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Aqueous organic solvent fractionation as means to improve lignin homogeneity and purity

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Abstract

Lignin's heterogeneous polymeric structure limit its utilisation in further processing for high-value applications. This paper describes a protocol for kraft lignin precipitation fractionation by water addition from aqueous ethanol, acetone or propyleneglycol monomethyl ether. The solvent-insoluble fractions possessed high molar mass, high polydispersity, high nitrogen and low sulphur content. Also lignin aggregation was observed when acetone was used. The molar mass of the precipitated fractions depended on the amount of water added in the precipitation step. The highly soluble lignin fractions possessed more carboxylic acid groups, higher amount of sulphur and more carbohydrates than other lignin fractions. The presented protocol is simple and easily up-scalable and tunable to fractionate lignin with green solvents when constant quality, high purity or high reactivity are needed.

Keywords

Kraft lignin; fractionation; molar mass; ethanol; acetone; propyleneglycol monomethyl ether

1. Introduction

Lignin is the second most abundant natural polymer after cellulose and it composes of ca. 20-30% of wood and most other lignocellulosic biomasses (Boerjan et al., 2003;

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Ragauskas et al., 2014). Lignin is considered as the most promising aromatic raw material to replace petrochemical-based feedstocks (Ragauskas et al., 2014). Currently, worldwide chemical wood pulping industry produces ca. 70 Mt of lignin which is mostly incinerated to generate energy. Novel technological solutions provide means to recover part of lignin from the existing process streams without impeding the energy or chemical balances of the mills (Tomani, 2010). In addition to pulping industry also lignocellulosic ethanol production is expected to produce another 62 million tons of lignin as side streams by 2022 (Ragauskas et al., 2014) These volumes illustrate the high availability of technical lignins, and it is expected that lignin will become a commercially relevant feedstock for a range of materials (Gellerstedt, 2015; Ragauskas et al., 2014).

Lignin is composed mostly of three types of phenyl propane units, i.e. p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, which differ by the number of methoxyl groups attached on the aromatic ring. H units have no methoxyl groups, G units possess one methoxyl group and S units possess two methoxyl groups attached on the aromatic ring. The relative content of these units depend mostly of plant species, as softwood lignin is composed mostly of G and some H units, hardwood lignin contains both G and S units and minor amount of H units and herbaceous lignins contain all three units in remarkable quantities (Vanholme et al., 2010). The phenyl propane units in lignin are interlinked via different, mostly ether, linkages (Boerjan et al., 2003). There is significant variation in lignin interunit linkages within trees and even cell wall layers (Vanholme et al., 2010) which indicates that lignin is inherently heterogeneous polymer. Furthermore, in chemical pulping processes the heterogeneity is increased due to incomplete impregnation of the chemicals in the feedstock. The heterogeneity is a challenge when lignin is used in material applications where constant molecular size, functionality and reactivity are required (Chatterjee and Saito, 2015; Gellerstedt, 2015; Norberg et al., 2013; Teng et al., 2013).

Ultrafiltration (Brodin et al., 2009; Norgren, Magnus, 2000; Sevastyanova et al., 2014; Toledano et al., 2010; Toledano et al., 2010), solvent fractionation (Boeriu et al., 2014; Cui et al., 2014; Duval et al., 2015; Li and McDonald, 2014; Lovell and Hibbert, 1941; Mörck et al., 1986; Ni, Y., Hu, 1995; Ropponen et al., 2011; Sadeghifar and Argyropoulos, 2016) and their combinations (Helander et al., 2013) are potential techniques to decrease the heterogeneity of lignin isolates. Ultrafiltration provides an efficient method to control the molar mass distribution of lignin by the selection of membranes with suitable cut-offs (Brodin et al., 2009; Sevastyanova et al., 2014; Toledano et al., 2010). A major advantage of this method is that the technology can be applied directly to cooking liquor at pulp mill without a need to adjust pH or temperature (Sevastyanova et al., 2014). On the other hand, the poor solubility of some lignins (e.g. hydrolysis lignin from ethanol production plant), fouling of the membranes and expensive instrumentation are major limitations for ultrafiltration.

Solvent fractionation is based on partial solubility of polymers into solvents. Several solvent fractionation methods have been developed to produce polymer fractions with narrow distribution of molar mass, branching or chemical composition (Francuskiewicz, 1994). Solvent fractionation of lignin can be performed either by selective dissolution of solid lignin or selective precipitation of dissolved lignin. In the pioneering work by Lovell and Hibbert (1941), lignin was first dissolved in methanol followed by fractionation using two immiscible solvents, carbon tetrachloride and chloroform. Later, Mörck et al. (1986) developed a sequential fractionation process using dichloromethane (DCM), isopropanol, methanol and methanol-DCM mixture to extract lignin fractions.

