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FRACTIONATION OF SPRUCE TRICHLOROACETIC LIGNIN†

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ABSTRACT

Fractionation of spruce lignin isolated b trichloroacetic acid at 90°C with organic solvents shows inhomogeneity of lignin. Diethylether extracts the biggest part of isolated lignin, whereas dichloromethane extracts part of lignin with greater Mw, Mn and Mz. Extracted fractions and insoluble residues were examined by FTIR spectroscopy showing that polar solvents extract fractions with more hydroxyl groups and lower trichloroacetylation degree than less polar organic solvents.

Keywords: extraction, organic solvents, lignin, trichloroacetic acid, GPC, FTI

INTRODUCTION

In the early 1940, Schütz succeeded in delignifying spruce wood with 80% chloroacetic acid at 113°C, but he concluded tha delignification of wood with 100% chloroacetic acid is not possible due to carbonisation of wood [1]. Our investigations show that the delignification of lignocellulose with haloacetic acids has some promises to become an organosolv pulping process [2,3]. After delignification of spruce wood with trichloroacetic (TCA) acid at 90°C cellulosic fibers with kappa number 11.5 and soluble

† Dedicated to memory of Professor Anton Šebenik

lignin are isolated. Composition and molecular weight of isolated lignin are comparable to other organosol lignins [4,5]. Lignin solubilisation process with haloacetic acids follows first order kinetics at the beginning, after that kinetics slowly becomes zero order. The activation energy for the first stage of the process is 104 kJ/mol [6], which is comparable to the activation energy for cleaving α-O-4 arylether bonds [7]. Isolated lignin is trichloroacetylated on aliphatic part of the C_9 unit. During TCA lignin fractionation according to Lindquist and Kirk [8], almost all chlorine is removed as trichloroacetic acid or its salt [4]. In order to obtain some insight into the composition of TCA lignin prior to it deesterification, its fractionation with neutral solvents was performed and the fractions were analyzed by FTIR spectroscopy and GPC.

EXPERIMENTAL

Materials

Spruce wood chips were supplied fro Goričane Mill and they were prepared in accordance with the TAPPI standard T 264 om-82 (1982). Extracted chips were vacuu dried overnight at 40°C and ground in "Micro-Hammer-Cutter" grinder. Fraction of 100-200 Mesh is used as spruce wood meal.

Methods

10 g of spruce wood meal (with 4% of humidity) is mixed with 100 g of TCA at 90°C. After 240 minutes of reaction time, delignification is stopped by cooling the reaction mixture. The reaction vessel is imersed in cold water and 20 ml of cold acetone are added. Suspension is filtered and liquor is vacuum evaporated until dark, high consistency liquid without smell of acetone is obtained. Lignin is precipitated by pouring the liquid in 2000 ml cold water. Lignin is filtered off and washed with warm water several times. After that lignin is air-dried overnight at 40°C. 25.5% (calc. on o.d. wood) of lignin is recovered.

4.67 g of lignin is exhaustively extracted in a Soxhlet extractor with pentane (5 hours), followed by diethylether (20 hours), dichloromethane (20 hours), acetone (5 hours), methanol (5 hours) and water (5 hours). After each extraction the residual lignin is dried and weighed. Approx. 10 to 20 mg of residual lignin is used for measuring of IR spectra. Each extraction liquor is vacuum evaporated. The isolated fraction of lignin is weighed and approx. 10 to 20 mg of each fraction is used to measure of the IR spectra, the rest o the sample is used for GPC analysis.

Analytical methods

FT-IR spectrometry. The sample is dried overnight in vacuo at 40°C. Pellets for absorbance measuring are prepared from approx. 10 to 15 mg dried sample and 100 g KBr. Absorbance FTIR spectra are measured on Perki Elmer's FT-IR spectrometer PE FTIR System 2000. Spectra are processed with GRAMS software. Ratios are calculated from baseline-corrected and to peak height at 1510 c^{-1} normalized spectra.

Gel Permeation Chromatography. Molar masses are determined on Pl gel mixed D equipped with an identica precolumn. Mobile phase i tetrahydrofuran with 1 ml/min of flow rate at 550 psi. Concentration of samples is 0.5 mg/ml and injection loop i 20 µl. Detection is carried out on Perki Elmer's DAD detector LC-235 at 280 nm. Calibration is done using narrow Mw standard peak position. Column is calibrated with polystyrene standards with molar weights of 390000, 51000, 3600, 600 and with benzene which has molar weight 78.

