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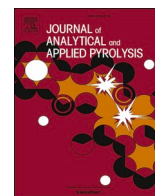


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Production of pyrolytic lignin for the phenolic resin synthesis via fast pyrolysis

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ABSTRACT

Recycling of waste wood into resol type phenol-formaldehyde (PF) resins via fast pyrolysis was demonstrated. Waste wood collected from the building demolition site in Finland was pyrolyzed with 20 kg/h circulating fluidized bed pyrolysis pilot unit. Pilot was operated with high organic liquid yield (60 wt% on average) and the produced fast pyrolysis bio-oil was fractionated by water addition into aqueous phase and water insoluble phase. The obtained fractions were characterized, and the water-insoluble viscous lignin fraction was used in the synthesis of PF-resins. Commercial phenol was successfully replaced by pyrolytic lignin fraction at 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% producing resins of low in free formaldehyde content, but resins with high replacement ratio exhibited higher viscosities. The use of H₂O/n-butanol mixture as solvent at a ratio 70:30 wt/wt% proved capable to prolong the storage time of the resin and helped to maintain the viscosity at acceptable values for at least 2 weeks before their use in the targeted application. Finally, the gluing performance of the resins was evaluated by measuring the tensile shear strength of lap joints formed by gluing 5 mm thick beech wood veneers. All the produced resins fulfilled a dry strength limit of ≥ 10 N/mm². Wet strength limit ≥ 7 N/mm² was fulfilled by the resins with the replacement ratio up 40 wt%, but resins with replacement ratio of 50 wt% had somewhat reduced wet strength. These results confirm a promising protentional application of pyrolysis derived lignin fraction in phenolic wood adhesives, at least in dry conditions.

1. Introduction

On the EU level, generation of non-hazardous waste wood from construction was approximately 8.5 million tons during 2020. Largest amount was produced in Germany (3.1 million tons), followed by Netherlands (1.6 million tons), and France (1.5 million tons). [1] Currently, the recycling rate of waste wood is low and most of it is used for energy. In some countries, waste wood is recycled into particle boards, but mainly rather clean fractions are used in these applications. [2] To increase the recycling rate of the end-of-life waste wood, utilization of chemical recycling technologies could be considered. One such technology is fast pyrolysis, where the feedstock is rapidly heated to 450 – 600 °C in the absence of oxygen and thermally degraded into small molecular mass components. Primary product is the fast pyrolysis bio-oil (FPBO), but also solid carbon rich char and non-condensable product gases are produced [3,4]. The product distribution is heavily affected by

the starting feedstock and process conditions [3].

The most mature technology for FPBO utilization is energy generation through combustion [5]. Standard EN 16900–2017, specifying the FPBO properties for the industrial boiler use, has been developed and published in 2017 [4,6]. Recently, Pyrocell and Preem have made advancements in the production of advanced biofuels through co-feeding the FPBO into a FCC system in Preems oil refinery [7,8]. Other less mature valorization pathways include hydroprocessing of FPBOs into transportation fuels [9–12], and gasification into syngas [13,14]. However, from the perspective of energy generation, the FPBOs are suboptimal due to the high oxygen and water content, poor thermal and storage stability as well as poor calorific value. Although significant advancements have been made in the production of advanced biofuels from the FPBOs, production of hydrocarbons will always need removal of most of the oxygen which is major element in FPBOs (up to 45 wt%, dry basis). Due to these reasons, applications where chemical

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characteristic and oxygen content of FPBOs are beneficial attributes are also worth to investigate further.

FPBOs are complex mixtures of different oxygenated components derived from the cracking reactions of the lignocellulosic macromolecules: cellulose, hemicellulose and lignin. In addition, extractives of lignocellulosics contribute to the FPBO yield and complexity and in the case of waste wood materials, coatings and resins, such as phenol-formaldehyde (PF) or urea-formaldehyde resins in fibreboard and plywood fractions, as well as other impurities present in wastes can increase the complexity of pyrolysis products even further [4,15,16]. Generally, the FPBO constituents can be divided into two groups. First group is the water solubles, which include polar oxygenated components such as acids, alcohols, aldehydes, ketones, phenols, furans, pyrans and mono- and oligomeric anhydrosugars. The second group is the water insolubles, which consists mainly of lignin derived oligomeric and polymeric matter, but also the water insoluble extractives such as resin acids, fatty acids and hydroxy acids. In addition to above mentioned components, FPBO includes significant amount of water, and smaller quantities of inorganic solids and ash. [17,18].