Similar strategies have been implemented over the years and the methods are based on organic solvents such as DCM, isopropanol, methanol, ethanol, acetone, diethyl ether, dioxane, tetrahydrofuran, butanone and hexane as pure solvents or as mixtures. (Arshanitsa et al., 2013; Dodd et al., 2015; Duval et al., 2015; Jiang et al., 2017; Li and McDonald, 2014; Ni, Y., Hu, 1995; Passoni et al., 2016; Ropponen et al., 2011) However, most of these solvents are classified as problematic or even hazardous (Prat et al., 2016) and therefore cannot be considered as green or safe options in lignin fractionation.

A fractional precipitation fractionation scheme for lignin was first proposed by Cui et al. (2014) who dissolved kraft lignin in acetone and then added hexane gradually to precipitate lignin fractions from the solution. Mixing two miscible solvents allowed the flexible manipulation of the yield and molecular composition of each lignin fraction and hence provided an attractive approach for lignin fractionation. A similar approach was applied by Sadeghifar et al (2017), who dissolved organosolv lignin into aqueous acetone followed by controlled lignin precipitation fractionation with water addition.

In this paper, we demonstrate a solvent fractionation method to separate kraft lignin in homogeneous fractions using aqueous solutions of ethanol, acetone or propyleneglycol monomethyl ether (PGME). The lignin precipitation fractionation was performed by first dissolving lignin in aqueous solvent followed by addition of water to controlled precipitation of lignin. The chemical structures of the produced lignin fractions were characterised to assess the performance of the process. This fractional precipitation procedure provides an easily controllable process to manipulate the yield and structural composition of produced lignin fractions without the use of harmful or hazardous solvents or expensive instrumentation.

2. Materials and Methods

2.1. Kraft lignin and its characterization

Dry softwood kraft lignin (dry matter 95%) was an industrial kraft lignin precipitated from softwood black liquor and kindly gifted by Metsä Fibre. Klason lignin content was determined gravimetrically after acid hydrolysis of the sample (Allsopp and Misra, 1940), and the hydrolysate was analysed to determine the acid soluble lignin using UV spectroscopy (Goldschmid, 1971) and carbohydrates using HPAEC-PAD (Tenkanen and Siika-aho, 2000).

Elemental analysis (C, H, N and S) was determined from 20-30 mg of ground and dried (105^{o}C for overnight) using FLASH 2000 series elemental analyzer.

UV absorption coefficient for the unfractionated kraft lignin was determined by dissolving 13.5 mg of lignin (o.d.) in 1000 ml NaOH solution (0.1M) at room temperature. The absorbance at 280 nm (0.350±0.020) designates the absorptivity value of 25.9 $l{\cdot}g^{-1}cm^{-1}$, which was applied to determine the concentration of dissolved lignin.

The molar mass distribution was defined by dissolving lignin in 0.1M NaOH solution at room temperature followed by size exclusion chromatography using UV detection at 280 nm (Baumberger et al., 2007). The molar mass calculations were performed based on external calibration of the method using polystyrene sulphonate standards.

The number of hydroxyl groups were determined with ^{31}P NMR spectroscopy by using the procedure by Granata and Argyropoulos (Granata and Argyropoulos, 1995) using a Bruker 500 MHz spectrometer. 1024 scans with pulse delay of 5 s, 90° pulse, line broadening of 2 and default baseline correction were used in spectral collection. The quantification limits applied were 150-145 ppm for aliphatic OH groups, 145-140.5

ppm for 3 and 5-subsituted phenolic OH groups, 140.5-138.5 ppm for guaiacylic OH groups, 138.5-137 ppm for p-hydroxyphenyl groups and 136-134 ppm for carboxylic acid groups.

2.2. Solvent fractionation of lignin

Lignin fractionation followed the scheme in Fig.1: 10 g (o.d.) of kraft lignin was mixed with 100 ml of aqueous ethanol (80 % by volume), acetone (60% by volume) or PGME (60% by volume) solution. The dispersion was mixed in an Erlenmeyer flask under magnetic stirring for 20 minutes at room temperature. The solution was centrifuged for 20 minutes and the supernatant was recovered. The insoluble lignin fraction was washed twice with aqueous solvent of same concentration, dried (in vacuum at 40^{o}C for 16-72 hours) and weighed.

A predefined volume of supernatant from the first fractionation stage was placed in Erlenmeyer flask followed by water addition to reach the desired solvent concentration (70% for ethanol and 50% for acetone or PGME). This solution was mixed for 20 minutes to allow lignin to precipitate followed by centrifugation and recovering the supernatant. The precipitate was washed twice with aqueous solvent, dried (40^{o}C vacuum) and weighed. Again, a predefined volume of supernatant was replaced in Erlenmeyer flask followed by water addition to precipitate a new fraction of lignin. These steps were repeated until solvent concentration of 50% was reached. At this stage the lignin concentration was so low that the precipitation fractionation was not practical to continue further. A new fractionation sequence was started by mixing 10 g of lignin with aqueous solvent (50% by volume) and repeating the fractionation as explained above. This way, the solvent volumes and lignin concentrations remained at practical level until solvent concentration of 10%. The last lignin fraction was recovered from this solution by evaporating the solvent under vacuum at 40°C.

