the lignin framework, decreasing condensation of the initial lignin and focusing the outcome on specific target molecules. Rh and Pt are catalysts that have shown a significant performance in the cleavage of lignin linkages (Bouxin et al., 2015; McVeigh et al., 2016). The outcome of those experiments showed that compared to platinum, rhodium had highest yield with 50/50 v.v IPA/water, clearly revealing differences between the metals. In addition, the variety of overall yields indicated that for catalytic runs the solutions used in the reactions were not inert and affected the selectivity of the metals differently. These results agreed with previous reports (Wang and Rinaldi, 2012) about the influence of solvents in the activity and selectivity of catalysts. Indeed, hydrogenolysis of diphenyl ether in the presence of a Raney nickel catalyst was favoured by the presence of solvents with Lewis acidity (Wang and Rinaldi, 2012). Curiously, in terms of individual yields, it was found that for Pt and Rh the main product was 2-methoxyphenol (1), resulting from a high selectivity of these metals for C-C cleavage and generation of a non-alkylated product. Particularly, in most reactions, Rh also favoured production of 2-methoxy-4-propylphenol (4), 4-ethylbenzene-1,2-diol (6) and 2-methoxy-4-(3-methoxypropyl)phenol (8). Although small variations across the processes occurred, in the presence of this metal, selective rupture of lignin linkages was achieved, generating the same main compounds. In other investigations, cleavage of C-O (β -O-4) and C-C (β -1) was also found (Yamaguchi et al., 2017) in the presence of various heterogeneous catalysts, including Rh. As a result, there were no hydrogenated molecules and Rh showed a good performance in C-C bonds cleavage (Yamaguchi et al., 2017). In this work, for reactions with 50% of acetone, compounds 4-ethyl-2-methoxyphenol (3) and 1,2-dihydroxybenzene (5) were not formed, showing that changes in solvent composition affected catalyst performance. These differences in solvent (from an alcohol to a ketone) structure and properties can change

the polarization and electrostatic interactions, then affecting distinctively lignin dissolution and reaction mechanisms.

For Pt/Al₂O₃ (Fig. 4a-4d), while using EtOH and acetone solvents most reactions favoured the production of 4-ethylbenzene-1,2-diol (6) and 2-methoxy-4-(3-methoxypropyl)phenol (8), whereas IPA led to the formation of 4-ethyl-2-methoxyphenol (3) and 1,2-dihydroxybenzene (5). It is important to highlight that with IPA, Pt had high selectivity for 2-methoxyphenol (1) and 1,2-dihydroxybenzene (5), which suggests hydrogenolysis in the presence of Pt was enhanced by IPA in its hydrogen donor capacity. Similarly, experiments (McVeigh et al., 2016) using an ammonia derived lignin with Pt/Al₂O₃ and IPA-water solutions produced 24.3 % of monomeric compounds and phenolics, while methanol-water solutions gave 16.4 % of products, showing different effects of solvent-water solutions in catalytic reactions. Further studies (Besse et al., 2017) showed efficient cleavage of C-C and C-O bonds in lignin model compounds in the presence of a Pt catalyst via hydrogenolysis, in a hydrogen rich environment. These studies revealed that having a catalyst in the reaction changed the selectivity and increased individual yields, signifying that solvolysis was not the predominant route by which these products were generated.

This particular hydrogenolysis processes of Kraft lignin occurred in a very competitive medium, in which hydrogen, solvents and lignin could potentially be competing for the same catalyst site. This can be related to the variety of results obtained in this study, leading to the assumption and discussion of each reaction as a unique system.