When the different fractions of the FPBO are in balance, FPBO will stay in one-phase. If bio-oil water content, for example due to high amount of feedstock moisture, is high enough, FPBO will phase separate into aqueous and organic fractions. [19,20]. Phase separation can also be forced by addition of water or it can take spontaneously place during the storage due to the aging reactions which disturb the phase equilibrium [21]. Pyrolysis of lignin rich feedstocks can also result in two-phase product due to the large amount of water insoluble components present in the produced FPBO [22]. Fractionation of the FPBO is a potential pathway, as it gives more freedom to optimize the valorization of different chemical groups present in FPBOs. For example, the water insoluble lignin fraction could be utilized to substitute phenol in the synthesis of PF-resins, which is the focus of this study.

Many different technical lignins, such as Kraft-lignin and lignosulfonates, have been used to substitute the phenol in PF-resins [23]. In addition, chemically modified lignins have been tested with the aim to increase the functionality and reactivity of lignins in the resin synthesis [24]. One such method is pyrolysis, which can reduce the molecule size of the lignin and hence increase the lignin reactivity. Several research groups have applied different bio-oils from various slow and fast pyrolysis processes to PF-resin synthesis [25–35]. In addition to the whole bio-oils, separated lignin fraction from the bio-oil has been tested. Aslan et al. (2015) substituted successfully 10 wt% of phenol by FPBO derived phenolic rich fraction in the synthesis of PF-resin. Sukhbaatar et al. (2009) separated the pyrolytic lignin from the pine wood FPBO by using mixture of water and methanol. Separated pyrolytic lignin was used to replace up to 30%, 40% and 50% of the phenol in PF resins and replacement rates up to 40% showed good performance when the resins were evaluated as oriented strand board corelayer binders. However, resins with 50% lignin replacement were found to give inadequate internal bonding.

The aim of this study was to produce FPBO from the waste wood and separate the water insoluble lignin fraction with water fractionation to be utilized in the PF-resin synthesis. Use of cheap waste wood as feedstock combined with simple water fractionation scheme could enhance the economic feasibility and sustainability of the process. In addition, the fractionation enables the separate valorization of the sugar stream, which could improve the economics even further. After the separation, lignin fraction was used in the resol type PF-resin synthesis to replace 10–50 wt% of the commercial phenol. Performance of produced resins were evaluated by gluing tests.

2. Materials and methods

2.1. Feedstock

Composition of ground and sieved starting feedstock (0.25 – 3.0 mm)

Table 1

Metal content of the feedstock (mg/kg dry basis).

Metal	Concentration	Metal	Concentration	Metal	Concentration
Al	269	Fe	109	P	51
As	125	K	278	Pb	1
Ca	1278	Mg	164	S	117
Cr	97	Mn	55	Ti	121
Cu	268	Na	134	Zn	118

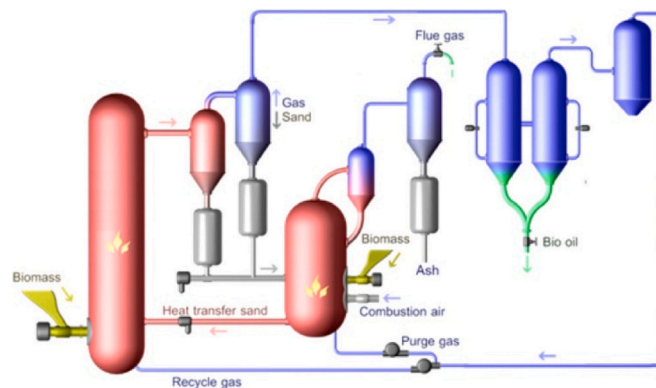


Fig. 1. Schematic flow diagram of the VTT's CFB pilot unit.

is presented in Table 3 and metal content in Table 1. Feedstock used was waste wood collected from the building demolition site located in Finland. Waste wood contained clean wood, painted/glued wood and plywood/chipwood fractions. Metal contents of the feedstocks were analyzed using microwave acid (HNO₃/HCl/HF) digestion (EN 13656:2020). Elemental composition (C, H, N, and O as difference) and ash were determined by methods SFS-EN 15104 and SFS-EN ISO 18122, respectively. Volatiles were measured by a thermogravimetric analyzer (TGA) according to the method by SFS-EN ISO 18123. The moisture content of feedstocks was followed daily during the pilot run with an Adam PMB Moisture Analyzer.