3. Results and discussion

3.1. Mass balances of lignin fractionation

The principle of precipitation fractionation is to dissolve the polymer in a solvent followed by addition of nonsolvent to precipitate fractions with narrow molar mass distribution (Francuskiewicz, 1994). Since lignin has high solubility in aqueous ethanol, acetone and PGME (Jääskeläinen et al., 2016), these three organic solvents were selected as fractionation media and water was applied as nonsolvent. The fractionation was initiated by first dissolving lignin as completely as possible but still close to the tipping point where small increase in water content results in significant precipitation of lignin. As was defined by the solubility tests earlier (Jääskeläinen et al., 2016), the optimal solvent concentration was 80% for ethanol and 60 % for acetone and PGME for this softwood kraft lignin, whereas lignin solubility in pure ethanol or acetone were lower. For PGME, a nearly quantitative dissolution was observed at water content of 0-40% (Jääskeläinen et al., 2016) indicating that this solvent provides a potential alternative to dissolve technical lignins with limited solubility in ethanol or acetone.

The insoluble lignin fraction composed of 32%, 16% and 0.8% of total lignin in ethanol (80%), acetone (60%) and PGME (60%) processes, respectively, as is illustrated Fig. 2. Addition of water, i.e. decreasing the solvent concentration, resulted in lignin precipitation and thus lignin fractionation. In the ethanol-based process, relatively low amount of lignin was precipitated in each step, whereas in acetone or PGME-based processes the yield of two first precipitated fractions covered 24-37% of total lignin each. This indicates that acetone and PGME-based processes were more sensitive to solvent concentration than ethanol-based process.

At solvent concentrations of ca. 20% lignin precipitation levelled off as further addition of water resulted in only negligible precipitation of lignin. Therefore, the last fractions were recovered by evaporating the aqueous solvent and the yield of these fractions were 9-13% on original lignin.

3.2. Molar mass

The solvent fractionation separated lignin into fractions mostly based on the molar mass, as illustrated in Fig.3. In ethanol and acetone-based fractionations, the insoluble fraction possessed significantly higher molar mass and polydispersity than the unfractionated lignin. However, in the PGME-based process, the insoluble fraction possessed nearly the same molar mass as the unfractionated lignin. However, this fraction possessed only less than 1% of the total unfractionated lignin.

The acetone-insoluble (60% ins) fraction possessed unexpectedly high molar mass and very high polydispersity (Fig. 3. and Table 1). Similar observation was not made in aqueous acetone fractionation for other types of technical lignins (Sadeghifar et al., 2017). It is likely that in this sample, lignin was aggregated since aggregation is known to take place in lignin solutions (Mantler et al., 1984). The formed lignin aggregates did not disaggregate when lignin was dissolved in 0.1M sodium hydroxide solution at room temperature for molar mass determination. However, heating lignin at 80°C in dilute alkaline conditions decreased the molar mass (Supplement information, S1), which supports the theory for aggregate formation in acetone-containing solution and their partial disruption under alkaline conditions. This result agrees with the knowledge that the dissociation takes place in alkaline solutions at low concentrations but only very slowly (Mantler et al., 1984). Interestingly, no aggregation was observed in other fractionation processes, but only in the acetone-based fractionations. The mechanism of the lignin aggregation is proposed to be π-π stacking (Deng et al., 2011; Mantler et al., 1984) and was also recently observed in pure acetone fractionation (Sadeghifar and Argyropoulos, 2016). In organic media, alkali lignin forms a sandwich-type head-to-tail stacking (J-aggregates) and these aggregates are reversible and can be disaggregated e.g. by addition of iodine which forms lignin-iodine charge-transfer complexes that cannot form novel π-π stacks (Deng et al., 2011). In addition, the disaggregation takes place slowly in alkaline solutions at low lignin concentrations (Mantler et al., 1984). In practice, the formation of aggregates affects lignin utilisation due to lowered solubility and reactivity and in most applications has a negative impact on lignin utilisation.

The average molar mass was the lower the lower was the solvent concentration in the precipitation step (Table 1). In general, the precipitated lignin possessed lower polydispersity than the unfractionated lignin or the insoluble lignin fraction. Therefore this protocol provides a method to produce a lignin fraction with desired molar mass and low polydipersity by tuning the solvent concentration in the precipitation step. In the last fractionation steps, the soluble lignin had weight average molar mass of ca. 1500 g/mol, which corresponds to lignin with ca. 8 monomeric units. However, this degree of polymerisation is indicative only, since the size exclusion chromatography was calibrated using polystyrene sulphonates and does not correlate exactly with the molar mass of lignin in this range (Baumberger et al., 2007).

