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Catalytic depolymerisation of isolated lignins to fine chemicals using a Pt/alumina catalyst: Part 1-Impact of the lignin structure

Florent P. Bouxin[a], Ashley McVeigh[a], Fanny Tran[b], Nicholas J. Westwood[b], Michael C. Jarvis[a] and S. David Jackson[a]

[a] WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow,

Glasgow, G12 8QQ

[b]School of Chemistry and Biomedical Sciences Research Complex, Purdie Building, University of St Andrews and EaStCHEM, North Haugh, St Andrews, KY16 9ST

Abstract

Four lignin preparations with different contents of alkyl aryl ether bonds were depolymerised using an alumina supported platinum catalyst. The results showed that the proportion of β-O-4 linkages is the crucial factor for both the yield and the nature of the monomeric products. Highly condensed lignin generated mainly non-alkylated phenolic products while uncondensed lignin generated mainly phenolic products retaining the 3-carbon side-chain. These phenolic products with the 3-carbon chain still attached were considerably less abundant than the maximum potential yield calculated from selective cleavage of alkyl aryl ether bonds by thioacidolysis, demonstrating that scope for improved yield remains. Although the catalytic conversion yield rose with increasing content of labile ether linkages in the lignin structure, optimisation of the catalytic depolymerisation was increasingly required to minimize side reactions. Gel permeation chromatography showed that the products converged towards the same molecular weight distribution regardless of the starting material. The full potential of the highly uncondensed lignin was reached only after the minimisation of condensation reactions during the catalytic conversion.

Keywords: Lignin, Catalytic depolymerisation, Condensation, Alkylphenols, Platinum

1   1. Introduction

2   It is widely agreed that the economic viability of biofuel production will depend on

3   adding value to the by-products. Amongst these, lignin, for long considered only as an energy

4   resource, attracts the most interest. Several approaches to upgrading lignin have been

5   described in recent reviews[1, 2]. Lignin can be converted to high-grade biofuel by pyrolysis

6   and deoxygenation[3-5] or converted to chemicals with higher added value using heterogeneous

7   catalysis[2]. The attractiveness of lignin lies its substituted aromatic structure which, after

8   efficient depolymerisation, should lead to substituted aromatic compounds. However, this

9   will heavily rely on a better understanding of the factors influencing the yield and distribution

10   of products.

11   Of the known approaches for lignin conversion using heterogeneous catalysis, Liquid

12   Phase Reforming (LPR) and hydrodeoxygenation (HDO) have been the most studied. LPR of

13   kraft lignin led to lower value products (guaiacol) in higher yield while HDO produced

14   higher value, more substituted products (alkylphenolic compounds) in lower yield[6]. Ethyl-

15   substituted[7] and propyl-substituted monomers[8] have been obtained by catalytic

16   hydrogenolysis of grass lignins, but the yield and distribution of products depended strongly

17   on the lignin structure. Recently two lignin preparations with substantial uncondensed (alkyl-

18   aryl ether) percentages were depolymerised using an alumina supported noble metal catalyst.

19   Although no attempt to the correlate conversion yield to the lignin structure was made, the

20   authors suggested that the presence of alkyl-aryl ether bonds was a key factor for the

21   conversion of lignin to monomers[9]. Complete cleavage of the alkyl-aryl ether bonds in a pure,

22   uncondensed lignin model compound was achieved using a carbon supported bimetallic

23   Zn/Pd catalyst in methanol at 150°C under 300 psi of H_2[10].

1   In hardwood species, native lignins are held together mainly by alkyl-aryl ether bonds

2   (up to 70% in some species)[11]. Unfortunately the pretreatment of lignin prior to

3   depolymerisation often leads to significant depletion of this type of bond and generates C-C

4   bonds that are harder to break[12, 13]. The resulting condensed lignin is less suitable for

5   conversion to aromatic chemicals. Severe pretreatment conditions (high temperature, acidic

6   medium) are the primary choice for second generation biofuel production but are well known

7   to increase lignin condensation[14]. The impact of the pretreatment on the catalytic conversion

8   of the lignin to products with added value has been reviewed[2]. Nevertheless the structure of

9   the lignin immediately before the catalytic conversion step is rarely taken into account. To

10   the best of our knowledge, no attempt has been made to investigate the impact of the lignin

11   structure on the yield and distribution of catalytically depolymerised products.

12   In this study four lignins with different degrees of condensation have been subjected to

13   catalytic depolymerisation using an alumina supported platinum catalyst. The lignins were

14   prepared using pretreatments with potential for the production of biofuels and co-products.

15   The purpose of this study was to evaluate the impact of the lignin structure on its suitability

16   for conversion to fine chemicals. The catalytic conversion was performed using a commercial

17   benchmark catalyst, Pt/alumina. The main objective was to understand the yield and

18   distribution of alkylphenolic products in relation to the initial degree of condensation of the

19   lignin.

20   2. Results

21   2.1. Characterisation of the lignin preparations

22   2.1.1. Sugar content and elemental analysis

23   The presence of sugars in the isolated lignin can be critical for the catalytic reaction.

24   The sugar compositions of the different lignins are shown in Table 1. The ammonia

1 percolation procedure yielded a lignin-carbohydrate extract from poplar that still contained

2 20% xylan. Its xylan content was reduced to less than 1% by a mild organosolv post-

3 treatment[15]. The poplar organosolv lignin had low sugar content and no further purification

4 step was needed. The commercial soda lignin from wheat straw had a higher sugar content

5 but not high enough to make it unsuitable for catalytic conversion.