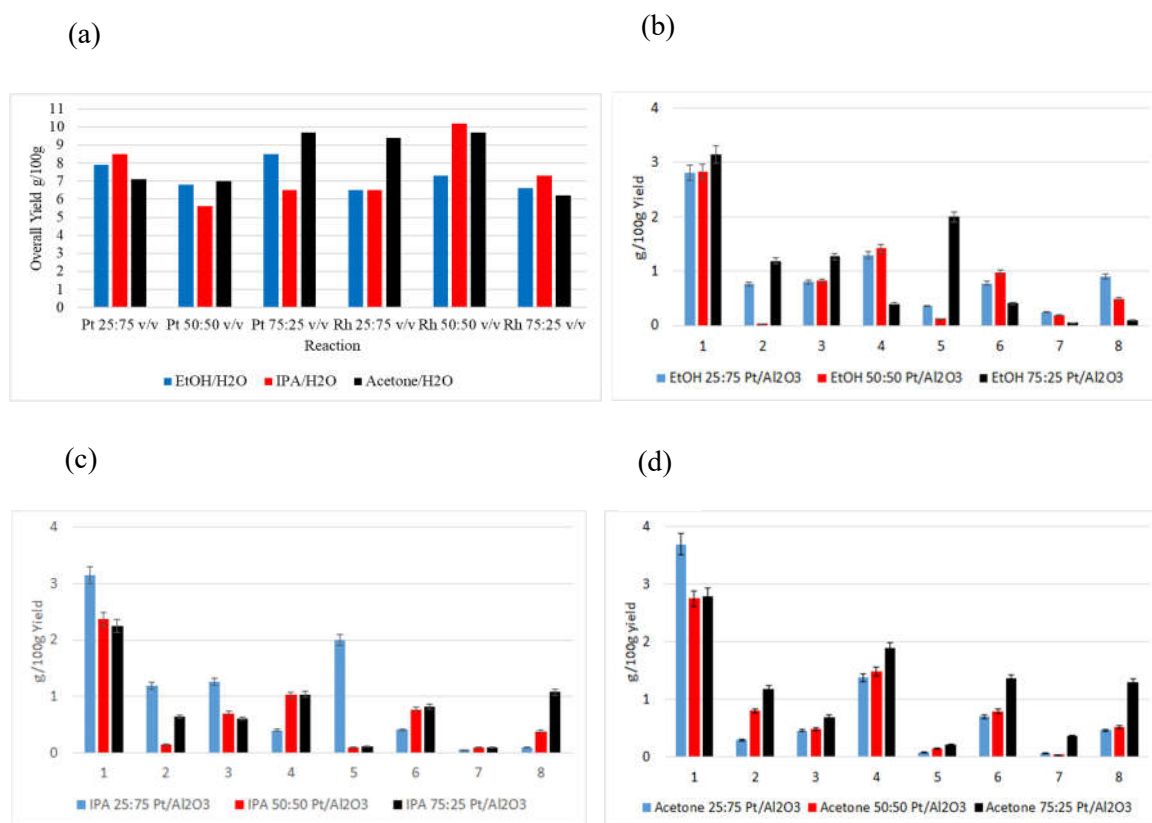
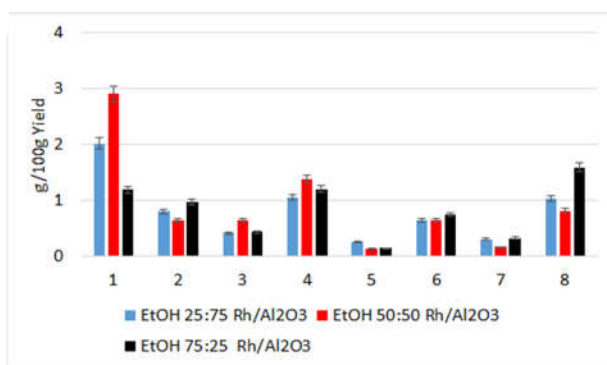
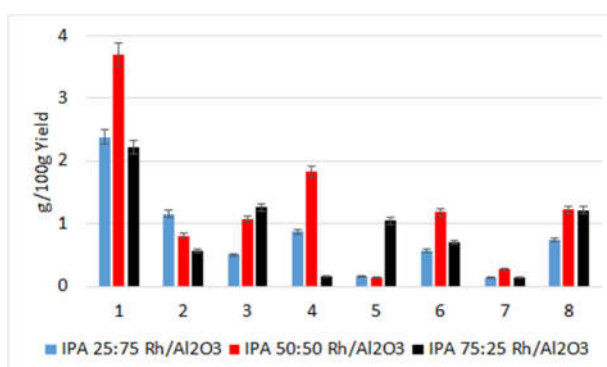


Fig. 4. (a) Overall yield from Pt/Al₂O₃ and Rh/Al₂O₃ in the presence of various solvent/water mixtures. Product distribution for reaction with Pt/Al₂O₃, (b) Ethanol/water v:v solutions; (c) IPA/water v:v solutions; (d) Acetone/water v:v solutions. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3-hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol.

(a)



(b)



(c)

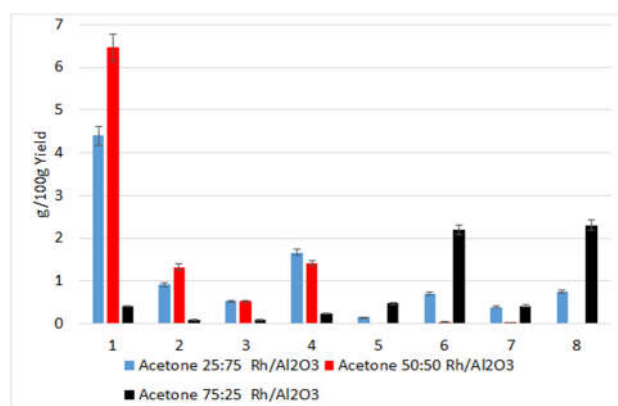


Fig. 5. Product distribution for reaction with Rh/Al₂O₃, (b) Ethanol/water v:v solutions; (c) IPA/water v:v solutions; (d) Acetone/water v:v solutions. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol.

The molecule 2-methoxyphenol (guaiacol) (1) was the main product of most reactions, hence, it can be intuitively understood that demethylation and dealkylation were the key routes involved in its formation. For this product, Rh showed considerable differences in selectivity dependent upon solvent, e.g. ~ 67 % with 50 % acetone/water but only ~ 4 % selectivity with 75 % acetone/water (Fig. 5c). This data indicated that for 2-methoxyphenol (1), Rh was involved in bond cleavage and it was significantly more affected by the type of solvent than was the case for Pt. Hence, if it is desired to produce a specific target molecule it is important to consider the combination of solvent and catalyst as a particular system.

As mentioned earlier it is clear that different reaction pathways dominate dependent upon the catalyst/solvent mix. In the present study, optimisation is required but it was found that a successful increase in the selective production of monomeric phenols could be achieved with the addition of catalyst and a suitable solvent mixture, which is encouraging especially for a lignin with a high degree of condensation such as KL.