3.3. Elemental composition of lignin fractions

Elemental compositions of the lignin samples reflect their chemical compositions. The carbon contents of the insoluble fractions from the first and last stages were lower than that of unfractionated lignin, whereas the selected middle fractions possessed higher proportions of carbon (Table 2). This result indicates that carbohydrates, which have much lower carbon content than lignin, are enriched in both high and low molar mass fractions. According to literature (Duval et al., 2015) the lignin fractions with high molar mass contain more carbohydrates than the unfractionated lignin. These carbohydrates were proposed to be covalently linked with lignin (Duval et al., 2015). The high content of carbohydrates in the low molar mass fractions were confirmed by lignin compositional analysis (Table 3).

Sulphur accumulated in the low molar mass fractions (Table 2). This result is consistent with other fractionation studies, which have illustrated that the sulphur content in the low molar mass lignin fraction is much higher than in the high molar mass fractions (Dodd et al., 2015; Sevastyanova et al., 2014).

Nitrogen was present in the initial lignin in only minute content, which is a typical level for kraft lignin (Tomani, 2010). Nitrogen originates most likely from the wood cell proteins. Interestingly, most of nitrogen retained in the insoluble fraction which is logical due to large polymeric size and low solubility of proteins.

3.4. Chemical composition of lignin fractions

Klason and acid-soluble lignin content is the most common method to define the total lignin content in a sample. The unfractionated kraft lignin revealed Klason lignin and acid-soluble lignin contents of 92.3% and 2.5%, respectively, which are typical values for kraft lignin which is precipitated from black liquor using CO_2 followed by acid wash (Brodin et al., 2009; Sevastyanova et al., 2014; Tomani, 2010).

The Klason lignin contents of the low molar mass fractions (10% sol) were only 57-67% on lignin (Table 3) which are very low when compared to typical values published for kraft lignin in literature (> 90 %) (Brodin et al., 2009; Duval et al., 2015; Fang et al., 2015; Helander et al., 2013; Li and McDonald, 2014; Sevastyanova et al., 2014). These lignins contained also extremely high proportions of acid-soluble lignin (16-21%) which are much higher than any corresponding values found in literature for kraft lignin. The highest acid-soluble lignin content reported for kraft lignin was 9.6%, and this was a kraft lignin fraction obtained by ethyl acetate extraction (Duval et al., 2015). Otherwise, typical kraft lignin fractions contain only 2-6% of acid soluble lignin. (Brodin et al., 2009; Fang et al., 2015; Helander et al., 2013; Li and McDonald, 2014; Sevastyanova et al., 2014)

The carbohydrate content of the unfractionated lignin was 1.1% which is a typical value for kraft lignin, although at the low side of the ordinary range (Tomani, 2010). The most soluble lignin contained surprisingly high amount of carbohydrates indicating the accumulation of carbohydrates in this fraction (Table 3). This result was unexpected, since it has been published by several authors (Duval et al., 2015; Mörck et al., 1986; Ropponen et al., 2011), that in other fractionation processes the carbohydrates are accumulated in the high molar mass lignin fraction.

The carbohydrate compositions in Table 4 reveal that the highly soluble lignin was enriched in galactose which is the most common carbohydrate covalently bound to softwood kraft lignin (Hortling et al., 2001).

3.5. Functional groups

The number of hydroxyl groups in aliphatic, phenolic and carboxylic acid moieties was determined using 31P NMR spectroscopy after derivatising the hydroxyl groups in the lignin samples with phosphorus-containing reagent. The NMR spectral shifts allow the differentiation of hydroxyl groups, namely aliphatic and aromatic hydroxyl groups and carboxylic acid groups (Granata and Argyropoulos, 1995) (Fig. 4). In addition, the different substitution pattern of the aromatic moieties (syringyl and condensed guaiacylic units, guaiacylic units and p-hydroxyphenyl units) are separated and they can all be quantified based on their chemical shifts (Granata and Argyropoulos, 1995). However, the poor solubility of selected kraft lignin fractions in DMSO restricted the analysis of the acetone (60%) and PGME (60%) insoluble fractions.

The ^{31}P NMR spectra of the lignin fractions from ethanol, acetone and PGME-based fractionations are shown in Fig. 4. It can be seen that the spectra from ethanol and PGME-based processes additional narrow bands occurred at 146-147 and 145-146 ppm, respectively, which are not present in other samples. These bands correspond to the shifts of phosphorylated alcohol groups in ethanol (146.3 ppm (Pu et al., 2011)) and PGME and therefore it is obvious that they originate from residual solvent present in the fractionated lignin despite of sample drying at 40^{o}C vacuum oven for at least 16 hours. The thermal desorption test of the lignin fractions (Kalliola et al., 2012) revealed, that the residual solvent was trapped in the lignin and was not removed even by heating the sample to 150^{o}C (Supplement information S2).