6 **Table 1**: Sugar content and elemental analysis of the different lignins [Standard

7 deviation in brackets]

|	Sugar content (g/100g of lignin)	Elemental analysis (mass %)			
		C	H	N	O
AFEX Wheat Straw	1.1 (0.1)	59.5	6.4	2.1	31.9
Soda Wheat Straw	2.6 (0.1)	61.3	5.6	0.9	32.2
Organosolv Poplar	0.4 (0.1)	63.9	6.0	0.4	29.7
Ammonia Poplar	0.5 (0.1)	60.2	6.0	1.8	31.9

8

9 The elemental compositions are typical of lignins previously reported[16]. The higher

10 nitrogen content of both lignins from ammonia-based pretreatments (AFEX wheat straw and

11 Ammonium Poplar) can be explained by incorporation of nitrogen from ammonia during the

12 pretreatment step.

13 2.1.2. Lignin uncondensed fractions

14 The uncondensed fractions (i.e. percent β-*O*-4 bonds) were estimated from the total

15 monomer yield generated by thioacidolysis of the lignins and are reported in Table 2. The

16 linkage percentages (β-*O*-4, β-β, β-5) were also calculated by NMR cross-peaks in the

17 aliphatic region[17] (Figure 1) and quantified using the G_2 and $S_{2,6}$ cross-peaks in the aromatic

18 region as reference[18]. The 2D NMR experiments measured the total quantity of β-*O*-4 bonds,

1 whereas thioacidolysis only took into account monomers linked by two β-*O*-4 bonds (the

2 uncondensed fraction). Despite the difference in what was measured, both techniques gave

3 values of the same order for the uncondensed fractions in the four lignins.
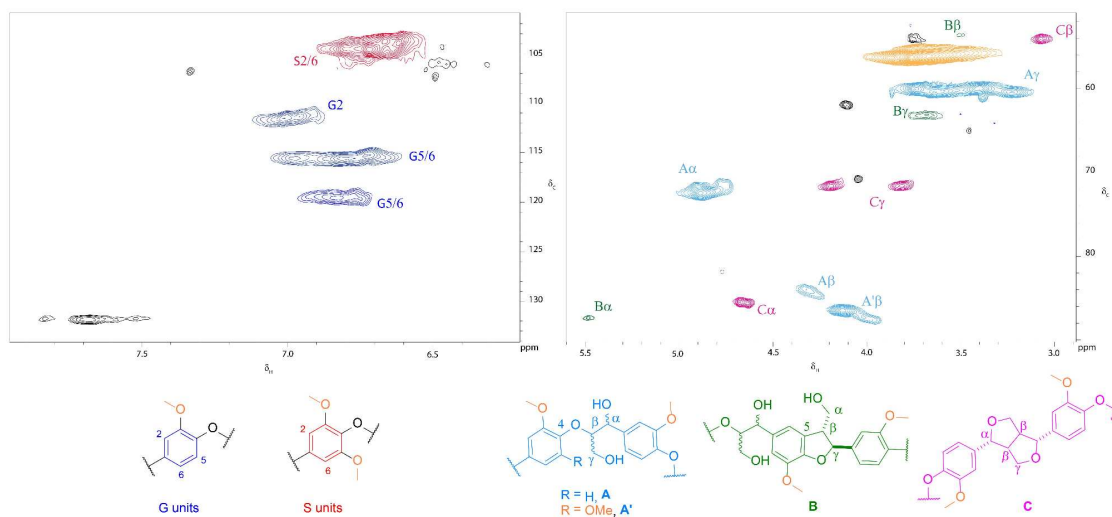
4

5 **Figure 1**: HSQC NMR spectrum of Poplar ammonia lignin. Contours are colour coded
6 according to the linkage they are assigned to. Black cross peaks correspond to
7 currently unassigned signals. NMR spectra were collected on a 500 MHz spectrometer
8 at a concentration of 100 mg of substrate in 0.6 mL of DMSO-*d*6.
9

10 As illustrated in Table 2, the Poplar ammonia lignin showed the highest content of β-

11 *O*-4 bonds (44.9 %), compared with only 3.7% in the wheat straw soda lignin. The difference

12 in uncondensed fraction comes partly from the feedstock type but principally from the

13 pretreatment conditions. It may be assumed that harsh alkaline conditions were responsible

14 for the condensation of the wheat straw lignin. In comparison the lignin obtained by mild

15 alkaline organosolv extraction of AFEX-pretreated wheat straw retained 37% of β-*O*-4

16 bonds, which can be explained by the relative lack of condensation during both the AFEX

17 pretreatment[19] and the subsequent lignin extraction step. After organosolv pretreatment of

18 poplar, the proportion of β-*O*-4 linkages was reduced to 12 %. This is expected since the

1 acidic conditions combined with high temperature (180°C) are known to cleave β-*O*-4

2 linkages leading to more condensed lignin[20]. Similar temperatures were applied during the

3 poplar percolation pretreatment but we have shown that the use of ammonium hydroxide, a

4 weaker base than sodium hydroxide, limits lignin condensation [15].

5 **Table 2**: Lignin β-linkage percentages and monomer ratios obtained by thioacidolysis and 2D

6 NMR [S: syringyl; G: Guaiacyl; H: p-hydroxycinnamyl units - Standard deviation in

7 brackets]

	Thioacidolysis		HSQC-NMR			
	β-*O*-4	S/G/H ratio	β-*O*-4	β-β	β-5	S/G/H ratio
Soda Wheat Straw	2.8 (0.3)	0.51/0.49/0	3.7	1.9	0.4	0.46/0.40/0.13
AFEX Wheat Straw	16.8 (0.4)	0.49/0.46/0.06	37.1	4.3	3.4	0.36/0.60/0.04
Organosolv Poplar	9.2 (0.2)	0.57/0.43/0	12.2	5.0	4.4	0.48/0.52/0
Ammonia Poplar	28.9 (0.3)	0.65/0.35/0	44.9	2.3	9.0	0.64/0.36/0

8

9 Monomer ratios were also obtained from the aromatic proton $S_{2,6}$ and G_2 of the 2D

10 NMR (Fig.1 and Fig S.1). The 2D NMR experiment measured the total amount of guaiacyl

11 and syringyl units, whereas thioacidolysis only took into account units linked by two β-*O*-4

12 bonds, which explains the differences in the monomer ratios. As shown in Table 2, the poplar