3.6 GPC analysis

Given that the system can re-polymerise, the products were compared to the starting KL using GPC. The analysis consisted of using equal amounts of Fraction 1 (which contained the fine chemicals) and Fraction 2 (heavier products) to provide an overall representation of molecular weight (Mw), molecular number (Mn) and polydispersity (IP) of lignin pre- and post-reaction. The results are reported in Table 4.

Table 4. GPC analysis of Kraft lignin and post reaction samples from solvolysis reactions (50/50) and catalysed reactions using Pt/alumina (also 50/50 solvent).

Reaction type	Molecular Weight (Mw, Da)	Molecular Number (Mn)	Polydispersity (Ip)
Kraft lignin, as sourced	4973	1236	4.0
EtOH/H ₂ O solvolysis	1296	589	2.2
EtOH/H ₂ O catalysed	1390	650	2.1
IPA/H ₂ O solvolysis	1155	584	1.9
IPA/H ₂ O catalysed	1029	571	1.8
Acetone/H ₂ O solvolysis	879	458	1.9
Acetone/H ₂ O catalysed	968	510	1.8

This analysis does not allow the identification of compounds but it revealed that compared to the initial lignin, the Ip value for the residual lignin after reaction indicated more uniform molecules after depolymerisation, with the value dropping from 4 to ~ 2. There was also a significant decrease in Mw after reaction and there is evidence of a solvent effect. Overall there was about a 75 % reduction in Mw after reaction for both solvolysis and catalysed reactions. Mw decreased in the order ethanol > IPA >> acetone, reinforcing the view that the solvent is a key aspect of the reaction system. However it is also clear that the catalyst effect is related to monomer selectivity rather than Kraft lignin depolymerisation.

3.7 Isotopic labelling studies of Kraft lignin

To improve our understanding of the influence of solvents and hydrogen in Kraft lignin depolymerisation, fully deuterated catalysed (FDC, replacing acetone, water and hydrogen with deuterated acetone ((CD₃)₂CO), deuterium oxide (D₂O) and deuterium (D₂) with Pt/Al₂O₃

catalyst), partially deuterated catalysed (PDC, replacing acetone and water with their deuterated forms but using H₂ gas) and fully deuterated non-catalysed (FDNC) reactions were performed and the results compared with a fully protiated equivalents (Fig. 6).

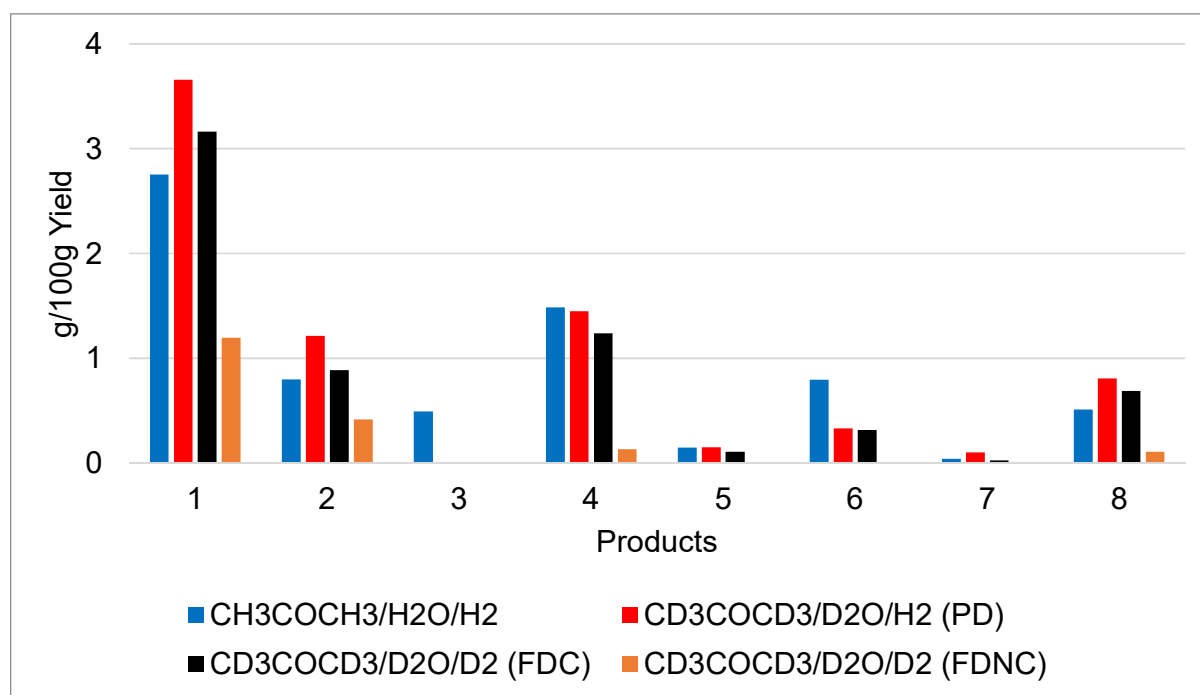


Fig. 6. Product distributions from isotopic reactions, catalyst Pt/alumina except for the fully deuterated non-catalysed (FDNC) reaction.