2.2. Pyrolysis and fractionation experiments

Pyrolysis experiments were carried out with the VTT's circulating fluidized bed (CFB) pilot unit with the feed capacity of 20 kg/h biomass feedstock (Fig. 1). The reactor (d = 64 mm, h = 9 m) was operated at atmospheric pressure and heated with the hot sand from the combustor. Sand used was quartz sand (0.1 – 0.6 mm, ρ = 2 600 g/dm³). The ground and sieved feedstock was introduced into the cold section of the riser reactor with a screw feeder and mixed with the cold fluidization gas stream coming from the reactor bottom. After the feedstock feeding point, feedstock particles were carried upwards by the fluidization gas to encounter the hot sand. Hot sand was fed into the reactor with a screw feeder, and the reactor temperature was controlled with the sand flow rate. After the introduction of hot sand, the mixture of solids was carried through the reactor to the cyclones. During this time, most pyrolysis reactions took place. The used pyrolysis temperature was 480 °C, and the superficial fluidization gas velocity was 7 m/s. The main part of the char particles and heat transfer sand were removed by two cyclones from the hot product gases and vapors before entering the liquid recovery system.

In the liquid recovery system, two scrubbers and one cooler were used. The vapors were condensed by using the pyrolysis liquid as a cooling agent. The temperature of the scrubbers was kept at 40 °C. A part of the non-condensable gases was used for fluidization, and the rest was burned in the combustor. Most of the ash from the feedstock ended with the char in the combustor. The combustor was operated as a bubbling fluidized bed, and the temperature was controlled to 700 °C by

feeding ground pellets into it. After the combustor, one cyclone and a hot gas filter were used to remove the fine dust and fly ash from the flue gases. Before the hot gas filter, flue gas was cooled to $< 250\text{ }^{\circ}\text{C}$ using a tube heat exchanger and water quench. Product yields are reported on the dry basis of the starting feedstock.

After the pyrolysis experiment the FPBO fractionation was carried out in 100 L Teflon coated vessel equipped with mixer. FPBO and water were weighted in the vessel to reach mass ratio of water and dry FPBO 1:1 and mixed for 1 h at room temperature. After mixing the phases were let to settle. Aqueous phase, i.e., the top phase, was removed by a pump and the water insoluble viscous lignin bio-oil fraction was emptied from the valve located at the bottom of the vessel.

2.3. Analytical methods for pyrolysis products

Physical characterization of the FPBO was carried out by employing modified standard methods [36]. The water content was analyzed by Karl Fischer titration using a Metrohm 795 KFT Titrino titrator (ASTM E 203). Elemental composition (CHN) was analyzed using an Elementar VARIOMAX CHN analyzer (ASTM D 5291), and the higher heating value (HHV) was measured using an IKA Werke C 5000 Control calorimeter (DIN 51900). The total acid number (TAN) comprising of carboxylic acid number (CAN) and phenolic number (PN) was determined with a 785 DMP Titrino analyzer (modified ASTM D 664), and the micro carbon residue (MCR) was determined using an Alcor Micro Carbon Residue Tester (ASTM D 4530). The ash content of the liquid was determined by combusting the residue from the MCR determination in a muffle furnace at $775\text{ }^{\circ}\text{C}$. The inorganic content of the liquids was analyzed according to standards DIN 51727 B:2011 (Cl) and DIN EN ISO 11885:2009 (other inorganics).

Once the water insoluble lignin fraction was separated from the FPBO, molecular weight, and aliphatic and phenolic OHs, as well as acid content of the separated lignin bio-oil were analyzed. For additional analyses lignin bio-oil (water insoluble) fraction was divided into DCM (dichloro methane) soluble and DCM insoluble fractions according to Oasmaa et al. [37]. Similarly, water soluble fraction was further fractionated into ether soluble and ether insoluble fractions. Molecular weight was determined for all fractions and low molecular weight compounds by gas chromatography/mass spectrometry GC/MS for DCM soluble and ether soluble fractions.