13 ammonia lignin had a higher relative percentage of syringyl units than the poplar organosolv

14 lignin. The high syringyl content of ammonia lignins has been observed previously and

15 attributed to mobilised syringyl lignin at particle surfaces[19]. The selective extraction of this

16 syringyl rich lignin is not fully understood but could be linked to thermal properties such as

17 glass transition temperature, which depends on the syringyl/guaiacyl ratio.
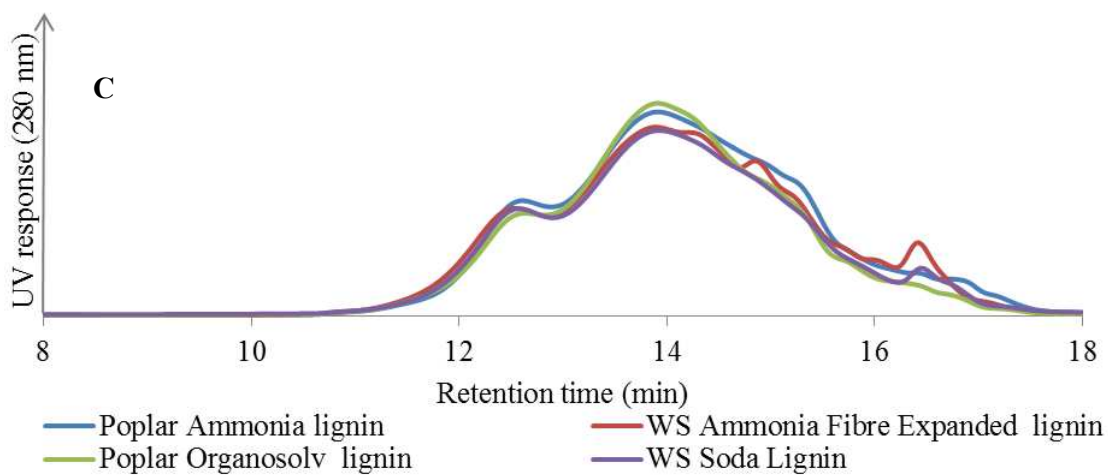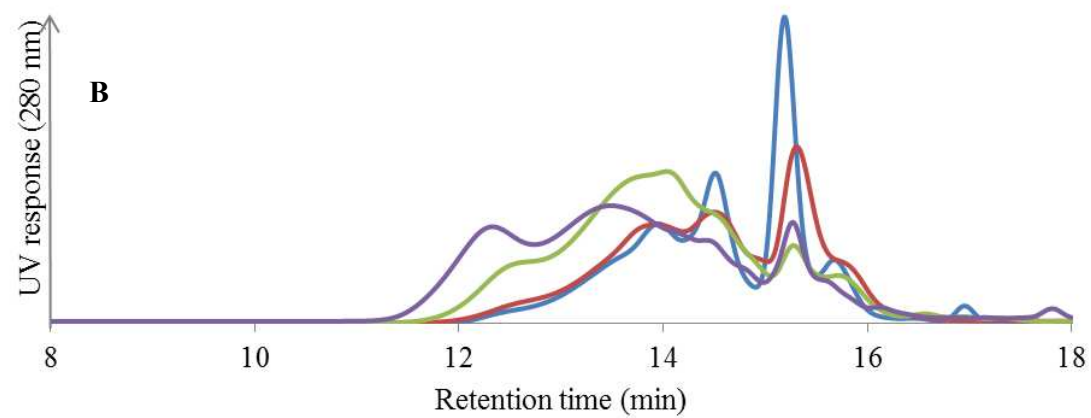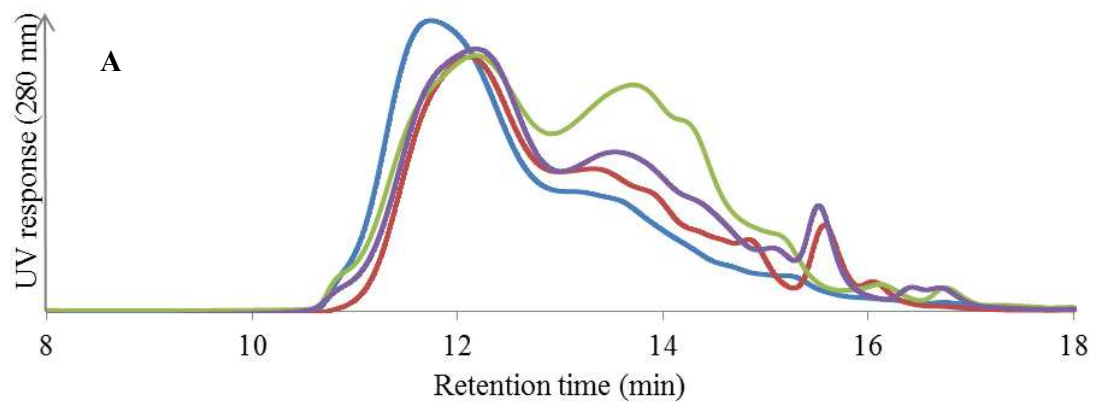
Fig 2. GPC profiles of acetylated starting lignin (A), thioacidolysis products (B) and acetylated products of the catalytic depolymerisation at 300 °C and 20 barg H_2 (C)

1

2   The GPC analysis of the AFEX and soda lignins from wheat straw (Fig. 2A) shows

3   that both lignins exhibited similar Mw profiles with the exception of the higher relative

4   abundance of the low Mw fraction eluting at 13-14 min from the soda lignin. In the case of

5   the poplar lignins, the high-temperature organosolv pretreatment led to partial cleavage of the

6   alky-aryl ether linkages and reduced the Mw of the lignin, as shown by the higher relative

7   intensity of the low Mw fraction eluting at 13-14 min, whereas the higher molecular weight

8   of the ammonia lignin suggested that in the alkaline medium the lignin was solubilised

9   without significant cleavage of the alkyl-aryl linkages.