RESULTS

Weight loss o trichloroacetic lignin sample during exhaustive extraction with organic solvents is presented in Table 1. On extraction of crude TCA lignin with the solvents presented in Table 1, several fractions are obtained. Ether and dichloromethane extrac more than half of crude lignin although the solubility of the extracted fractions in these solvents is low and extracted lignin precipitated during extraction. The left side o

Figure 1 presents FTIR spectra of crude TCA lignin and of residual lignin after the extraction of crude TCA lignin, whereas lignin fractions extracted with solvents mentioned in Table 1 are presented on the right side.

Table 1 Weight changes in lignin sample during extraction with organic solvents.

Solvent	Extraction time (h)	Weight loss (%)
Pentane	5	2,3
Diethylether	20	27,3
Dichloromethane	20	25,6
Acetone	5	4,6
Methanol	5	6,5
Water	5	6,6

It can be seen on the left side of Figure 1 that by extraction of TCA lignin the relative amount of hydroxyl groups (peak at 3414 cm^{-1}) and polysaccharides (characteristic peaks at 1450 and 890 cm^{-1}) is increasing in the residue, whereas the relative amount o trichloroacetyl groups (peaks at 1761, 824 and 675 c $^{-1}$), aromatic structures (peak at 1510 c $^{-1}$), guaiacyl groups (peak at 1272 c $^{-1}$), as well as ether structures (peak at 1232 c $^{-1}$) is decreasing. Peak height ratio $_{1330}/A_{1272}$ representing the ratio o sum of syringyl (S) and condensed guaiacyl ($G_{cond.}$) to guaiacyl groups is decreasing too. By extracting final lignin residue with warm water, 6,6% of acylated polysaccharides are recovered and 26,5% remains insoluble in the above-mentioned solvents.

On the right side of Figure 1, the FTIR spectra of extracted lignin are shown. Pentane extract of crude TCA lignin contains virtually no OH groups, ether extract of the residue after pentane extraction contains small amounts of OH groups and the relative amount o OH groups in extract increases with increasing polarity of the solvent. Contribution o the CH_x groups, on the other hand, is the highest in the pentane extract and decreases with increasing polarity of the solvent. Intensity of peaks indicating the presence o trichloroacetyl groups is the highest in the ether extract followed by the pentane, dichloromethane, acetone extract and is the lowest in the methanol extract. Other characteristics are as follows.

- In pentane extract, broad band around 2600 c $^{-1}$ represents hydroxyl stretching i carboxyl groups. An additional peak at 1761 shows trichloroacetylation of the extract.
- Peaks at 1703 cm^{-1} and 1677 cm^{-1} show carbonyl groups. The peak representing aromatic skeletal vibrations at 1507 is relatively weak. The signal at 1365 cm^{-1} is resolved and represents C-H in CH_3 rather then phenolic OH because of a missing signal at 3414 c $^{-1}$. The signal at 2936 representing aliphatic C-H groups is relatively high. The resolved signal at 1086 cm^{-1} represents C-O i aliphatic ether and trichloroacetylated aliphatic OH groups. The signal at 1330 c $^{-1}$ which represents the sum of syringyl units (S) and condensed guaiacyl units ($G_{cond.}$) is small and not clearly shown without using deconvolution technique. The pentane extract spectrum is very similar to the spectrum of spruce pitch treated with TC and containing some aromatic impurities [9].
- In diethylether extracts aromatic C_9 unit (peak at 1513 c $^{-1}$) highly trichloroacetylated on aliphatic part (peaks at 1761, 824 and 675 c $^{-1}$). The aromatic part has free hydroxyl groups (peak at 3451 cm $^{-1}$). The signal at 1083 cm^{-1} indicates existence of the C-O bonds, the signal at 1128 c $^{-1}$ indicates syringyl and condensed guaiacyl moeities in the fraction. The latter is supported also by a high signal at 1227 cm^{-1}. Signals at 1270 cm^{-1} to 1220 cm^{-1} are also risen due to carbonyl and carboxyl groups. The spectrum of ether extract has severa similarities with the spectrum o cinnamyl alcohol with trichloroacetylated primar aliphatic hydroxyl group.
- The spectrum o dichloromethane extract is comparable to the spectrum of the ether extract. The main difference is in different relative absorbances of peaks. The most evident difference is a relatively higher signal at 1272 c $^{-1}$ if compared to signals at 1761 cm^{-1} and 1227 cm^{-1}. The signal at 1128 cm^{-1} can be noticed indicating a few molar % o syringyl units [10] in the extract, whereas signal a 1330 cm^{-1} cannot be noticed.