For the molar mass measurements, the samples were dissolved in 0.1 M NaOH and filtered ($0.45\text{ }\mu\text{m}$). The molar mass measurements were performed with size exclusion chromatography (SEC) using 0.1 M NaOH eluent (pH 13, 0.5 mL/min , $T = 25\text{ }^{\circ}\text{C}$) and PSS MCX 1000 & 100000 Å columns. The elution curves were detected using Waters 2998 Photodiode Array detector at 280 nm. The molar mass distributions (MMD), number average molar mass (Mn), weight average molar mass (Mw) and polydispersity (PD) were calculated against polystyrene sulphate standards (eight standards with a range of $3420\text{--}148,500\text{ g/mol}$) and using Waters Empower 3 (Milford, MA, USA) software. Phenolic and aliphatic hydroxyl groups and acids were analyzed by ^{31}P NMR. For ^{31}P NMR analyses, each pyrolysis lignin sample was accurately weighted (25 mg) and dissolved in N, N-dimethylformamide ($150\text{ }\mu\text{L}$) in 4 mL vial. After total dissolution, pyridine ($100\text{ }\mu\text{L}$), internal standard solution (ISTD) (200 μL) endo-N-Hydroxy-5-norbornene-2,3-dicarboximide (e-HNDI, 0.005 mmol) in pyridine/ CDCl_3 (1.6/1, v/v) and $\text{Cr}(\text{acac})_3$ solution ($50\text{ }\mu\text{L}$) (11.4 mg/1 mL) in pyridine/ CDCl_3 (1.6/1, v/v) were added. Then, phosphitylation reagent ($150\text{ }\mu\text{L}$) 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane [P.R.(II)] was added dropwise. Finally, CDCl_3 ($300\text{ }\mu\text{L}$) was added to the solution and clear brown to black solution was achieved. Freshly prepared samples were measured with ^{31}P NMR immediately after preparation at room temperature. Bruker 500 MHz NMR spectrometer was used for the measurement. Chemical shifts are reported relative to the sharp signal (132.2 ppm) originating from the reaction between water and P.R. II. Following NMR parameters were used: scans = 1024, pulse delay = 5 s, 90° pulse and line

broadening = 2 and default baseline correction. ^{31}P NMR measurement is based on the method developed by Granata and Argyropoulos [38].

Water soluble low molecular weight compounds were determined directly from the water extract by using Agilent 7890 A GC combined with an Agilent 5977B mass selective detector (MSD). Separation of compounds was performed applying a high polarity fused silica capillary column J&W HP-INNOWax ($60\text{ m} \times 0.25\text{ mm}$, film thickness $0.25\text{ }\mu\text{m}$) by using carrier gas (Helium) flow of 1.2 mL/min . The oven temperature program was following: initial temperature of $60\text{ }^{\circ}\text{C}$ was held 1 min, then the column was heated to $230\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C/min}$, and kept at this temperature for 30 min. The compound detection with mass scan range of m/z between 27 and 300 (EI 70 eV) was used. Before analysis internal standards 1-butanol and isovaleric acid were added to the sample. For the quantification, calibration solutions of compounds in the range of $10\text{--}200\text{ mg/l}$ were prepared.

Low molecular weight pyrolysis derivatives of polysaccharides and lignin were analysed as their trimethylsilyl derivatives with an Agilent 7890 A GC equipped with an Agilent 5975 C inert MSD and a DB-5 MS capillary column ($30\text{ m} \times 0.25\text{ mm}$, film thickness $0.25\text{ }\mu\text{m}$) by Borrega et al. [39]. For the separation of compounds oven temperature program was following: 1 min at $70\text{ }^{\circ}\text{C}$, $10\text{ }^{\circ}\text{C/min}$ to $300\text{ }^{\circ}\text{C}$, and 10 min at $300\text{ }^{\circ}\text{C}$ and carrier gas (Helium) flow was 0.9 mL/min . The compound detection with mass scan range of m/z between 40 and 800 (EI 70 eV) was used. The MS identifications were based on the use of a commercial Wiley database and reference literature [40]. Before analysis water soluble sugar fraction and DCM soluble lignin fraction were dried. Thereafter, 5 mg of sample and internal standard were trimethylsilylated in pyridine (0.2 mL) with 0.2 mL of N,O-bis(trimethylsilyl) trifluoroacetamide, containing 10% of trimethylchlorosilane. Semi-quantitative analysis of major compounds present in sample were done using salicylic acid (20.0 g/l) and D-(+)-arabitol (20.1 g/l) as the internal standards for lignin and polysaccharide derivatives, respectively.

2.4. Preparation of PF and Lignin-PF resins

The isolated lignin bio-oil was used for the synthesis of PF-resins. Sodium hydroxide, paraformaldehyde, formaldehyde (solution 39%w/v), phenol and n-butanol were of reagent grade and used as received. PF resins were prepared in a five-neck glass reactor apparatus equipped with a temperature sensor for continuous temperature control, vertical condenser, adjustable mechanical stirrer, and heating mantle. The steps followed for the synthesis of the PF resins are described below:

I. Phenol, paraformaldehyde (or formaldehyde solution), lignin bio-oil (in case of resins with partial phenol replacement) and solvent were loaded in the reactor. The mixture was homogenized for 30 min with constant stirring and heated up to $40\text{ }^{\circ}\text{C}$ to dissolve the reagents.