10

11   2.2. Catalytic conversion of lignin preparations

12

13   2.2.1.   Molecular weight distributions of the depolymerised products

14

15   The four lignin preparations were subjected to catalytic conversion at 300 °C under 20

16   barg of H_2 and their products of reaction analysed by gel permeation chromatography. For

17   comparison, the thioacidolyzed products of the four different lignins were also analyzed by

18   GPC (Fig. 2C). The GPC analysis of the catalytic depolymerisation products was performed

19   on the combined methanol/water- and acetone-soluble products. This allowed the analysis of

20   the total products, as no residual lignin insoluble in acetone was found. Moreover, the mass

21   loss from the catalyst on acid washing was in the same range from each substrate and

22   suggested that only 3% of the lignin deposited on the catalyst (Fig. S.2). The GPC analysis

23   gave an overview of the mass distribution but quantification of the monomeric fraction was

24   inaccurate due to peak width and variation of UV responses between molecules. GC analysis

25   was therefore performed to quantify the monomers. After selective cleavage of alkyl-aryl

1   ether bonds by thioacidolysis, it was evident that the wheat soda lignin in particular retained a

2   high-Mw (Fig 2B) peak, eluting at 12-13 min, that presumably corresponded to the abundant

3   condensed fraction in this lignin preparation. However in the GPC profiles of all the other

4   depolymerised lignins, a high-Mw peak eluting at 12-13 min was present (Fig 2C),

5   converging towards constant relative intensity for all four samples. It can be inferred that

6   where there was a large uncondensed fraction before catalytic reaction, a substantial part of

7   this fraction was converted to condensed material of high Mw rather than to monomers. In

8   the case of the initially condensed wheat soda lignin, however, there was little uncondensed

9   material and thus little scope for further condensation; and slight degradation of some of the

10 C-C linkages in the condensed fraction occurred, leading to a minor loss of relative intensity

11 in the high-Mw GPC peak (Fig 2C).

12 Thus hydrogenolysis was more efficient than thioacidolysis for the depolymerisation of the

13 highly condensed Soda lignin. However, when the starting material was less condensed, e.g.

14 the AFEX and ammonia lignins, hydrogenolysis was less efficient than thioacidolysis in

15 breaking down the lignin to low molecular weight fragments.

16

17   2.2.2. Yields and distribution of catalytically depolymerised products from the

18   different lignins

19   The analysis of the monomeric fraction of the depolymerised products was performed

20 by GC/MS and permitted identification of 18 monomeric aromatic structures, which are

21 illustrated in Figure 3. The major products were alkylated phenolic compounds belonging to

22 the class described previously[6, 7, 10]. The absence of hydrogenation of the aromatic ring can be

23 inferred from the abundance of cross peaks in the 2D NMR aromatic region (Fig. S.3) and

24 from the absence of cyclohexanols. Deoxygenation was mainly restricted to the alkyl chain,

1   as no hydrocinamyl structures were produced from Poplar lignin. Moreover, except for the

2   Organosolv lignin, no significant difference in the syringyl/guaiacyl ratio was observed after

3   catalytic depolymerisation compared to thioacidolysis (Table S.1).

4

1: $R_1=R_2=H$; $R_3=CH_3$ 11: $R_1=R_2=OCH_3$; $R_3=H$
2: $R_1=R_3=H$; $R_2=OCH_3$ 12: $R_1=R_2=OCH_3$; $R_3=CH_3$
3: $R_1=R_3=H$; $R_2=OH$ 13: $R_1=R_2=OCH_3$; $R_3=CH_2CH_3$
4: $R_1=H$; $R_2=OCH_3$; $R_3=CH_3$ 14: $R_1=R_2=OCH_3$; $R_3=CH_2CH_2CH_3$
5: $R_1=H$; $R_2=OCH_3$; $R_3=CH_2CH_3$ 15: $R_1=R_2=OCH_3$; $R_3=CH=CHCH_3$
6: $R_1=H$; $R_2=OH$; $R_3=CH_2CH_3$ 16: $R_1=R_2=OCH_3$; $R_3=CH_2CH_2CH_2OCH_3$
7: $R_1=H$; $R_2=OCH_3$; $R_3=CH_2CH_2CH_3$ 17: $R_1=R_2=OCH_3$; $R_3=CH_2CH_2CH_2OH$
8: $R_1=H$; $R_2=OCH_3$; $R_3=CH=CHCH_3$ 18: $R_1=OCH_3$; $R_2=OH$; $R_3=CH_2CH_2CH_2OH$
9: $R_1=H$; $R_2=OCH_3$; $R_3=CH_2CH_2CH_2OCH_3$
10: $R_1=H$; $R_2=OCH_3$; $R_3=CH_2CH_2CH_2OH$

5   **Figure 3**: Products identified after catalytic depolymerisation of different lignins

6   As opposed to the GPC analysis, the quantification of the monomers gave significant

7   differences. As illustrated in Table 3, the blank reaction without catalyst showed the lowest

8   overall yield of 3.5% and mainly generated guaiacol and syringol. In the presence of catalyst,

9   the overall yield increased up to 14% for the Poplar ammonia lignin, which was nearly three

10   times the yield obtained for the soda Wheat straw lignin. In previous studies, the

11   hydrodeoxygenation of lignins using the same type of catalyst was conducted at lower

12   temperature (200 ºC) which, with other influences such as lignin structure, could explain the

13   lower yield obtained [6].