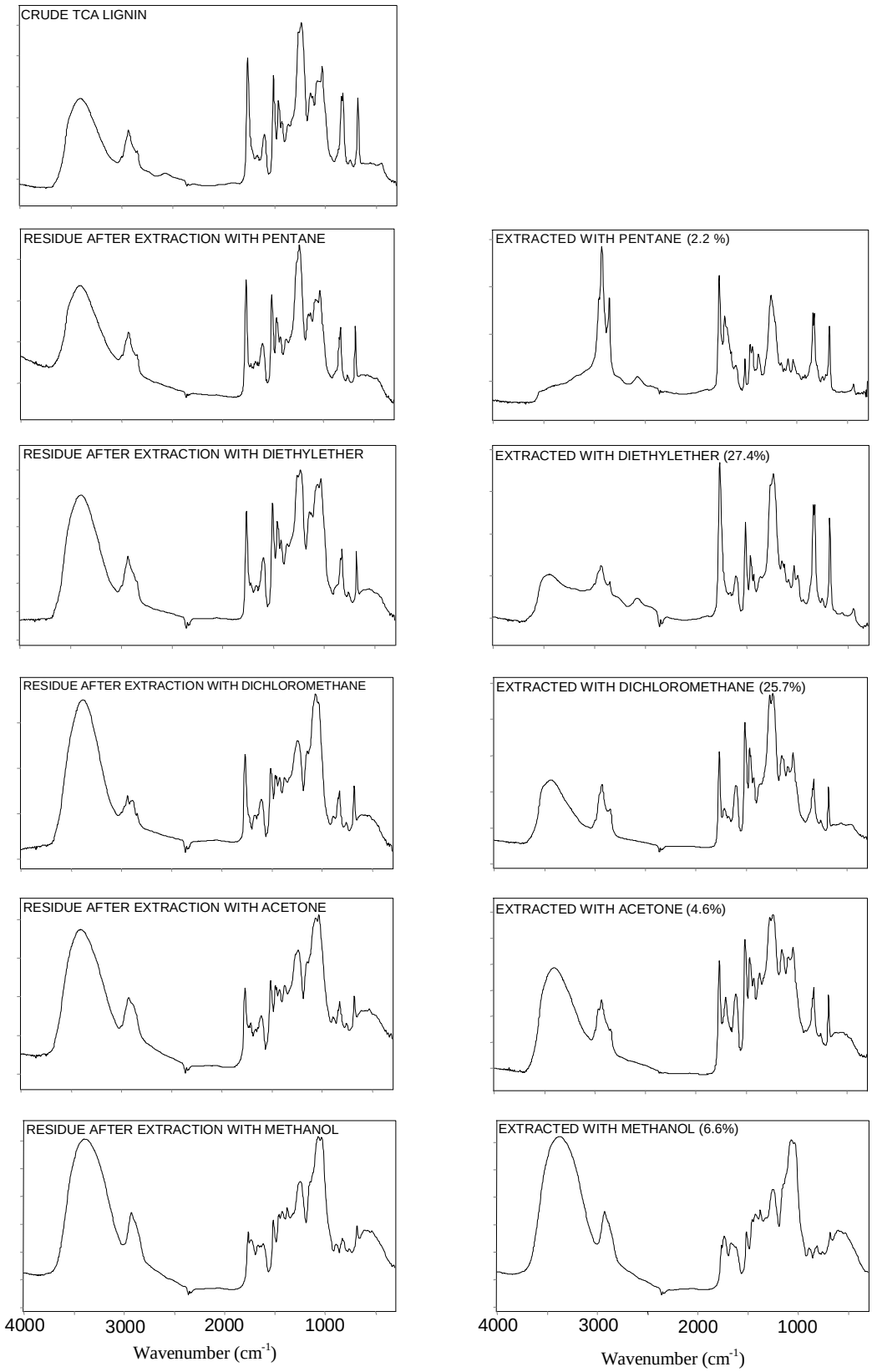

Figure 1 FTIR spectra of (left) residual lignin after extraction of crude TCA lignin in series with different solvents and (right) extracted lignin.