II. The first part of NaOH solution 50 wt% (1/3 of total amount) was added dropwise and the temperature was kept below $100\text{ }^{\circ}\text{C}$. After the addition of NaOH was completed, the mixture was heated gradually up to $90\text{ }^{\circ}\text{C}$ (during 30–40 min). When the temperature reached $90\text{ }^{\circ}\text{C}$, the mixture was kept under stirring for 60 min and then cooled down to $60\text{--}70\text{ }^{\circ}\text{C}$.

III. With the reaction mixture at $60\text{ }^{\circ}\text{C}$ the second part of NaOH solution (2/3 of total amount) was added dropwise and the mixture was heated up to $100\text{ }^{\circ}\text{C}$ under stirring. Again, the temperature was increased stepwise, as the temperature control is critical. The temperature was gradually increased during 30–40 min and it was maintained to $100\text{ }^{\circ}\text{C}$ for 1 h, until the free formaldehyde reached the desirable value (lower than 2.3% w/w).

IV. When the free formaldehyde content was below 2.3%, the mixture was cooled to room temperature and discharged. At the final cooling step, it is desirable to achieve a quick decrease of the temperature (preferably during 30 min), considering that it is critical to decrease the rate of the polycondensation reaction. Following the described synthetic route, the overall time required for the synthesis of lignin bio resin is approximately 5–6 h.

Table 2
Mass balances from the pyrolysis pilot experiment.

Stage	Length, h	Feed, kg/h	Temp. °C	Organic liquids, wt% db	Pyrolytic water, wt% db	Gases, wt% db	Char by difference, wt% db
1	40	18.7	483	57.9	12.1	11.1	18.9
2	40	20.4	480	62.0	11.3	11.0	15.7

db = dry basis

Table 3
Analyses for the feedstock used in the pilot experiment, for the FPBO and for the coke causing the blockages on wet basis.

Sample	Feedstock	FPBO	Coke in pump lines
Moisture/water, wt%	5.2	20.3	n.m.
Ash, wt%	0.8	0.06	n.m.
C, wt%	50.8	42.9	58.8
H, wt%	6.1	7.3	6.3
N, wt%	0.6	0.5	1.3
HHV, MJ/kg	20.22	18.23	n.m.
LHV, MJ/kg	18.89	16.65	n.m.
Volatiles, wt%	80.1	n.m.	n.m.
Solids, wt%	n.a.	0.1	n.a.
TAN, mg KOH / g	n.a.	140	n.a.
CAN, mg KOH / g	n.a.	65	n.a.

n.m. = not measured, n.a. = not applicable

Finally, the resin was stored in a closed container and kept at room temperature.

2.5. Resin characterization and gluing validation

The produced resins have been characterized by assessing their free formaldehyde content, non-volatile content, viscosity, and pH. The pH value was measured with a Jenway 570 pH Meter. The viscosity was determined using a Brookfield RV DV-II+ Pro viscometer and the non-volatile content was measured using a Kern DBS moisture analyzer. Free formaldehyde was determined by titration using the ISO 11402 – Hydroxylamine hydrochloride method, and IR spectra were recorded in a Bruker ALLPHA II FT-IR spectrometer.

The gluing performance of the resins was evaluated by measuring the tensile shear strength of lap joints formed by gluing 5 mm thick beech wood veneers (EN 205:2003). The resin to be tested was applied at 150 g/m² to both surfaces to be glued together and then in a hotplate press the laminate was cured at 200°C and 20 bar for 5 min. Before cutting out the glued wood samples to be tested, the laminated wood was equilibrated at 20°C and 65% relative humidity for 7 days. Samples for humidity resistance were immersed in deionized water at 20°C for 24 h before testing. The breakage tensile force was measured on an Instron dynamometer 5569.

Table 4
Yield of different fractions from the fractionation of the pyrolysis oil by water addition.

	Moisture	C	H	N	O	Total quantity	Water	Organics	Yield of organics, dry basis
	wt%	wt% dry	wt% dry	wt% dry	wt% dry	kg	kg	kg	wt% dry
<i>Materials IN</i>									
FPBO	17.5	52.0	6.4	0.6	41	46.4	8.1	38.3	-
Water	100	-	-	-	-	30.2	30.2	0.0	-
SUM	-	-	-	-	-	76.6	38.3	38.3	-
<i>Materials OUT</i>									
Aqueous fraction	58.7	48.7	5.2	1.3	45	62.2	36.5	25.7	67.1
Water insoluble fraction (lignin bio-oil)	11.5	66.8	6.7	0.9	26	13.7	1.6	12.1	31.7
SUM	-	-	-	-	-	75.9	38.1	37.8	98.8

3. Results and discussion

3.1. Pyrolysis experiments

Totally 100 h long pilot experiment was carried out where 80 operational hours in two continuous 40-hour periods was reached, with 20-hour maintenance break between the operational periods. Pilot was operated with high organic liquid yield (60.0 wt% of dry feedstock on average) which was comparable with high quality feedstocks, such as pine saw dust or de-ashed straw [17,19,20,41,42]. Average yields of pyrolytic water, gases and char were 11.7, 11.1 and 17.3 wt%, respectively (Table 2). Yields of these by-products were also on the similar levels with high quality biomass feedstocks. Thus, it can be stated that the performance of the pilot in respect to product yields was on excellent level.