Table 5 reports the kinetic isotopic effects found for individual molecules. Solvent kinetic isotopic (SKIE) effects are useful tools for an understanding how solvents influences a reaction. The results from this study showed that product distribution/selectivity was dependent on the type of solvent used. Therefore by analysing the changes in the rate of protiated and deuterated products it was possible to determine whether positive kinetic isotopic effects ($KIE > 1$), inverse isotopic effects ($KIE < 1$) or no kinetic isotopic effect ($KIE = 1$) were involved in the formation of individual molecules.

Table 5. Kinetic isotopic effect values for PDC (partially deuterated catalysed), FDC (fully deuterated catalysed) and FDNC (fully deuterated non-catalysed) using 50/50 acetone/water.

Compound code	Monomer (Standard deviation)	PDC	FDC	FDNC
		KIE values		
1	2-methoxyphenol (0.1)	0.8	0.8	4.4
2	4-methyl-2-methoxyphenol (0.05)	0.7	1.0	2.3
3	4-ethyl-2-methoxyphenol (0.01)	ND	ND	ND
4	4-propyl-2-methoxyphenol (0.04)	1.0	1.2	8.4
5	1,2-dihydroxybenzene (0.01)	1.0	1.3	ND
6	4-ethylbenzene-1,2-diol (0.08)	2.4	2.5	ND
7	4-(3-hydroxypropyl)-2-methoxyphenol (0.01)	0.4	1.7	ND
8	4-(3-methoxypropyl)-2-methoxyphenol (0.03)	0.6	0.7	4.2

ND, not detected in deuterio experiments.

The fully deuterated non-catalytic reaction shows significant KIEs for all products, indicating that deuterium is involved in the rate determining step. These results show the strong influence of solvent in product formation of non-catalysed experiments and confirmed that the mechanism was not simply thermolysis. The solvents role could be mainly associated to stabilisation of reaction intermediates, promotion of H/D exchange or even acting directly in the mechanism of bond cleavage (Seoud et al., 1997). These results yielded the valuable mechanistic evidence that solvents were not only dissolving lignin, but affecting the rate of reaction and product formation, this was in accordance with variation in product distribution from solvolysis. The concentration of lignin was not considered a determining aspect for the KIE, as changes in lignin mass (from 0.25g-1g) were carried out in previous investigations

(McVeigh et al., 2016), at the same reaction conditions with protiated solvents, and it was found no change in the rate.

When Pt/Al₂O₃ was present only the production of 4-ethylbenzene-1,2-diol exhibited a significant KIE. Therefore, although the processes produce the same range of compounds it is clear that the mechanisms have changed. Comparing PDC and FDC most molecules presented similar values of KIE, showing that by changing hydrogen for deuterium there was little influence in the formation of compounds 2-methoxyphenol (1), 4-ethylbenzene-1,2-diol (6) and 4-(3-methoxypropyl)-2-methoxyphenol (8). For compounds 4-propyl-2-methoxyphenol (4) and 1,2-dihydroxybenzene (5) the presence of deuterium resulted in a change from no kinetic isotopic effect to a positive KIE while products 4-methyl-2-methoxyphenol (2) and 4-(3-hydroxypropyl)-2-methoxyphenol (7) also had influence of deuterium in their formation changing to positive KIE. Importantly, the use of hydrogen became essential for the generation of specific compounds. This is in agreement with previous investigations (McVeigh et al., 2016) using the same experimental set up and protiated solvents, varying starting hydrogen pressure from 0 barg, 10 barg, 20 barg and 30 barg, and it was found that the higher the pressure, the higher the product yield. Hence, it could be assumed that hydrogen was involved in dissociative adsorption, promoting hydrogenolysis.

3.8 Characterisation of Pt/alumina post-reaction

After use, a selection of solvent/catalyst samples were characterised to determine whether or not the catalyst had undergone physical or chemical change during the reaction. BET analysis showed a slight increase in surface area and decrease in the pore volume for all catalysts analysed. To analyse the physical stability of the support, XRD analyses of spent catalysts were carried out. Aqueous environments at high temperatures can affect stability of alumina supports and its hydration, however, no evidence of support instability was found with the

analyses showing no differences compared to the starting material. The catalysts used in this work had a mixture of delta and theta alumina phases but they were mostly composed of the more stable θ -alumina. In addition, the reaction environment containing oxygenates and carbonaceous species could have helped to improve stability decreasing the possibility of hydrolysis of alumina (McVeigh et al., 2016). It has been reported that catalyst deactivation can be caused by the presence of carbonaceous materials over the catalyst surface and especially in supports with acidic characteristics (Argyle and Bartholomew, 2015). Therefore analyses of Al_2O_3 for Kraft acetone/ H_2O 50:50 v/v and Pt/ Al_2O_3 in reactions with Kraft in FDC and PDC, acetone/ H_2O , ethanol/ H_2O and IPA/ H_2O 50:50 v/v were carried out in order to investigate this. Elemental analysis confirmed the presence of carbon, hydrogen and nitrogen (Table 6) on the catalyst. The values across the catalyst samples were similar giving a surface species with a general formula of $\text{CH}_{1.3}$. Most values were similar, apart from the reaction with acetone and Al_2O_3 , which had a slightly higher carbon laydown. This is quite common as addition of the metal to the support will reduce the acid site density, therefore the type of solvent involved in the reaction did not influence the amount of carbon deposited. It is interesting to note that the content of species deposited from FDC and PDC experiments were similar to the protiated reactions, indicating no KIE for carbon deposition. TPO analysis of these catalysts showed a main combustion event at ~ 700 K, which matched with the derivative weight profile (this profile was generally similar for all samples).