- In acetone extract, an intensive signal at 1698 c $^{-1}$ that may represent aliphatic aldehyde or ketone, is noticed. This part of lignin spectrum is more intensive i acetone extract than in dichloromethane extract. The resolved signal at 1365 cm^{-1} indicates phenolic OH groups. The signal at 1330 cm^{-1} which represents syringyl units (S) or condensed guaiacyl units (G) can be noticed in IR spectrum. On the other hand the signal at 1143 cm^{-1} representing guaiacyl units is clearly resolved. Intensities of signals at 1271 cm^{-1} and 1227 cm^{-1} are almost equal. Lignin is partly trichloroacetylated (peaks at 1761, 824 and 675 c $^{-1}$).
- Fraction of lignin dissolved in methanol gives rise to a signal in IR spectrum at 1730 cm^{-1} that shows nonconjugated carbonyl groups. The signal at 3414 c $^{-1}$ is relatively high, compared to the signal at 1510 cm^{-1}. Signals at 1272 cm^{-1} and 1140 cm^{-1} are unresolved, and the signal at 1030 cm $^{-1}$ is more intense comparable to the signal at 1272 cm^{-1}. Signals at 1375, 1062, 1030 and 893 cm $^{-1}$ indicate polysaccharides. The spectrum of methanol extract is similar to the spectrum o carbohydrates isolated with water.

Table 2 Molar weights and polydispersity of the extracted lignin fractions

Solvent	Mw	Mn	Mz	Mw/Mn
Crude TCA lignin	3287	1142	8138	2,88
Diethylether	2088	1032	3977	2,02
Dichloromethane	3968	1525	8329	2,60
Acetone	3440	973	7666	3,53
Purified TCA lignin	2188	1117	3573	1,96

Table 2 presents average molar weights of extracts. Dichlorometane extract is characterised by higher Mw, Mn and Mz than other extracts. Diethylether extracts lignin fraction with lowest Mw, Mn, Mz and polydispersity. On the other hand, the polydispersity of acetone extract is the highest. Compared to crude TCA lignin, the source of extracts, dichlormethane extract has higher average molar weights bu slighty lower polydispersity. According to Lundquist and Kirk [8] TCA lignin fraction obtained by purification has slightly higher Mw and Mn, and slightly lower Mz and polydispersity than ether extract of crude lignin.

DISCUSSION

When crude TCA lignin is subjected to purification according to Lundquist and Kirk [8], four fractions are obtained: ether soluble, chloroform soluble/ether insolubl , water soluble, and insoluble fraction. During this purification procedure trichloroacetyl groups are largely removed from lignin [4]. The knowledge of the distribution of trichloroacetyl groups among the lignin fractions could be of interest when trying to elucidate what is going on during TC delignification. To retain trichloroacetyl groups on fractionation of lignin, a series of neutral solvents of increasing polarity and boiling point has been applied for extraction fractionation of crude TCA lignin. The solvents were chosen to perform extraction as close as possible to the room temperature using a nonsolvent (pentane) followed by increasingly better solvents and ending with highly polar poor solvents. The results presented in Table 1 and Fig. 1 indicate that pentane removes a small lipophilic part of crude lignin and pentane extract is composed mostly of TCA-modified pitch containing predominantl nonaromati CH_x groups. TCA may thus be appropriate to delignify woods containing high quantities of pitch, lipids, and other extractives. Other solvents of the tested extraction series do fractionate the isolated lignin. Diethylether and dichloromethane remove approximately one quarter of originally present crude TCA lignin each. Approximately one quarter of originally present crude TCA lignin remains undissolved after extraction with the series of solvents presented in Table 1. Regarding MW distribution, Table 2, diethylether removes lignin fractions of lower MW and more homogeneous ones than other solvents. The more polar the solvent or the higher boiling in the series, the less homogeneous are the obtained fractions. Of the tested solvents, dichloromethane removes lignin fractions of highest MW. Better solvents like, e.g., tetrahydrofuran (THF) were not tested in this case since THF is one o the best (and thus the least selective) solvents for TCA lignin [4].

From the FTIR spectra presented in Figure 1 some typical absorbance ratios have been calculated that are presented in Table 3. Ratios in Table 3 are orientative, because carbonyl and trichloroacetyl groups may affect peaks on the mentioned wavenumbers.