However, the maintenance break during the pilot run was not planned and it was caused by the blockages in the liquid recovery system. Extensive amount of coke was formed in the first scrubber where the hot vapors were cooled and condensed. These solids blocked the top part of the scrubber and the pump lines in the scrubber bottom. During the maintenance break, the system was cleaned, but the phenomena repeated itself during the second 40 h operational period. The solids were analyzed after the experiment, and it was found out that the nitrogen content of the solids was higher than in the feedstock and in the FPBO (Table 3). One possible explanation could be that the nitrogen containing resins in demolition wood are contributing to the solids formation. Although solids and coke formation in the scrubber is typical when the hot vapors are cooled down, this extensive solid formation has not been observed previously with biomass feedstock.

3.2. Fractionation of pyrolytic lignin

Fractionation of water insoluble lignin bio-oil was carried out by water addition into the pyrolysis oil. The results are presented in Table 4. Totally, 46.4 kg of pyrolysis oil with water content of 17.4 wt% was mixed with 30.2 kg of water resulting in the water/organics ratio of 1:1. After mixing and settling, 62.2 kg of aqueous fraction and 13.7 kg of water insoluble lignin bio-oil fraction was obtained. If the division of the pyrolysis oil organics is considered, 31.7 wt% of organics was captured within the water insoluble lignin bio-oil fraction, meaning that 67.1 wt% of the organics were deposited on the aqueous fraction. Organics of the aqueous fraction were richer in oxygen compared to water insoluble fraction (45 wt% vs. 26 wt%), whereas the water insoluble fraction was richer in carbon (66.8 wt% vs. 48.7 wt%). Results are logical, as the

Table 5
Identified GC-eluted organic compounds in different FPBO fractions.

Compounds	In dry FPBO, wt %	Compounds	In dry FPBO, wt %
Water soluble aqueous phase		Water insoluble lignin bio-oil	
Light volatiles	37.8	DCM soluble (LMW lignin and extractives)	22.3
Alcohols and acids	9.3	Lignin derived monophenols	0.9
<i>Methanol</i>	0.6	<i>Hydroxyphenylethanol</i>	0.07
<i>2-Propanol</i>	2.1	<i>Hydroquinone</i>	0.03
<i>Acetic acid</i>	6.14	<i>Catechol</i>	0.09
<i>Propionic acid</i>	0.36	<i>4-Methylcatechol</i>	0.08
<i>Isobutyric acid</i>	0.02	<i>3-Methylcatechol</i>	0.02
<i>Butyric acid</i>	0.06	<i>Guaicol</i>	0.03
<i>Pentanoic acid</i>	0.02	<i>4-Methylguaiaicol</i>	0.07
<i>Hexanoic acid</i>	0.04	<i>4-Ethylguaiaicol</i>	0.02
Aldehydes, ketones, furans, pyrans	12.5	<i>Eugenol</i>	0.04
<i>Acetaldehyde</i>	0.18	<i>Isoeugenol</i>	0.11
<i>Glycolaldehyde (dimer)</i>	7.38	<i>Vanillin</i>	0.08
<i>2-Propanone</i>	0.08	<i>Vanillic acid</i>	0.05
<i>2-Butanone</i>	0.02	<i>Acetylguaiaicol</i>	0.04
<i>1-Hydroxy-2-propanone (acetol)</i>	2.40	<i>Guaiaicylacetone</i>	0.03
<i>1-Hydroxy-2-butanone</i>	0.21	<i>Dihydroconiferyl alcohol</i>	0.04
<i>1,2-Cyclopentanedione</i>	0.04	<i>Coniferylaldehyde</i>	0.10
<i>3-Methyl-1,2-cyclopentanedione</i>	0.16	Dilignols	0.09
<i>Furfural</i>	0.18	<i>4,4'-Dihydroxy-3,3'-dimethoxystilbene</i>	0.09
<i>5-Methylfurfural</i>	0.02	Anhydrosugars	0.19
<i>5-Hydroxymethylfurfural</i>	0.34	<i>1,6-Anhydro-β-D-mannopyranose</i>	0.05
<i>2-Acetylfuran</i>	0.03	<i>1,6-Anhydro-β-D-glucopyranose (Levogluconan)</i>	0.14
<i>2-Furanmethanol</i>	0.03	Extractives and derivatives	0.58
Lignin derived monophenols	0.71	<i>Nonadioic acid</i>	0.03
<i>Phenol</i>	0.03	<i>Oleic acid</i>	0.06
<i>2-Methylphenol</i>	0.01	<i>Pimaric acid</i>	0.05
<i>3-Methylphenol</i>	0.01	<i>Isopimaric acid</i>	0.03
<i>4-Methylphenol</i>	0.03	<i>Palustric acid</i>	0.02
<i>Guaiaicol</i>	0.15	<i>Dehydrodehydroabietic acid</i>	0.05
<i>4-Methylguaiaicol</i>	0.11	<i>Dehydroabietic acid</i>	0.19
<i>4-Ethylguaiaicol</i>	0.01	<i>Abietic acid</i>	0.07
<i>Eugenol</i>	0.02	<i>7-Oxodehydroabietic acid</i>	0.08
<i>Isoeugenol</i>	0.13	<i>Unidentified LMW compounds in LMW lignin</i>	0.29
<i>Vanillin</i>	0.18	DCM insoluble (HMW lignin)	9.7
<i>Syringol</i>	0.02		
<i>4-Methylsyringol</i>	0.01		
Ether insoluble (Sugar-like)	30.2		
Alcohols, acids, aldehydes	0.87		
<i>Ethylene glycol</i>	0.13		
<i>Glycolic acid</i>	0.19		
<i>Glycolaldehyde dimer</i>	0.31		
<i>2,5-Dihydroxypentanoic acid</i>	0.08		
<i>1,4-anhydro-3-deoxypentitol-2-carboxylic acids</i>	0.16		
Anhydrosugars	1.88		
<i>1,6-Anhydro-β-D-galactopyranoside</i>	0.07		
<i>1,4-anhydro-D-galactopyranose</i>	0.03		
<i>1,6-Anhydro-β-D-mannopyranose</i>	0.34		