Table 6. Elemental analysis of spent Al₂O₃ and Pt/Al₂O₃.

Type of reaction	C (%)	H (%)	N (%)
Spent Al₂O₃ catalyst support			
Kraft Acetone/H ₂ O	11.9	1.3	Not detected
Spent Pt/Al₂O₃			
Kraft EtOH/H ₂ O	8.9	0.9	Not detected
Kraft IPA/H ₂ O	8.4	1.0	0.03
Kraft Acetone/H ₂ O	9.3	1.1	0.03
Kraft Partially deuterated	8.7	0.9	0.04
Kraft Fully deuterated	9.2	0.9	0.03

This is consistent with the literature where weight losses at similar temperatures and systems have been reported to be associated with hydrocarbonaceous materials (Bouxin et al., 2017).

It is important to highlight that small combustion events appeared at different temperatures, with weight losses at ~ 397 K, 407 K and ~800 K. Overall it is clear that multiple carbon species were present. Raman spectroscopy gave a weak G-band at ~1590 cm⁻¹ on all the catalysts revealing the presence of some graphitic species.

4. Conclusions

The depolymerisation process conditions used generated phenolic monomers in the presence and absence of catalyst. The use of solvents to dissolve lignin was expected to help in the interaction between lignin and the solid catalyst, interestingly this appears to the case as individual yields were dependent upon an appropriate combination of catalyst and the ratio of solvents. KIEs revealed that solvents and hydrogen were significantly engaged in the cleavage of C-C and C-O-C bonds of KL, resulting in phenolic monomers. For KL, products were small-

chain, substituted phenols, mainly 2-methoxyphenol (guaiacol). Carbonaceous species were detected over the spent Pt/alumina.

E-supplementary data of this work can be found in online version of the paper.

Acknowledgements

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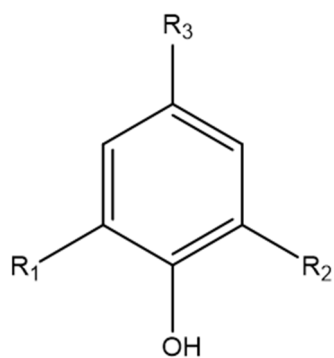


Fig. 7. Basic lignin monomeric motif (for a G-unit $R_1 = H$ and $R_2 = OCH_3$).

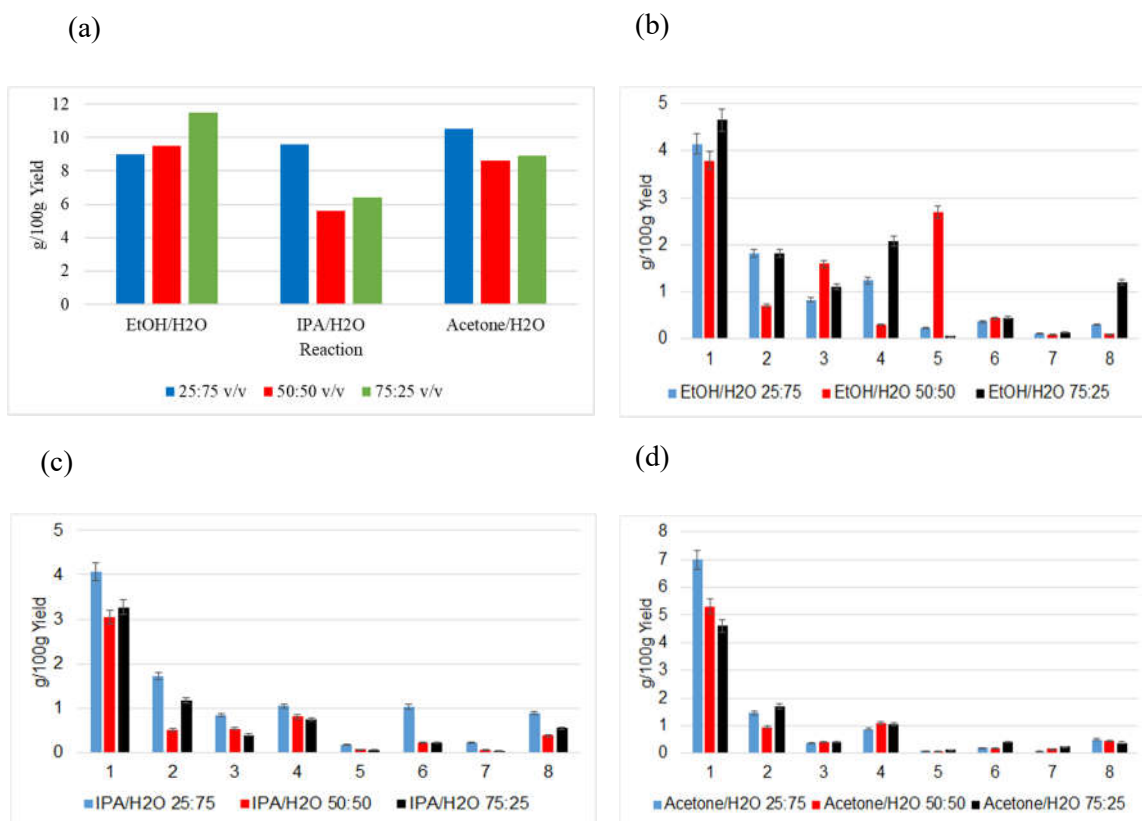


Fig. 8. (a) Overall yield of aromatic monomers from non-catalysed hydrogenolysis of Kraft lignin with different solvent mixtures. Product distribution in the presence of: (b) Ethanol/water v:v solutions; (c) IPA/water v:v solutions; (d) Acetone/water v:v solutions. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol.