14

15

16

17

1 **Table 3**: Identification and quantification of the main monomeric products from catalytic

2 depolymerisation of different lignin preparations at 300 °C and 20 barg H_2

N°	NAME	Ammonia Poplar (no Cat)[a]	Ammonia Poplar	Organosolv Poplar	Ammonia Fibre Expanded WS	Soda WS
1	Methylphenol	n.d.	n.d.	n.d.	0.06	0.08
2	Guaiacol (G)	0.45[b]	0.45	0.46	0.68	0.79
3	Catechol	0.12	0.13	0.12	0.19	0.21
4	MethylG	0.10	0.20	0.30	0.37	0.30
5	EthylG	0.18	0.53	0.44	2.05	1.10
6	EthylCatechol	n.d.	n.d.	n.d.	0.11	0.07
7	PropylG	n.d.	0.85	0.56	0.84	0.19
8	PropyenylG	0.15	0.85	0.28	0.63	0.08
9	3-MethoxypropaneG	n.d.	0.47	0.12	0.53	n.d.
10	3-HydroxypropaneG	n.d.	0.66	0.20	0.29	0.07
11	Syringol (S)	1.65	1.75	0.97	0.86	1.47
12	MethylS	0.21	0.56	0.46	0.23	0.29
13	EthylS	0.28	1.01	0.45	0.62	0.61
14	PropylS	0.08	2.68	1.14	0.75	0.28
15	PropenylS	0.26	1.70	0.52	0.60	0.08
16	3-MethoxypropaneS	n.d.	0.86	0.22	0.41	n.d.
17	3-HydroxypropaneS	n.d.	1.30	0.24	0.24	0.03
18		n.d.	n.d.	0.09	0.25	0.07
	Total	**3.48**	**14.02**	**6.56**	**9.68**	**5.74**

3 [a]: Blank of reaction without catalyst; [b]: g/100g of lignin

4   In order to compare the catalytic depolymerisation yields with the degree of

5 condensation as measured by wet chemical analysis (thioacidolysis) both sets of data were

6 converted to µmol/g of lignin monomers taking into account the molecular weight of each
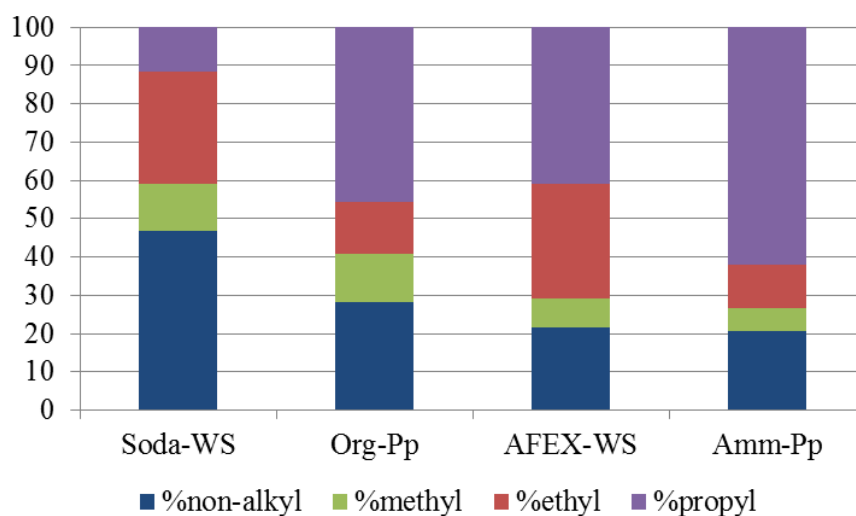
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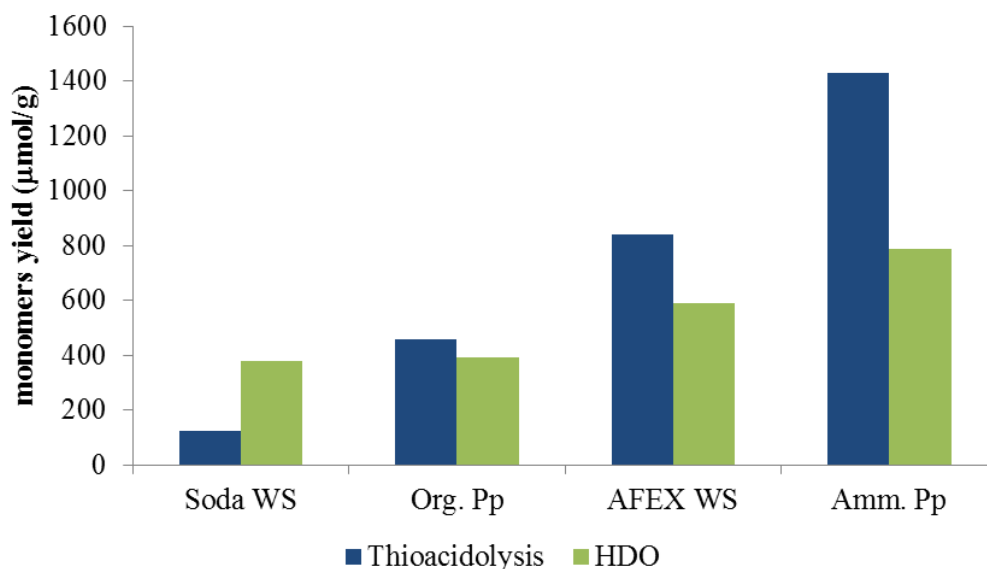
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2   **Figure 4**: Overall yields of monomers from thioacidolysis and catalytic conversion of

3   different lignin preparations [blue stick: Thioacidolysis products; green stick: Depolymerised

4   products]

5   In thioacidolysis, the selective cleavage of β-*O*-4 bonds generates products with an

6   intact propyl side chain[21]. This approach may be envisaged as a model reaction for the

7   conversion of uncondensed lignin to monomeric propylphenol compounds and compared to

8   the catalytic reaction. As illustrated in figure 4, the catalytic conversion yield was higher than

9   the thioacidolysis yield for highly condensed lignin (Soda Lignin). When the uncondensed

10   fraction of the lignin was greater, the catalytic conversion yield increased but at a lower rate

11   than the thioacidolysis yield. The thioacidolysis yields from the soda lignin were three times

12   lower than from the organosolv lignin, while the catalytic yields were the same. A number of

13   potential side-reactions in the catalytic conversion of condensed lignins are not paralleled in

14   thioacidolysis, such as loss of the γ-carbon. Moreover, abnormal constituents such as ferulic

15   acid, coniferaldehyde and benzaldehyde units lead to monomers that are not taken into

16   account in the thioacidolysis yields. For example, wheat lignins are rich in ferulic acid which

1   can undergo decarboxylation, explaining the abnormal amount of ethylguaiacol (see Table 3).

