

# Solvent pre-treatment of lignin for obtaining of low viscosity lignopolyols by oxypropylation for synthesis of polyurethanes

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**Abstract.** Wheat straw lignin was pre-treated by organic solvents of different polarity: ethylacetate, ethylmethylketone and ethylmethylketone/water mixture, using sequential extraction technique. The total yield of fractions was ~ 40% (w/w). In comparison with non-treated lignin the solvent soluble fractions have lower molecular weights, lower polydispersity and average functionality indices. The low viscosity lignopolyols with lignin substituent content up to 40%, suitable for rigid polyurethane foams obtaining were produced by the oxypropylation of isolated fractions. The non-soluble in organic solvents lignin residue represent a purified natural aromatic amorphous cross-linked polymer. Therefore besides oxypropylation its application as filler of thermostable polymers with enhanced flammable resistance could be beneficial biorefinery approach.

## 1. Introduction

Lignin comprising 15 – 25% of lignocellulosic feedstocks such as agricultural materials or forest resources, offer a number of attractive features as starting material for production of polymers and chemicals of aromatic nature.

The difficulties with lignin conversion into value added products is connected with high intrinsic heterogeneity of lignin in situ and its strengthening in the process of their isolation from plant tissue. Structural and functional heterogeneity of lignin is conditioned by the diversity of phenyl – propan moieties forming of lignin structure and combination of them in different ratio depending on plant origin, type of links between moieties, cross linking and severity of processes used for lignin isolation. Different approaches were used for overcoming negative impact of lignin heterogeneity incl. structural moieties (by introduction of novel additional functional groups and extension of chain) with respect to selected task and fractionation by different methods: ultrafiltration, selective precipitation, permeation chromatography.

The object of this study was combination of above mentioned approaches for obtaining of liquid polyols with enhanced content of lignin prospective for PU synthesis from pure soluble technical wheat straw lignin. The sequential extraction of lignin with solvent of increasing hydrogen – bonding capacity was used for pretreatment and obtaining of lignin fractions of reduced heterogeneity, meanwhile for following modification of fractions was realized using propylene oxide, that provide introduction of high active in reaction with isocyanate secondary OH- groups in exchange of phenolic one [1].



## 2. Experimental

### 2.1. Materials

BIOLIGNIN<sup>TM</sup> was extracted at pilot scale from wheat straw using a mixture of acetic acid/formic acid/ water at the CIMV pilot plant (Pomacle, France). Purity of the lignin was about 95% [2]. Initial BIOLIGNIN<sup>TM</sup> was washed with water to set free lignin from organic acids, then dried at 50°C and grinded. Fractions, isolated by sequential fractionation [3] of initial BIOLIGNIN<sup>TM</sup> (F0) using ethylacetate (F1), ethylmethylketone (F2) and ethylmethylketone/ water (90/10, v/v) mixture (F3) and residue (F4) were dried in oven at 70°C and after that fractions was dried in vacuum at 50°C.

### 2.2. Oxypropylation reaction conditions

The initial lignin (L) and isolated fractions were oxypropylated in 1L Parr high pressure reactor. Lignopolyols, differing by the lignin content in the initial reaction mixture from 10 to 40% (based on the dry mass of lignin), were synthesized. In all cases propylene oxide (PO), air dried lignin (5% moisture) and KOH (5% based on the dry mass of lignin) were loaded into the reactor, sealed and heated under stirring to 160 – 176 °C, when exothermic process started then heating is switched off. The reactor pressure increased and then dropped to a value close to atmospheric pressure. Showing that the reaction is over, the KOH was neutralized by acetic acid. The ensuing products were recovered of the unreacted PO by vacuum removal [3].

### 2.3. Characterization of lignopolyols obtained

The viscosities of lignopolyols was determined by means of rotation viscosimetry [HAAKE Viscotester 6L/R plus] at 25 °C. The hydroxyl index ( $I_{OH}$ ) were determined via acetylation of samples with Ac<sub>2</sub>O followed by potentiometric titration of free acetic acid in excess with 0.1 N NaOH in water. Potassium acetate (KAc) content in lignopolyols (ethanol solution) was determined by potentiometric titration (Radiometer analytical TIM 840 equipped with glass electrode) with 0.1 N HCl. The moisture of lignopolyols obtained was determined using Carl Fisher titration Coulometric KF titrator 275 KF

### 2.4. Characteristics of Lignin-PO copolymers [3]

Liquid – liquid extraction was used for lignin copolymer isolation from reaction mixture. Lignopolyol was dissolved in methanol and then hexane was added. The mixture was stirred 3h and then hexane phase was separated. Extraction with hexane was repeated one more time. Hexane was distilled and high molecular polypropylene glycols (PPG) content was determined gravimetrically. Methanol solution was concentrated using rotation evaporator. Concentrated methanol solution was precipitated in cold acidic water. Lignin - PO copolymer was filtered, washed and dried.