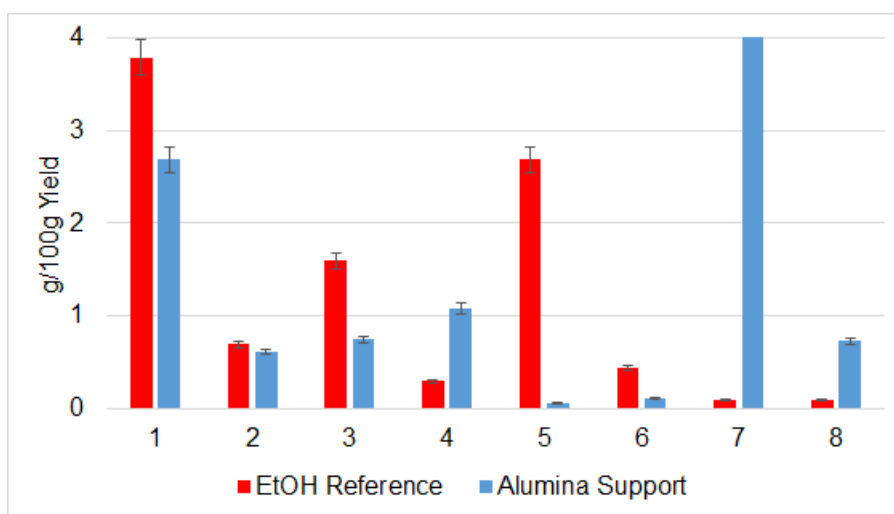


Fig. 9. Effect of Al_2O_3 in the depolymerisation of Kraft lignin in the presence of EtOH/ H_2O 50:50 v/v. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol

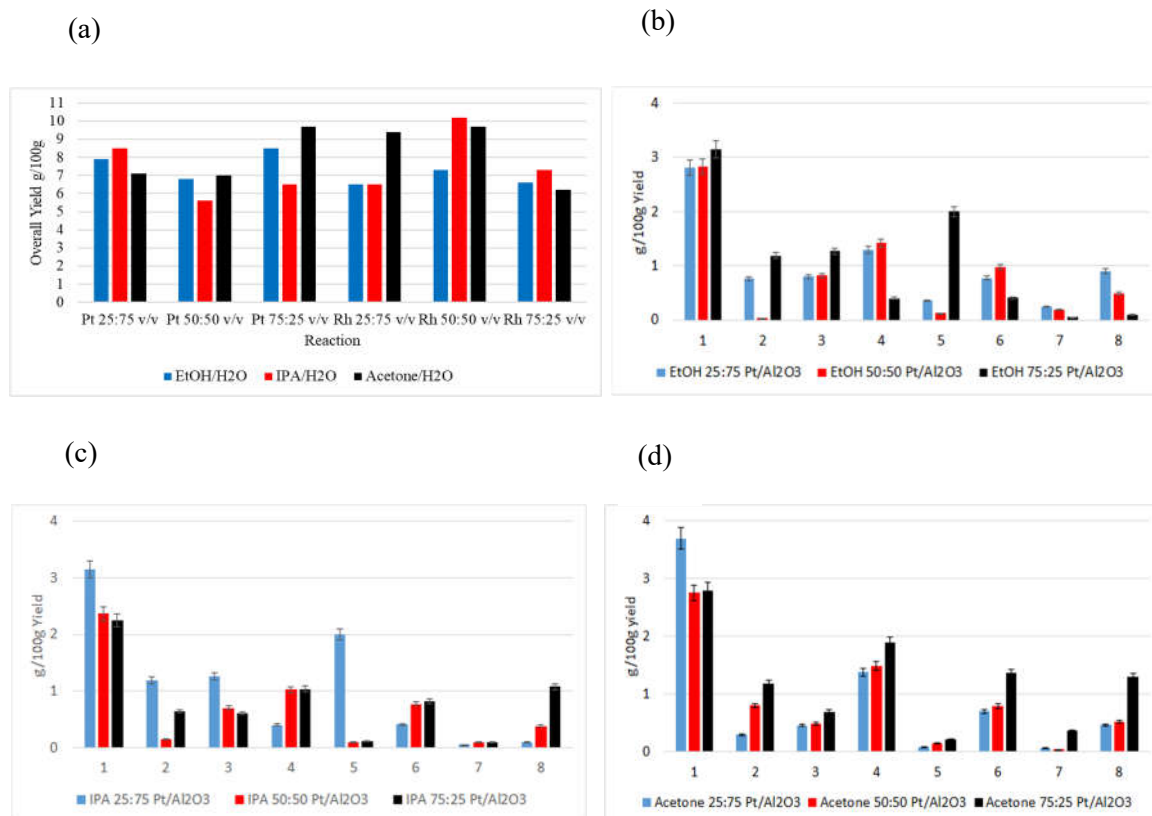
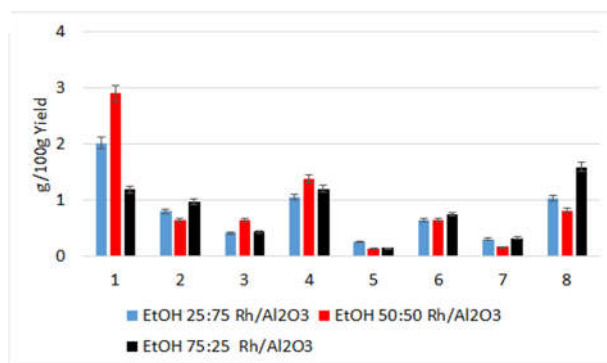
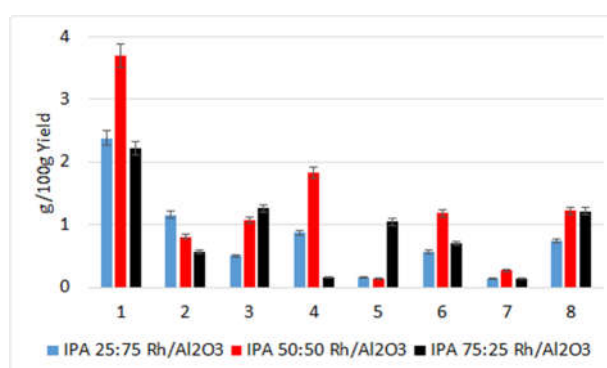