The solvent was not covalently linked, since the solvent-originating free hydroxyl group could be observed in the ^{31}P NMR spectra, which would not be present if the alcohol would be etherified in lignin. Therefore it is likely that the solvent was adsorbed to lignin with physical interactions that restricted its evaporation during heating.

The residual ethanol and PGME contents in the samples were quantified by integrating these solvent bands in the ^{31}P NMR spectra (Table 5). The residual solvent content varied between 1.3 and 5.0% for ethanol and 7.2 and 7.8% for PGME-based samples. The higher PGME content compared to ethanol could be explained by its higher boiling point, but otherwise no clear trend in solvent concentrations as function of the fractionation process could be assessed. The content of residual acetone in the samples from the acetone-based processes cannot be measured by this ^{31}P NMR spectroscopic method due to the lack of hydroxyl groups in acetone.

The aliphatic hydroxyl groups in the lignin samples originate either from free hydroxyl groups in the side chain of the phenylpropane units or any residual carbohydrates in the sample. No clear trends in the content of aliphatic hydroxyl groups could be observed (Table 5), except that in the low molar mass fractions (10% sol) the number of aliphatic hydroxyl groups was high. This agrees with the high content of carbohydrates in these samples. On the other hand, this result does not agree with other fractionation studies, in which low molar mass lignin fractions have been found to possess less aliphatic hydroxyl groups than lignin with higher molar mass (Cui et al., 2014; Sadeghifar et al., 2017) .

The phenolic hydroxyl groups in lignin can be classified based on the aromatic substitution of the phenolic units. The amount of syringyl units is low by nature in softwood lignin and therefore the spectral range that corresponds to 3,5-disubstituted units originate mostly from condensed phenolic units. The value for kraft lignin (1.20 mmol/g) is at the same range that has been published for residual kraft lignin earlier

(Jääskeläinen et al., 2003). In the ethanol-based fractionation these units were highest in the insoluble residue and lowest in the most water-soluble fraction. Surprisingly, this trend could not be observed for acetone or PGME fractionations.

Guaiacyl-type of phenols are the most prominent phenolic unit in softwood lignin. The content of free phenolic guaiacyl units increased steadily as the fractionation proceeded (Table 5). The most soluble lignin fractions contained significantly higher amount of guaiacylic phenols than other lignin fractions. This result is logical as the molar mass of lignin in these samples was also remarkably lower. When lignin is depolymerised by the cleavage of β-aryl ether linkage, the most common interunit linkage in lignin, the molar mass is reduced and a novel phenolic hydroxyl group is introduced. Hence, the lower the molar mass, the higher the number of phenolic hydroxyl groups. This correlation is also visualised graphically in Fig. 5 which summarises the relation between the weight average molar mass and the number of guaiacylic hydroxyl groups in lignin. This correlation is similar as has been observed with other lignin fractionation processes (Cui et al., 2014).

The number of carboxylic acid structures was the highest in the last fractions which also supports the high solubility of these fractions aqueous systems with high water content. The result is consistent with the solvent process by Cui et al. (2014) who also illustrated that the low-molar mass fractions contain a high number of phenolic hydroxyl groups and carboxylic acid moieties. On the other hand, this result is clearly different than has been obtained by ultrafiltration, where the content of carboxylic acid groups was not affected by fractionation, i.e. the amount of carboxylic acid groups was nearly constant in each lignin fractions regardless of the molar mass (Sevastyanova et al., 2014).

4. Conclusions

The proposed lignin precipitation fractionation scheme is based on the use of safe green solvents. The aqueous solvent protocol allows the fractionation of wet lignin, which is typical when lignin is recovered from an industrial source. In addition, the chemical recovery and recycling of one organic solvent simple when compared to fractionation processes that utilise several organic solvents. The gradient mixing of the solvents enables an easy tuning of the process and the number of precipitation steps can be freely selected depending on the purity, molar mass and solubility requirements set for the final lignin product. The paper describes a selection of three different solvents which all produced lignin fractions with similar properties.

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Figure captions

Fig. 1. Schematic description of the aqueous ethanol solvent fractionation. The same principle was applied for aqueous acetone and aqueous PGME fractionations, except that lignin was dissolved directly in 60% solvent concentration.

Fig. 2. Yield of solid (insoluble or precipitated) lignin fraction from ethanol, acetone and PGME processes. * denotes the lignin recovered from the solution after solvent evaporation.

Fig. 3. Molar mass distributions of precipitated lignin fractions. The green curve denotes the molar mass distribution of the unfractionated kraft lignin.

Fig. 4. ^{31}P-NMR spectra of initial kraft lignin, and lignin fractionated with ethanol, acetone and PGME. The asterisks denote the residual solvent observed in the aliphatic range of the spectra.

Fig. 5. Correlation between the molar mass and the number of guaiacylic hydroxyl groups in the unfractionated lignin and in lignins fractionated with aqueous ethanol, acetone and PGME.