The ratios of absorbance of aliphatic to aromatic CH_x groups are quite similar i diethylether-, dichloromethane-, and acetone- extracts. Thus, after removal o lipophilic matter with pentane, the mentioned solvents remove predominantly lignin-like compounds. Methanol, on the other hand, removes predominantly non-lignin matters. In the extraction residue the compounds containing aliphatic CH_x groups accumulate, bu the residue after extraction with methanol displays a lower ratio of aliphatic to aromatic groups than methanol extract.

Table 3. Absorbance ratios representing some indication of relative differences in degree o esterification, ratio of aliphatic to aromatic units, and of degree o condensations.

	Ratio of aliphatic to aromatic signals A_{2936}/A_{1510}		Esterific.of C_9 unit. A_{1761}/A_{1510}		Degree of esterific. A_{3414}/A_{1761}		Content of phen. OH groups A_{1365}/A_{1510}		Content of C-O groups A_{1086}/A_{1510}		S/G ratio A_{1330}/A_{1269} [10]	
	Res.	Ext.	Res.	Ext.	Res.	Ext.	Res.	Ext.	Res.	Ext.	Res.	Ext.
Crude Lig.	0,65		1,10		0,81		0,41		0,56		0,42	
Pentane	0,32	6,16	0,94	4,89	0,77	0,01	0,53	0,96	0,88	1,01	0,41	0,09
Ether	0,50	0,55	0,97	1,41	1,03	0,40	0,61	0,45	1,07	0,44	0,53	0,33
CH_2Cl_2	0,51	0,50	1,07	0,82	1,23	0,69	0,74	0,46	1,46	0,56	0,59	0,42
Acetone	0,72	0,50	1,00	0,91	1,26	0,85	0,86	0,70	1,53	0,77	0,63	0,57
Methanol	0,70	0,93	1,01	0,95	1,23	1,75	0,84	1,14	1,50	2,71	0,62	0,62
Residue	0,35		0,83		0,84		0,74		1,02		0,68	

The ratio of signals o phenolic OH vs. aryl (A_{1365}/A_{1510}) indicates that ether- and dichlormethane- extract contain comparable amount of aryl OH groups per C_9 unit. This ratio is high in pentane extract as a consequence of high amount of aliphatic structures. The same may be the reason for the increasing this ratio in the acetone and the methano extracts.

Regarding the degree o trichloroacetylation of C_9 units, diethylether removes lignin units esterified to a higher degree, whereas the degree o esterification of C_9 units removed afterwards by more polar solvents seems comparable.

The ratio of signals of free to trichloroacetylated OH groups in the extracts is increasing with increasing polarity of solvents in the extraction series. In the residues it increases until the extraction with dichloromethane, after extraction with acetone it becomes lower and does not change on the extraction with methanol

Spruce lignin has low syringyl content. Therefore the ratio of signals S/G (A_{1330}/A_{1269}) [10] shows mainly the ratio of condensed G vs. G groups. This ratio indicated that lignin containing guaiacyl moieties substituted on position 5 is extracted better with more polar solvents. The ratio of signals ($_{1086}/A_{1510}$) representing the ratio of ether contents vs. aromatic structures increases with the increasing polarity of the solvent, being especially high in methanol extract.

CONCLUSION

To prevent the loss o trichloroacetyl groups, trichloroacetic lignin can be fractionated b extraction using a series of neutral solvents. Pentane removes predominantly lipophilic non-lignin matters, the majority of lignin is extracted by diethylether and dichloromethane. The extracts are characterised by relatively low Mw and polydispersity. The latter is increasing with solvent polarity, whereas the degree o trichloroacetylation is decreasing. Lignin fractions having higher S/G ratio are extracted better in more polar solvents. Taking all the data together indicates that although the removal of esterified lignin fractions is an important part of the extraction-fractionation process, the process is much more complex and deserves more detailed study.

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POVZETE

Frakcionacija smrekovega lignina izoliranega z triklorocetno kislino pri 90°C z organskimi topili kaže na nehomogenost lignina. Dietilete ekstrahira največji del izoliranega lignina, medtem ko diklorometan ekstrahira del lignina z največjo Mw, Mn in Mz. Ekstrahirane frakcije in netopni ostanki so bili analizirani z FTI spektroskopijo. Rezultati analiz kažejo, da polarna topila ekstrahirajo frakcije z več hidroksilnimi skupinami in nižjo stopnjo trikloroacetilacije kot manj polarna organska topila.