Fig. 10. (a) Overall yield from Pt/Al₂O₃ and Rh/Al₂O₃ in the presence of various solvent/water mixtures. Product distribution for reaction with Pt/Al₂O₃, (b) Ethanol/water v:v solutions; (c) IPA/water v:v solutions; (d) Acetone/water v:v solutions. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol.

(a)



(b)



(c)

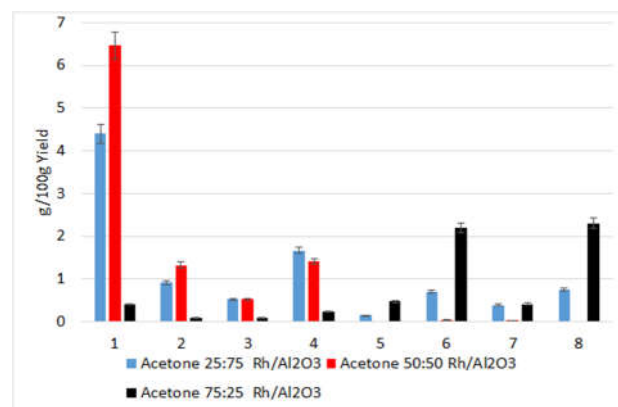


Fig. 11. Product distribution for reaction with Rh/Al₂O₃, (b) Ethanol/water v:v solutions; (c) IPA/water v:v solutions; (d) Acetone/water v:v solutions. Products identified by GC-MS, (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4-propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3-hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol.

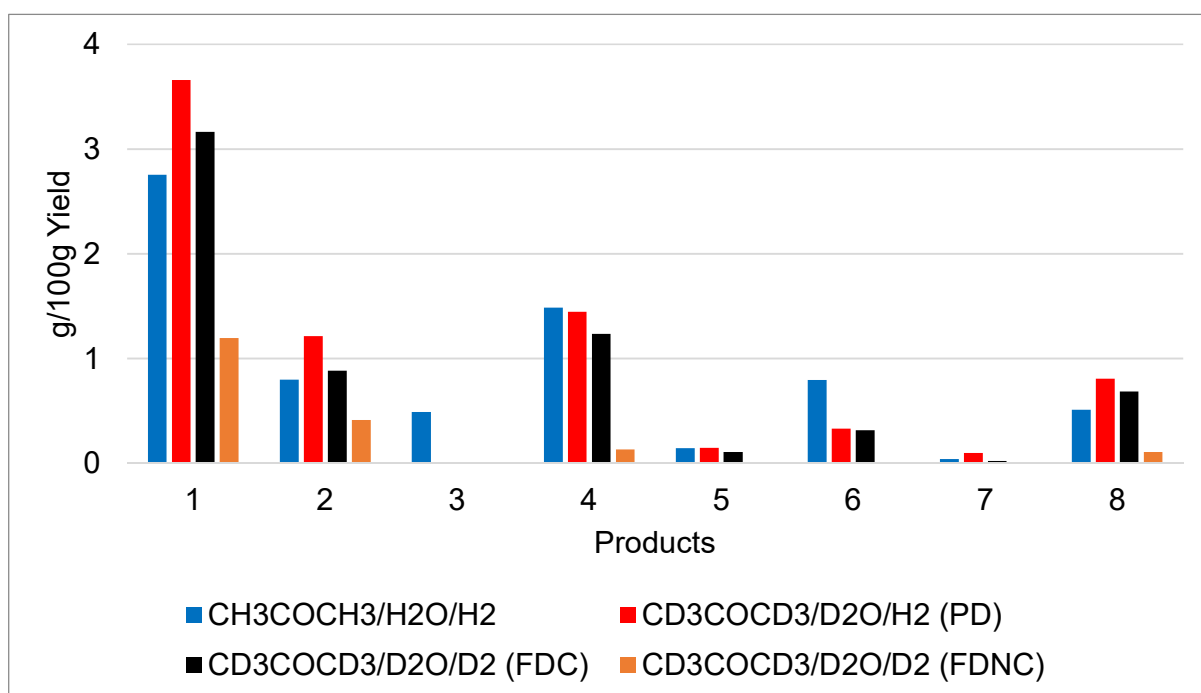


Fig. 12. Product distributions from isotopic reactions, catalyst Pt/alumina except for the fully deuterated non-catalysed (FDNC) reaction.