Table 1. Number average and weight average molar mass and polydispersities of lignins from different fractionation steps.

	M_n (g/mol)	**M_w (g/mol)**	**PDI**
Kraft lignin	2100	4100	1.98
Ethanol			
80%ins	3000	7600	2.54
70%prec	3600	5300	1.48
60%prec	3000	4300	1.41
50%prec	2400	3300	1.38
40%prec	2000	2800	1.40
30%prec	1700	2200	1.33
20%prec	1500	2000	1.32
10%prec	1500	2000	1.34
10%sol	1100	1500	1.36
Acetone			
60%ins	3400[a]	18900[a]	5.62[a]
50%prec	3000	6000	1.97
40%prec	2300	3500	1.55
30%prec	1800	2700	1.46
20%prec	1600	2300	1.41
10%prec	1500	2100	1.40
10%sol	1100	1600	1.44
PGME			
60%ins	1900	4300	2.24
50%prec	2900	6700	2.31
40%prec	2400	3900	1.66
30%prec	2000	2800	1.45
20%prec	1700	2400	1.42
10%prec	1600	2200	1.40
10%sol	1200	1700	1.43

[a] aggregation of lignin

Table 2

Table 2. Carbon, hydrogen, nitrogen and sulphur composition of selected lignin fractions.

	Carbon, %	**Hydrogen, %**	**Nitrogen, %**	**Sulphur, %**
Kraft lignin	65.0	5.7	0.12	1.62
Ethanol				
80% ins	64.3	5.7	0.15	1.48
50% prec	68.1	5.9	0.14	1.63
10% sol	58.9	6.2	0.08	2.88
Acetone				
60% ins	56.0	6.1	0.33	0.74
50% prec	66.4	5.8	0.14	1.45
10% sol	63.9	6.0	0.12	1.59
PGME				
60% ins	59.7	6.1	0.43	1.10
50% prec	65.9	5.9	0.12	1.35
10% sol	59.1	5.9	0.09	2.75

Table 3

Table 3. Klason lignin, acid-soluble lignin and carbohydrate content of the most soluble lignin fractions.

	Klason lignin, %	**Acid soluble lignin, %**	**Carbohydrates, %**
Kraft lignin	92.3	2.5	1.1
Ethanol 10%sol	57.0	20.5	5.7
Acetone 10%sol	64.4	16.9	6.1
PGME 10% sol	67.1	15.6	5.3

Table 4. Carbohydrate content (% on lignin fraction) and composition (% on total carbohydrates, in parenthesis) in unfractionated kraft lignin and in selected lignin fractions. Ara = arabinose, Gal = galactose, Glu = glucose, Xyl = xylose, Man = mannose.

	Ara, %	**Gal, %**	**Glu, %**	**Xyl, %**	**Man, %**
Kraft lignin	0.2 (18%)	0.3 (27%)	0.1 (9%)	0.3 (27%)	<0.1 (9%)
Ethanol 10% sol	1.00 (18%)	2.42 (42%)	0.25 (4%)	1.64 (29%)	0.15 (3%)
Acetone 10% sol	0.99 (16%)	2.89 (47%)	0.26 (4%)	1.60 (26%)	0.16 (3%)
PGME 10% sol	0.86 (16%)	2.55 (48%)	0.21 (4%)	1.39 (26%)	0.12 (2%)

Table 5

Table 5. Number of aliphatic and phenolic hydroxyl groups and carboxylic acids in selected lignin fractions. Cond PhOH = free phenols in condensed syringyl units; G-PhOH = free phenols in guaiacylic structures and p-PhOH = free phenols in *para*-hydroxyphenyl structures and COOH = carboxylic acids.

	Solvent %	**Aliph OH mmol/g**	**Tot PhOH mmol/g**	**Cond PhOH, mmol/g**	**G-PhOH, mmol/g**	***p*-PhOH, mmol/g**	**COOH, mmol/g**
Kraft lignin	-	1.17	2.76	1.20	1.39	0.17	0.28
Ethanol							
80% ins	3.8	1.85	3.43	1.69	1.49	0.25	0.33
70% prec	1.8	1.50	2.75	1.36	1.24	0.16	0.20
60% prec	1.7	1.40	2.53	1.20	1.16	0.17	0.23
50% prec	1.3	1.29	2.82	1.26	1.40	0.17	0.29
40% prec	1.6	1.37	3.01	1.26	1.56	0.18	0.37
30% prec	5.0	2.09	2.94	1.08	1.70	0.16s	0.40
10% sol	1.6	2.22	4.05	1.05	2.72	0.28	0.71
Acetone							
60% ins	is	is	is	is	is	is	is
50% prec	-	1.28	2.62	1.24	1.21	0.17	0.26
40% prec	-	1.13	2.94	1.30	1.46	0.18	0.32
30% prec	-	1.06	2.87	1.17	1.53	0.18	0.33
10% sol	-	2.25	4.04	1.21	2.52	0.32	0.63
PGME							
60% ins	is	is	is	is	is	is	is
50% prec	7.3	1.97	2.33	1.10	1.09	0.13	0.20
40% prec	7.2	1.86	2.63	1.18	1.30	0.15	0.24
30% prec	7.8	1.88	2.74	1.14	1.41	0.18	0.29
10% sol	4.0	1.89	3.95	1.21	2.43	0.31	0.56