2   Moreover, small quantities of guaiacol and syringol are produced even from condensed parts

3   of the lignin structure. As illustrated in figure 5, guaiacol and syringol together accounted for

4   47 % of the molar quantity of depolymerised products from soda lignin while they only

5   accounted for 28 %, 22% and 21 % of the total molar fraction for the organosolv, AFEX and

6   ammonia lignins, respectively. In contrast the relative proportion of propylphenolics

7   increased from 12 % to 62 % of the total on going from the soda lignin to the ammonia
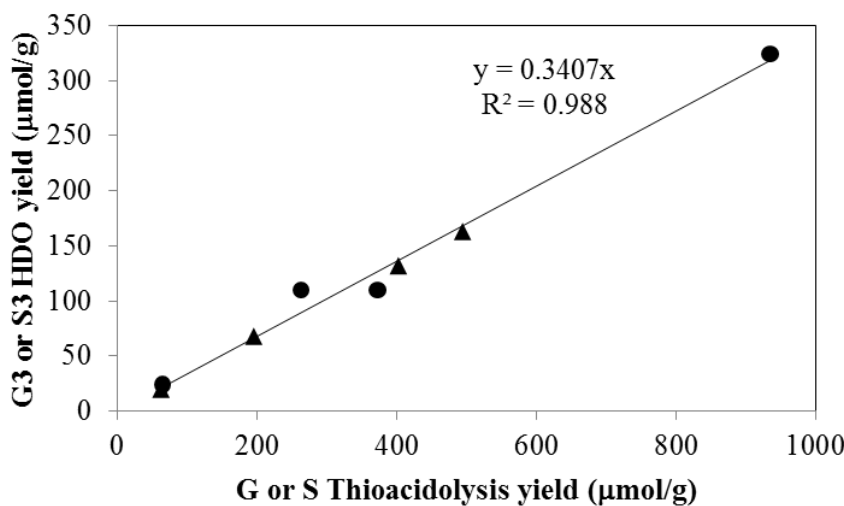
8   lignin.

9

10   **Figure 5**: Relative molar proportion of catalytic depolymerisation products from

11   different lignins [blue : non-alkyl; green: methyl; red: ethyl; purple: propyl]

12   As the ethyl, methyl and non-alkylated phenolic compounds can come from the

13   condensed fraction of the lignin, only the proportion of propylphenolic compounds generated

14   can be directly correlated to the amount of β-O-4 linkages in the starting lignin material. As

15   illustrated in Figure 6, there is an excellent correlation between the thioacidolysis and

16   catalytic depolymerisation yields of the products with 3-carbon side chains when either

17   guaiacyl or syringyl units are considered. This observation suggests that both guaiacyl and

1 syringyl units undergo the same type of complex reactions at the same rate. The catalytic

2 depolymerisation yield of propylphenolic compounds was three times lower than its potential

3 maximum yield as deduced from thioacidolysis.

The plot shows G3 or S3 HDO yield (μmol/g) on the y-axis versus G or S Thioacidolysis yield (μmol/g) on the x-axis, with the regression line:

$$y = 0.3407x$$
$$R^2 = 0.988$$

4

5 **Figure 6**: Correlation between thioacidolysis and catalytic depolymerisation yields of

6 the propylphenolic products. (Circle: Sum of S3 type HDO products; Triangle: Sum of G3

7 type HDO products)

8

9 **3.   Discussion**

10 The results presented above show that the structure of the lignin greatly affects the

11 nature and yield of monomeric depolymerised products. Consequently, the cost efficiency of

12 the lignin isolation method – usually dominated by the efficiency of conversion of the

13 associated cellulose to biofuel - must be balanced against the potential to generate products of

14 higher added value.

15 Compared to the analytical technique of thioacidolysis, the catalytic conversion was

16 non selective towards uncondensed linkages, giving rise to both cleavage and condensation.

1   In consequence, the catalytic conversion was less efficient for depolymerising uncondensed

2   lignins. In other words catalytic conversion of lignin to fine chemicals is most promising

3   when the starting lignin is uncondensed, but condensation of the lignin during the catalytic

4   step then leads to the greatest unfulfilled potential. Lignin condensation during this step is as

5   much an issue as during the isolation of the lignin. As illustrated in Figure 7, competition

6   between depolymerisation and condensation is the key problem in the conversion of lignin

7   into fine chemicals.

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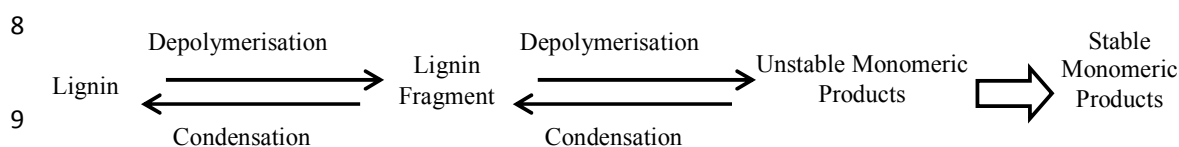
10   **Figure 7**: Lignin depolymerisation / condensation scheme

11   This competition exists at all stages of the process, from feedstock pretreatment to

12   catalytic depolymerisation. The ammonia percolation pretreatment, in which the lignin was

13   continuously removed from the reaction vessel as soon as it became soluble, avoided

14   condensation by limiting both depolymerisation and the simultaneous generation of unstable

15   intermediates[15]. During catalytic conversion, depolymerisation is the aim and the generation

16   of unstable products cannot be avoided. The key effect of the hydrogenolysis was to reduce

17   condensation of the products by fast stabilisation (hydrogenation) of reactive intermediates.