Lignin - PO copolymer glass transition ( $T_g$ ) temperature was determined by DSC analysis using with Mettler Toledo Star DSC823 instrument. Scans were recorded from -70°C to 200°C under N<sub>2</sub> atmosphere with a heating rate of 10 °C/min in an alumina crucible. For each experiment, 8mg dried specimens were used.

Determination of methoxyl and oxypropyl group content, is based on the Baker's method [3] where final step – detection of reaction products containing methyl iodide and isiodopropane, was change on chromatograph. The samples was mixed with hydroiodic acid in a vial with a pressure-resistant seal and heated in oil bath. The vial was cooled in ice–water and chloroform containing 1-iodopropane as an internal standard (IS) was added immediately with a syringe through the sealed cap. The reaction products and the IS were extracted with chloroform, dried over anhydrous sodium sulphate, and subjected to GC analysis.

The ratio of the peak areas of methyl iodide, isopropyl iodide to that of IS was calculated by the Agilent 6850 software. The system was calibrated with vanillin.

AU (arbitrary units): a ratio of peak area of isopropyl iodide to that of the internal standard on chromatograms.

### 3. Results and discussion

#### 3.1 The characteristics of lignin fractions

The BIOLIGNIN<sup>TM</sup> is not fully soluble in most common organic solvents (tetrahydrofuran, dioxane, acetone, ethanol, methanol, ethyl acetate and other). Sequential extraction used ethylacetate, ethylmethylketone and ethylmethylketone/water mixture allow to isolate 36% of lignin as organo-soluble fraction (the content of lignin residue (F4) after solvent pre-treatment was 64,1%) characterized by 3 times lower heterogeneity (Mw/Mn) and molecular mass and decreased of OH groups per macromolecule unit (average functionality). In the result of fractionation was obtained 3 soluble lignin fractions with reduced heterogeneity and functionality (Table 1).

Table 1.

Characteristics of BIOLIGNIN<sup>TM</sup> and isolated organosoluble fractions

Sample	Yield, %	Mn, g/mol	Mw, g/mol	Mw/Mn	M <sub>EQ</sub> , g/mol	Average functionality
BIOLIGNIN <sup>TM</sup> (F0)	100	900	17800	19,8	122	7,3
Ethylacetate fraction (F1)	11,2	270	1500	5,4	236	1,2
Ethylmethylketone fraction (F2)	9,2	380	2500	6,6	148	2,7
Ethylmethylketone/water fraction (F3)	15,5	670	4500	6,7	135	4,9

- The data of molecular weight distribution were kindly presented by RG Gosselink (Wageningen, The Netherlands)
  - Mn – number average molecular weight;
  - Mw – weight average molecular weight;
  - Mw/Mn - polydispersity index (PDI);
  - M<sub>EQ</sub> – amount of material containing 1mol of functional groups (OH groups).

It was suggested that ethylacetate (F1) and ethylmethylketone (F2) fractions with lower functionality have to give lower cross-linked polyurethanes (PU) in comparison with others samples.

#### 3.2. Lignins oxypropylation and characteristics of lignopolyols obtained

The oxypropylation of BIOLIGNIN<sup>TM</sup> and separated fractions made at different lignin/PO ratio (L/(L+PO)) (Table 2). As the result of oxypropylation reaction lignins the phenolic OH groups were transformed into secondary aliphatic OH groups high reactive towards isocyanate. Lignopolyols obtained from organic soluble fractions did not contain non-liquefied solid fractions that is significant advantage of this fractions as starting raw material for lignopolyols synthesis in comparison with unfractionated lignin (F0) or residue (F4).

Increase of lignin content in reaction mixture entail increasing of hydroxyl value (I<sub>OH</sub>) of polyols obtained providing higher activity in PU formation. Together with that increasing of potassium acetate content in obtained lignopolyols with increasing of lignin content in them was observed. The presence of catalyst (KAc) active in polyurethanes and isocyanurate formation can be considered as an advantage in preparation of high active polyurethane systems usable for processing them into rigid polyurethane (PUR) foams (Table 2).