Figure 1

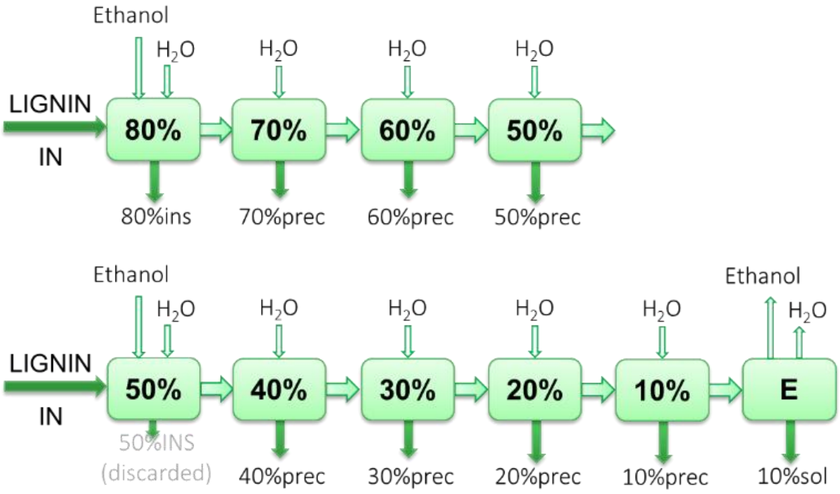

Fig. 1.

Figure 2

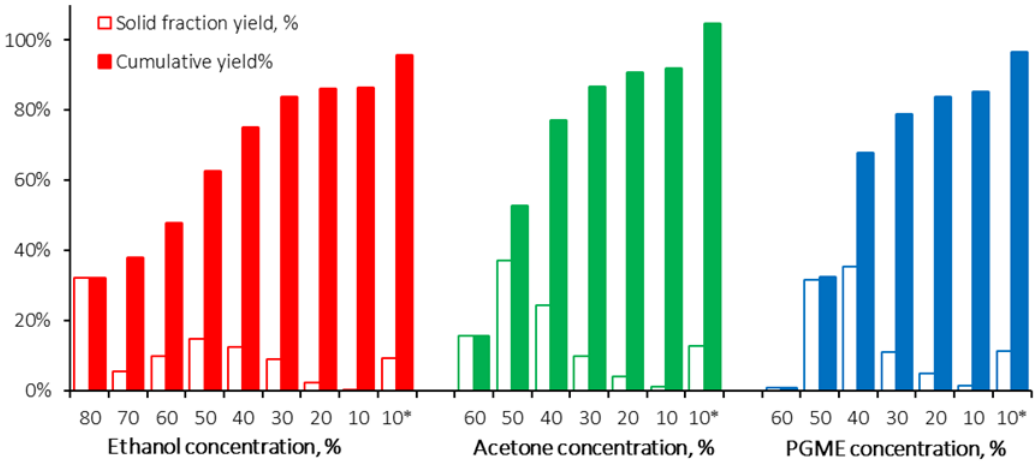

Fig 2.