Table 5 (continued)

Compounds	In dry FPBO, wt %	Compounds	In dry FPBO, wt %
<i>1,6-Anhydro-β-D-glucopyranose (Levogluconan)</i>	1.45		
<i>Cellobiosan</i>	0.29		
<i>Cellobiose</i>	0.03		
<i>Unidentified LMW compounds in sugar fraction</i>	1.41		

water-soluble organics in pyrolysis oils typically contain polar oxygen rich compounds, such as sugar derivatives, acids, aldehydes, ketones, furans and pyrans. On the other hand, water insoluble lignin fragments with varying molecular size are richer in carbon [17].

For the detailed chemical characterization by GC/MS and molecular mass analyses, the obtained water soluble and insoluble fractions were further solvent fractionated according to Oasmaa et al. [37]. The water insoluble lignin bio-oil was further extracted with DCM to obtain DCM soluble and DCM insoluble fractions. The quantity of DCM soluble fraction was higher than the DCM insoluble fraction. The DCM soluble fraction was lower in molecular weight compared to the DCM insoluble fraction and contained the major proportion of lignin monomers and the extractives of the FPBO (Table 5). In addition, aqueous fraction was divided into ether soluble light volatiles and ether insoluble sugar rich fractions. The content of ether soluble fraction was slightly higher than the ether insoluble fraction. As expected, this ether soluble fraction was lower in molecular weight compared to the ether insoluble fraction. Ether soluble fraction was enriched with low molecular weight oxygenates (acids, alcohols, ketones, aldehydes, and furans) whereas ether insoluble contained anhydrosugars and oligomeric fragments of polysaccharides. Small quantity of lignin derived products could be determined from the water-soluble fraction due to the hydrophilicity of certain phenolic compounds. Whereas small quantity of anhydrosugars were determined from the DCM soluble fraction indicating the incomplete separation of the water soluble and water insoluble fragments. Further washing of water insoluble fraction with water would probably improve the purity.

The utilization of the aqueous phase was not in the scope of this project but is an important aspect when the whole concept is evaluated. Based on the composition, one robust utilization pathway could be aqueous phase reforming of organics into hydrogen [43], but also further solvent fractionation to separate valuable chemicals could be considered. Recently, several research groups have used different water insoluble ionic liquids to separate components such as phenolics and aromatics [44–46] as well as acetic acid, glycolaldehyde and acetol [47] from the pyrolysis derived aqueous phases. In addition, more conventional organic solvents such as toluene to separate phenolics [48], ethyl acetate to separate acetic acid [49] or n-butanol to separate furfural, 5-HMF, weak acids and phenolics [50] has been evaluated. Sugar rich fraction could be suitable for fermentation processes [46,50].