18   However, the results showed that condensation still predominated during the catalytic

19   reaction.

20   Further optimisation of the catalytic conversion of lignin to fine chemicals will require

21   that the condensation process be prevented. For a decade it has been known that one of the

22   condensation pathways is nucleophilic attack on the benzylic position of the lignin structure

23   (Fig. 8)[22, 23]. This type of reaction predominates in acid catalysed organosolv reactions.

1 During catalytic conversion, the slightly acidic alumina support may promote the acid-

2 catalysed alkylation of the benzylic position, as has been previously reported for the

3 condensation of benzylphenyl ether on zeolite HSZM-5 in aqueous medium[24].

4
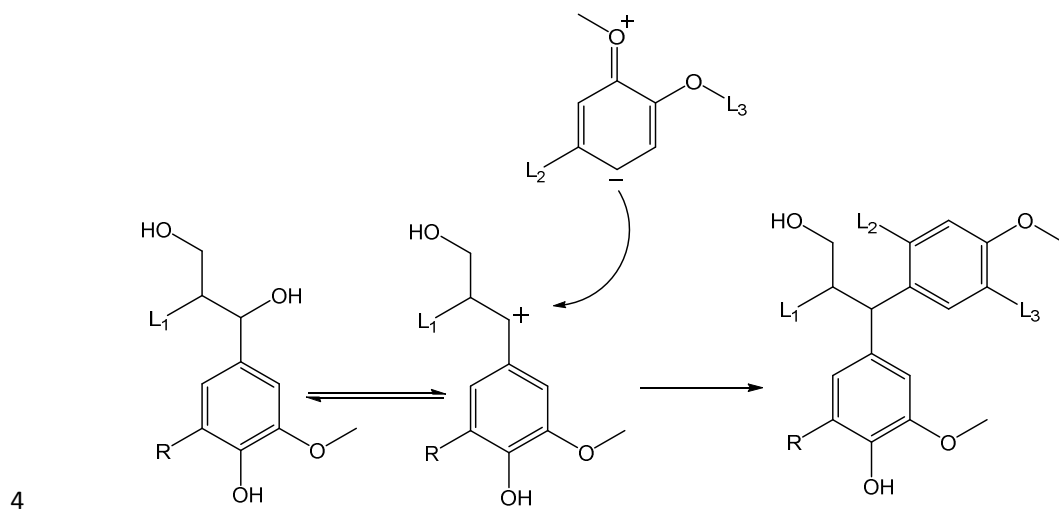
5 **Figure 8**: Condensation of the lignin via benzylic carbonium ion formation after heterolytic

6 cleavage of the benzylic C-O bonds [L_1, L_2, L_3 = Lignin fragments ; R = H or OMe]

7 In the case of bio-oil deoxygenation, a two-temperature process has been suggested

8 with the aim of stabilizing the reactive species and thus avoiding condensation[25]. A similar

9 approach to stabilisation of lignin before hydrogenolysis will be considered in a future paper.

10 Another explanation for the low conversion of lignin can be inferred from the blank reaction

11 where no catalyst was added to the medium. GPC analysis of the ammonia lignin subjected to

12 these conditions showed similar molecular weight distribution to the catalytic products (data

13 not shown), implying that condensation could also occurred in solution. In that case, slow

14 adsorption of lignin fragments on the catalyst could also be the limiting factor for lignin

15 conversion. A similar observation motivated other authors to subject lignin to liquid phase

16 reforming (LPR) followed by HDO[26]. While the lignin products changed, the two step

17 process did not improve the overall yield compared to the LPR alone. In other words, LPR

18 treated lignin, probably more condensed, was also less suitable for HDO conversion.

1   It can be expected that conversion of highly uncondensed lignins, such as AFEX or

2   ammonia lignin, will require gentle and carefully optimised conditions to achieve selective

3   cleavage of C-O bonds and generate high yields of fine aromatic chemicals. In the case of

4   more condensed lignins such as soda or organosolv lignins, harsher conditions are required to

5   cleave C-C bonds or other cracking approaches should be envisaged.

6   3. Conclusion

7   Lignin structure, in particular the abundance of β-O-4 linkages, had a major impact on the

8   yield and distribution of products after catalytic depolymerisation. Increasing the degree of

9   condensation in the initial lignin structure reduced the total yield of monomers and also

10   reduced the proportion of monomers retaining the three-carbon alkyl side-chain, which have

11   particular potential for conversion to fine chemicals. When the initial lignin structure was

12   relatively uncondensed, condensation during the catalytic step reduced the yields of alkylated

13   monomers. Optimisation of lignin breakdown, especially from highly uncondensed lignin,

14   requires more selective cleavage methods to minimise condensation. It may be advantageous

15   to adopt a multi-stage breakdown strategy with increasing severity of conditions at each

16   stage.

17

18

19   4. Experimental

20   4.1. Materials

21   Hybrid poplar sawdust was provided by a UK sawmill. The sawdust was sieved and the

22   particle size range from 125μm to 1080 μm was used. The dry matter content of the poplar

23   sawdust was 92.6 %. Ammonia fibre expanded (AFEX) wheat straw was obtained from Prof.

1   Bruce Dale, Michigan State University. Protobind 1000 lignin (Soda Lignin) was purchased

2   from Green Value (Switzerland).

3   The alumina supported platinum catalyst was obtained from Johnson Matthey (reference

4   number 1074). The catalyst was sieved between 250 to 425 μm, pre-reduced at 250 °C and

5   stored under air. The platinum dispersion, as measured by carbon monoxide chemisorption,

6   was 56 %, while the catalyst had a BET surface area of 119 $m^2.g^{-1}$, a pore volume of 0.49

7    $cm^3.g^{-1}$ and an average pore diameter of 11 nm. All other reagents and solvents were

8   purchased from Sigma-Aldrich and used without further purification.