The water content in lignopolyols is varied in the range of 0.02-0.4% that meet the requirements to polyetherpolyols suitable for PUR foams production [5].

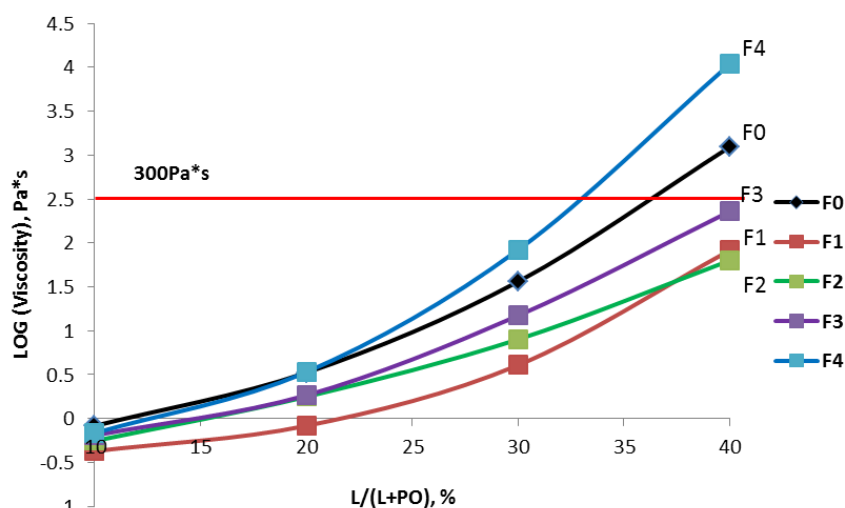
Table 2.

Characteristics of lignopolyols obtained

Sample	L/(L+PO), (w/w), %	Nonsoluble fraction, %	I <sub>OH</sub> , mgKOH/g	Moisture ×10 <sup>-2</sup> %	KAc content, %	Content %	
						Copolymer	PPG*
F0	10	1-5	245±5	6.2±0.5	1,10±0,01	21,1±1,7	25,9±1,9
	20		358,5±2,2	6.7±0.5	1,75±0,03	32,4±0,7	16,5±1,9
	30		411±5	8.00±0.20	2,44±0,07	39,10±0,10	11,8±0,6
F1	10	0,0	168±6	2.90±0.10	1,01±0,01	42,9±2,4	33,2±1,0
	20		228±4	6.8±0.3	1,56±0,01	31,9±1,7	24,70±0,20
	30		315±7	3.0±0.6	2,17±0,10	35±4	26,4±1,8
	40		352,3±1,7	4.70±0.10	2,60±0,22	38,4±2,1	23,3±1,1
F2	10	0,0	172,2±0,6	1.90±0.10	0,83±0,01	20,1±1,2	19±3
	20		254,7±2,2	2.40±0.10	1,48±0,01	50±8	20,9±1,4
	30		330,4±2,2	5.8±0.20	2,20±0,10	40,0±1,0	15±3
	40		394±4	3.30±0.10	2,86±0,02	47,3±0,20	11,1±0,7
F3	10	0,0	196±17	8.90±0.10	0,89±0,01	19±3	30±3
	20		320±12	8.00±0.10	1,64±0,01	34,7±1,5	23,7±2,6
	30		411,2±1,1	9.30±0.10	2,5±0,5	39,0±1,0	16,5±1,8
	40		463,9±1,7	5.2±0.3	3,05±0,05	41±3	9,4±0,6
F4	10	0,5-3	234±3	7.5±0.4	0,85±0,02	15,8±1,8	22,1±0,8
	20		357±5	11.70±0.10	1,69±0,02	37±6	15,7±0,9
	30		415±6	40.4±3.3	2,50±0,10	41±6	12,30±0,10

\* - High molecular hexane soluble polypropylene glycols

The lignopolyols synthesized on the basis of organic solvents soluble lignin fractions characterized with lower viscosity in comparison with viscosity of unfractionated lignin based polyols at the same lignin content in its (Figure 1).