Table 1. Standard deviation values of individual molecules from Kraft lignin depolymerisation. Compounds: (1) 2-methoxyphenol, (2) 4-methyl-2-methoxyphenol (3) 4-ethyl-2-methoxyphenol, (4) 4propyl-2-methoxyphenol, (5) 1,2-dihydroxybenzene, (6) 4-ethylbenzene-1,2-diol, (7) 4-(3hydroxypropyl)-2-methoxyphenol (8) 4-(3-methoxypropyl)-2-methoxyphenol

Compound							
1	2	3	4	5	6	7	8
Standard Deviation							
0.1	0.05	0.01	0.04	0.01	0.08	0.01	0.03

Table 2. Identified compounds from the depolymerisation of Kraft lignin

Compound Code	R ₁ /R ₂ /R ₃ group	Compound Name
(1)	R ₁ =R ₃ =H; R ₂ =OCH ₃	2-methoxyphenol (guaiacol)
(2)	R ₁ =H; R ₃ =CH ₃ ; R ₂ =OCH ₃	4-methyl-2-methoxyphenol
(3)	R ₁ =H; R ₃ =CH ₂ CH ₃ ; R ₂ =OCH ₃	4-ethyl-2-methoxyphenol
(4)	R ₁ =H; R ₃ =CH ₂ CH ₂ CH ₃ ; R ₂ =OCH ₃	4-propyl-2-methoxyphenol
(5)	R ₁ =R ₃ =H; R ₂ =OH	1,2-dihydroxybenzene (catechol)
(6)	R ₁ =H; R ₂ =OH; R ₃ =CH ₂ CH ₃	4-ethylbenzene-1,2-diol
(7)	R ₁ =H; R ₂ =OCH ₃ ; R ₃ =CH ₂ CH ₂ CH ₂ OH	4-(3-hydroxypropyl)-2-methoxyphenol
(8)	R ₁ =H; R ₂ =OCH ₃ ; R ₃ =CH ₂ CH ₂ CH ₂ OCH ₃	4-(3-methoxypropyl)-2-methoxyphenol

Table 3. Overall yield of reference and Al₂O₃ experiments in the presence of EtOH/H₂O, IPA/H₂O and acetone/H₂O 50:50 v/v.

Reaction Type	Overall yield (g/100 g)	
	Solvolysis	Al₂O₃
Kraft lignin EtOH/H ₂ O	9.5	9.7
Kraft lignin IPA/H ₂ O	5.6	6.9
Kraft lignin Acetone/H ₂ O	8.6	8.7

Table 4. GPC analysis of Kraft lignin and post reaction samples from solvolysis reactions (50/50) and catalysed reactions using Pt/alumina (also 50/50 solvent).

Reaction type	Molecular Weight (Mw, Da)	Molecular Number (Mn)	Polydispersity (Ip)
Kraft lignin, as sourced	4973	1236	4.0
EtOH/H ₂ O solvolysis	1296	589	2.2
EtOH/H ₂ O catalysed	1390	650	2.1
IPA/H ₂ O solvolysis	1155	584	1.9
IPA/H ₂ O catalysed	1029	571	1.8
Acetone/H ₂ O solvolysis	879	458	1.9
Acetone/H ₂ O catalysed	968	510	1.8

Table 5. Kinetic isotopic effect values for PDC (partially deuterated catalysed), FDC (fully deuterated catalysed) and FDNC (fully deuterated non-catalysed) using 50/50 acetone/water.

Compound code	Monomer (Standard deviation)	PDC	FDC	FDNC
		KIE values		
1	2-methoxyphenol (0.1)	0.8	0.8	4.4
2	4-methyl-2-methoxyphenol (0.05)	0.7	1.0	2.3
3	4-ethyl-2-methoxyphenol (0.01)	ND	ND	ND
4	4-propyl-2-methoxyphenol (0.04)	1.0	1.2	8.4
5	1,2-dihydroxybenzene (0.01)	1.0	1.3	ND
6	4-ethylbenzene-1,2-diol (0.08)	2.4	2.5	ND
7	4-(3-hydroxypropyl)-2-methoxyphenol (0.01)	0.4	1.7	ND
8	4-(3-methoxypropyl)-2-methoxyphenol (0.03)	0.6	0.7	4.2

ND, not detected in deuterio experiments.

Table 6. Elemental analysis of spent Al₂O₃ and Pt/Al₂O₃.

Type of reaction	C (%)	H (%)	N (%)
Spent Al₂O₃ catalyst support			
Kraft Acetone/H ₂ O	11.9	1.3	Not detected
Spent Pt/Al₂O₃			
Kraft EtOH/H ₂ O	8.9	0.9	Not detected
Kraft IPA/H ₂ O	8.4	1.0	0.03
Kraft Acetone/H ₂ O	9.3	1.1	0.03
Kraft Partially deuterated	8.7	0.9	0.04
Kraft Fully deuterated	9.2	0.9	0.03