Figure 3

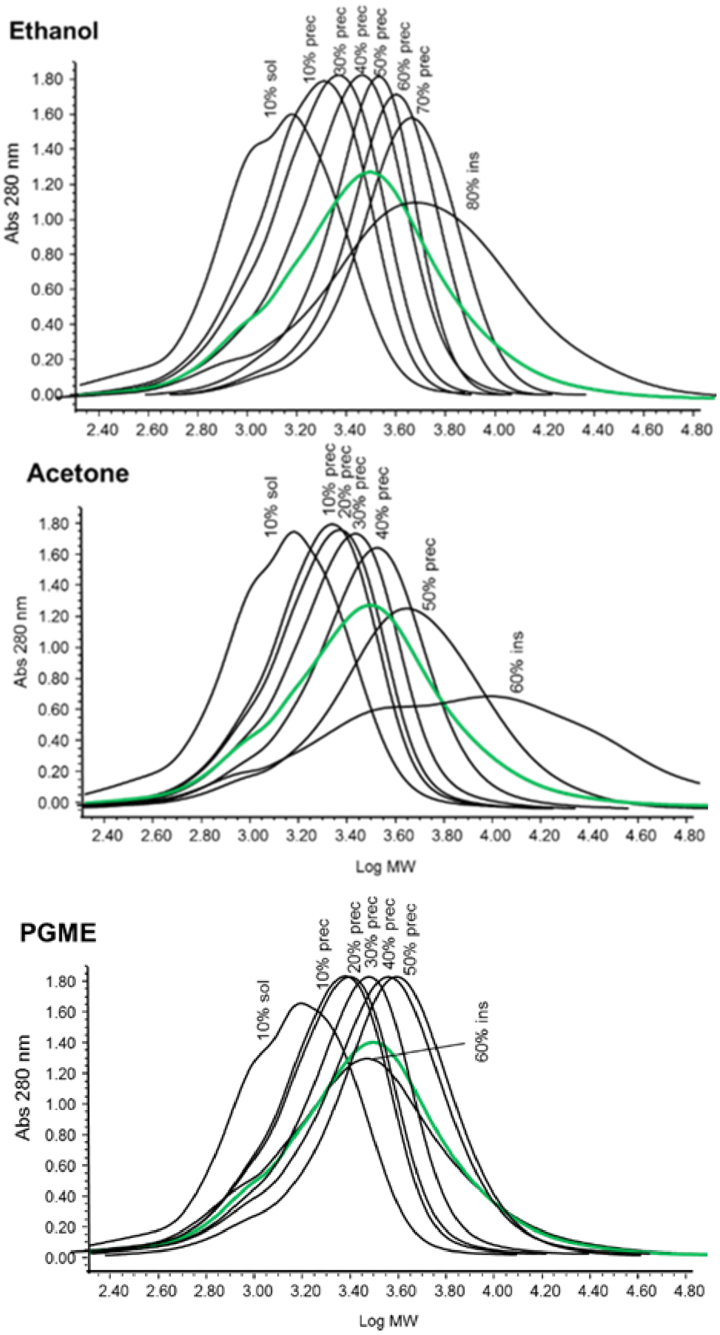

Fig. 3

Figure 4

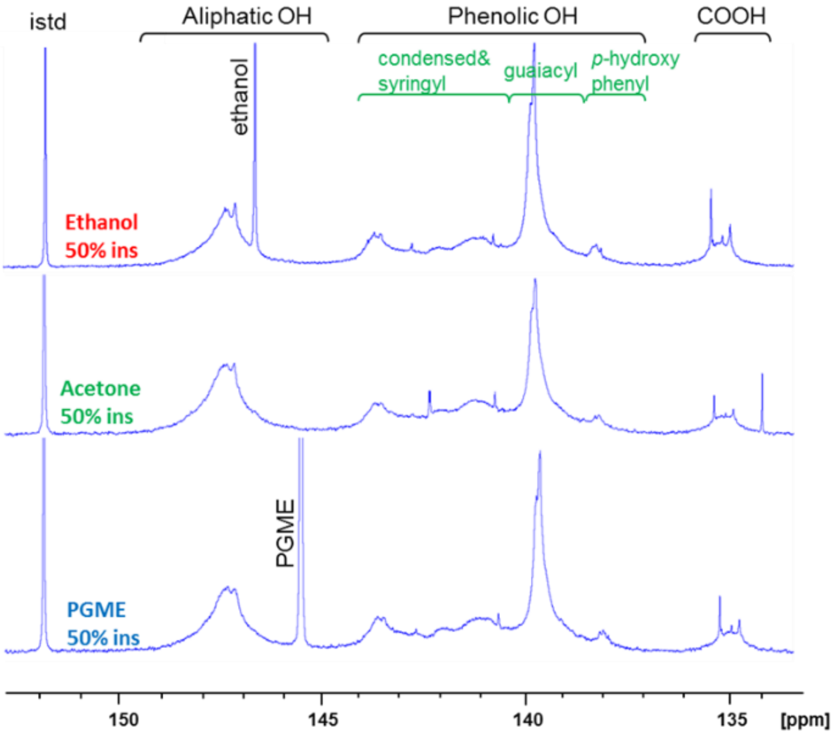

FIg 4.

Figure 5

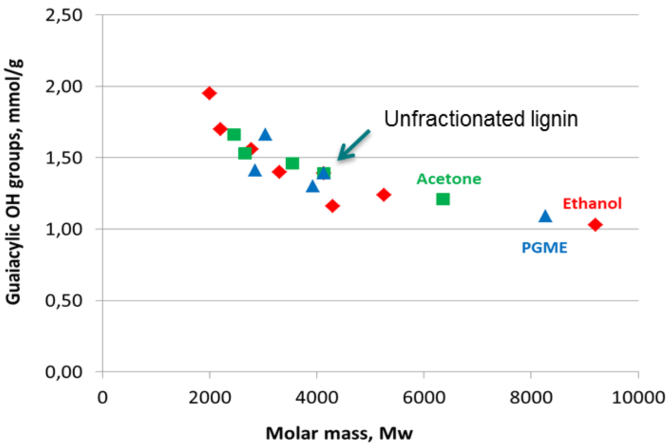

Fig 5