**Figure 1.** Viscosity of lignopolyols synthesized on the basis of BIOLIGNIN™ and its fractions

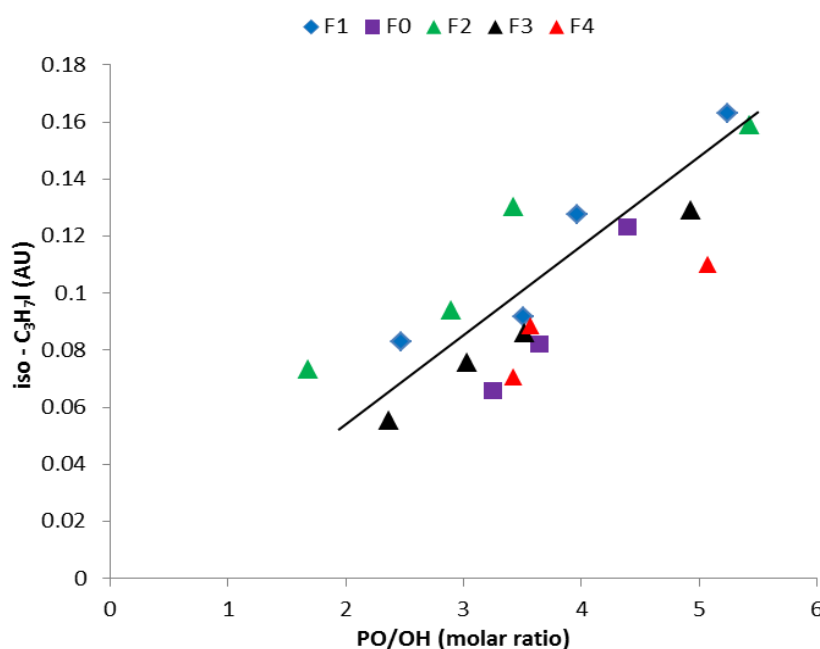
It is recognized that viscosity is one of the main characteristics of polyols determining the suitability for rigid polyurethane foam production in industry. Lignin component content in reaction mixture can be increased up 40% not exceeding 300Pa\*s recognized as a limit viscosity for polyols in PUR foam industry [6, 7]. The results obtained allow to suggest the possibility to increase the lignin constituent content in lignopolyols up to 50%.

### 3.3. Lignin-propylene oxide copolymer characteristics

It was established that the lignopolyols obtained consist from lignin - PO copolymer, high molecular PPG soluble in hexane and low molecular PPG soluble in water. With increasing of L/(L+PO) values the lignopolyols obtained were steadily enriched in copolymer fractions (Table 2).

The mass balance of process of lignopolyols extraction indicated also the presence in lignopolyols of propylenglycol and its low molecular derivatives soluble in water, but insoluble in hexane. To evaluate the extent of lignin modification in results of oxypropylation the separated lignin - PO copolymers properties were studied in more details.

GC analysis of products obtained at copolymers treatments with HI has shown that the aliphatic OH groups in copolymers are represented mainly by secondary alcohol groups. The methoxyl and isopropyl groups of copolymers were determined in one attempt. It was found that copolymer methoxyl group amount increases, with increasing of L/(L+PO) ratio.



**Figure 2.** The isopropyl iodide content in products of copolymer treatment by HI vs PO units attached to one OH group of lignin

The growth of content of isopropyl groups in copolymers is accompanied by relative decreasing of -OCH<sub>3</sub> groups due to reduction of phenylpropane unit concentration in copolymers as the result of PO grafting on to OH functionality of lignins.

The calculation made on the basis of OCH<sub>3</sub> groups content in copolymers have shown, that per one OH group of lignin 2 till 5 PO molecules are grafted (Figure 2). The degree of molar substitution decreases in the following row F4>F2>F3>F1>F0.

The decreasing of lignin-PO copolymers T<sub>g</sub> with increasing of isopropyl chain length of copolymer was established by DSC method, confirming the lignin modification

#### 4. Conclusions

In contradiction to direct BIOLIGNIN™ oxypropylation, the fractionation and following oxypropylation of lignin fractions is the attractive approach to obtain lignopolyols with increased content up to 40% of renewables in composition, but with reduced viscosity, corresponding to industrial requirements  $\leq 300$  Pa\*s. The lignopolyols obtained from fractions, isolated with organic solvent pre-treatment, do not contain non-liquefied solid fractions.

The lignopolyols obtained is consisting of lignin – PO copolymers, high and low molecular polypropylene glycols. PO grafting onto lignin OH groups was confirmed by independent physical-chemical methods: GC, FT-IR and DSC. The characterization of rigid polyurethane foams obtained from above mentioned lignopolyols is under development. The non-soluble in organic solvents lignin residue could be considered a purified natural aromatic amorphous cross-linked polymer. Therefore besides oxypropylation its application as filler of thermostable polymers with enhanced flammable resistance could be beneficial biorefinery approach. As an additional direction the carbonized material production using non-soluble lignin residue as a raw material could be proposed.

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