9   4.2. Lignin preparation

10   Three of the four tested lignins were prepared in house, as described below.

11   4.2.1. Lignin isolation from AFEX wheat straw

12   Following Lawther et al.[27], the AFEX Wheat straw was extracted under reflux at 5%

13   loading with 0.5N sodium hydroxide in ethanol/water (6/4: v/v). After this mild extraction

14   step, the mixture was filtered on a Buchner funnel and the residue washed with ethanol/water

15   (6/4). After neutralisation of the filtrate to pH 6, hemicelluloses were precipitated by adding 3

16   volumes of ethanol. The precipitate was removed by centrifugation and the supernatant was

17   concentrated and acidified to pH 2. The precipitated lignin (AFEX WS) was recovered by

18   centrifugation, washed with deionised water and freeze dried.

19   4.2.2. Acid organosolv lignin from poplar

20   This lignin was prepared by a well-established organosolv process[28] as previously

21   described[29]. In a stainless steel reactor, poplar sawdust was mixed with ethanol/water (6/4 ,

22   v/v) containing sulphuric acid (1.25 % w/w of poplar). The reactor was rotated on a motor-

23   driven shaft inside a programmable oven. The reaction was conducted at 180 C for 1h. After

1   cooling, the mixture was filtered on a Buchner funnel and the filtrate diluted in 3 volumes of

2   water (pH 2). The precipitated lignin (Organosolv Poplar) was recovered after centrifugation,

3   washed with deionised water and freeze dried.

4   4.2.3. Ammonia lignin from poplar

5   Ammonia Lignin was prepared as reported previously[15]. Briefly, aqueous ammonia

6   (15 % w/v) was percolated through the poplar sawdust at 180 °C, 20 barg and 3 ml.min^{-1} flow

7   rate with a total liquid/solid ratio of 10:1. The percolated liquor was concentrated and

8   acidified to pH 2. The precipitate was recovered by centrifugation and briefly hydrolysed

9   with mild ethanolic acid to remove carbohydrate impurities. The lignin was then precipitated

10   in three volumes of water (pH 2, HCl). The purified lignin was recovered by centrifugation,

11   washed three times with deionised water and freeze dried.

12

13   4.3. Catalytic conversion of the lignin

14   The catalytic depolymerisation reactions were conducted in a 300ml 316 stainless

15   steel Parr batch autoclave reactor equipped with a Parr model 4842 digital temperature

16   controller ±2°C. During a typical experiment 0.5 g of lignin was added to the autoclave along

17   with 0.1 g 1 % w/w Pt/Al$_2$O$_3$ and 100 ml methanol-water mix (50:50 v/v). The reactor was

18   purged with hydrogen and pressurised to 20 barg. The reaction was performed at 300°C with

19   mechanical stirring (1000 rpm) and stopped after 2h (plus 30min ramp time).The reaction

20   mixture was filtered on sintered glass (porosity 3) to remove the catalyst and insoluble

21   products, then the residue was washed with acetone to solubilise higher molecular weight

22   lignin fragments. The fraction soluble in methanol-water was centrifuged to remove finely

23   dispersed solids. An aliquot of the solution was then mixed with a known quantity of internal

1 standard, acidified to pH 3 and extracted with dichloromethane/dioxane (8/2 v/v). After

2 evaporation of the solvent, the products were solubilised in 2ml dichloromethane.

3

4   4.4. Analytical methods

5

6   The sugar analysis, gel permeation chromatography and thioacidolysis of lignins have

7 been described in a previous paper[15]. For GPC analysis of the catalytic conversion products,

8 equal volumes of the methanol-water and acetone solubles were mixed together, evaporated

9 to dryness, acetylated, and solubilised in THF before injection. GC/MS analysis of the

10 catalytic conversion products was performed as follows. An aliquot (10µl) of the products

11 extracted in dichloromethane was added to 30µl pyridine and 70µl TMS. Qualitative and

12 quantitative analyses were performed using a Shimadzu GC-MS-QP2010S coupled to a

13 Shimadzu GC-2010 GC equipped with a ZB-5MS capillary column (30m x 0.25mm x 0.25

14 µm). The quantification of the products was measured on the TIC and based on reference

15 compounds with hexadecane as an internal standard.

16   NMR spectra were acquired on a Bruker Avance III 500 MHz spectrometer equipped

17 with a BBFO+ probe. The central DMSO solvent peak was used as internal reference (δ_C

18 39.5, δ_H 2.49 ppm). The ^{1}H,^{13}C-HSQC experiment was acquired using standard Bruker pulse

19 sequence 'hsqcetgpsp.3' (phase-sensitive gradient-edited-2D HSQC using adiabatic pulses

20 for inversion and refocusing). The composite pulse sequence 'garp4' was used for broadband

21 decoupling during acquisition. 2048 data points was acquired over 12 ppm spectral width

22 (acquisition time 170 ms) in the F2 dimension using 24 scans with 1 s interscan delay and

23 the d4 delay was set to 1.8 ms (1/4J, J = 140 Hz). Spectral width of 170 ppm, 256 increments

24 were acquired in F1 dimension (acquisition time 5.6 ms) resulting in a total experimental

1   time of 2 h. The spectrum was processed using squared cosinebell in both dimensions and

2   LPfc linear prediction (32 coefficients) in F1. Volume integration of cross peaks in the HSQC

3   spectra was carried out using MestReNova software[17].

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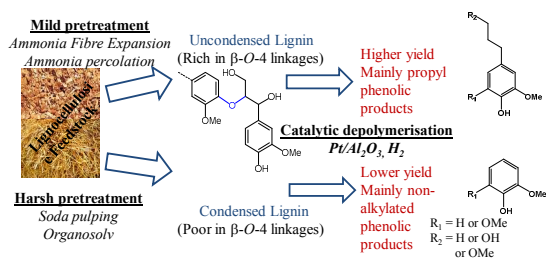
Catalytic depolymerisation of lignins with different β-O-4 linkages percentages affected both the yield and the nature of aromatic monomeric products