In addition, the weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PD) were analyzed for all FPBO fractions (Fig. 2 and Table 6). Aqueous fraction contained lower molecular weight components as expected. Biomass lignin on the other hand was converted into low molecular weight fragments in pyrolysis ($M_w = 1681$ Da, PD = 3.8). Therefore, the average molecular weight of lignin was rather low compared to molecular masses of Kraft lignin. For example, Crestini et al. [51] reported $M_w = 6000$ and PD = 6.2 for soft wood Kraft lignin. The low molecular weight with narrow polydispersity value can enhance the reactivity of lignin in resin synthesis.

Furthermore, for the extracted water insoluble lignin fraction, aliphatic and phenolic OH's were analyzed by P NMR (Table 7 and

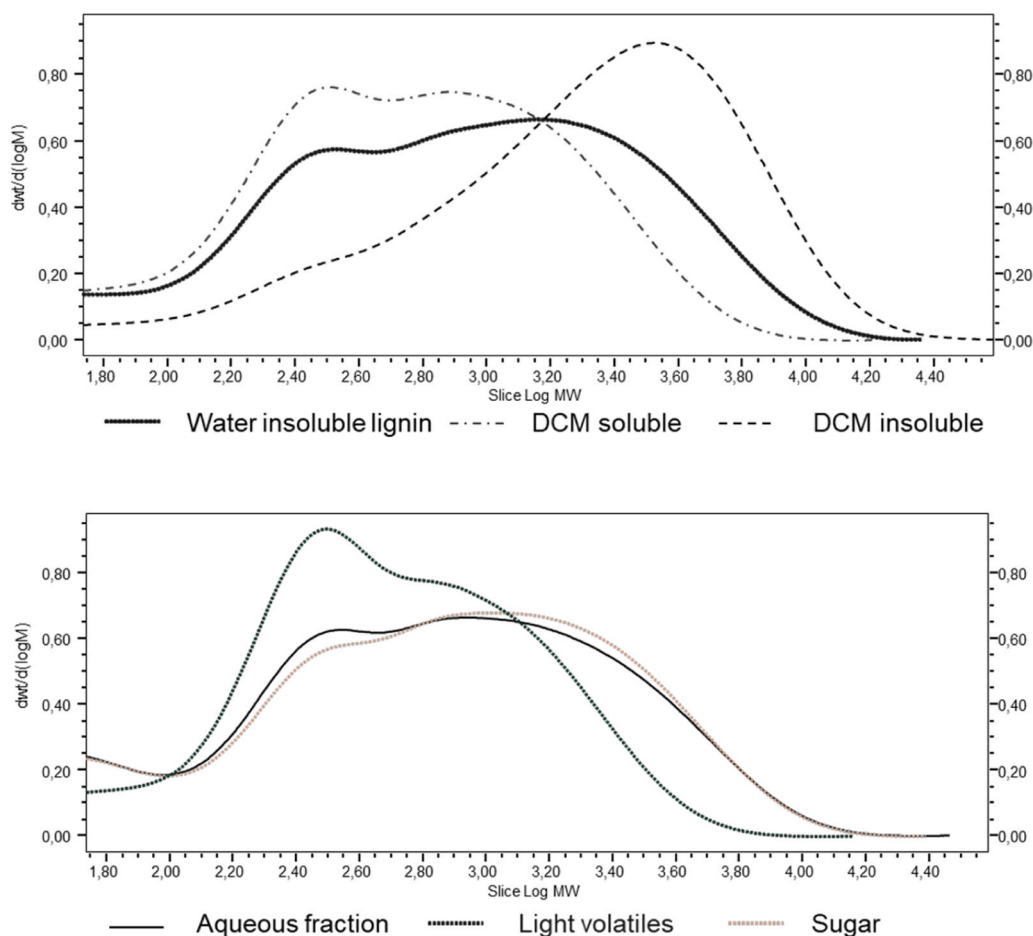


Fig. 2. Molecular masses of the different FPBO fractions. LMW = low molecular weight, HMW = high molecular weight.

Table 6

Number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity (PD) for the FPBO fractions.

	Mn	Mw	PD
Water insoluble lignin	441	1681	3.8
DCM insoluble	880	3241	3.7
DCM soluble	362	1018	2.8
Aqueous fraction	385	1476	3.8
Light volatiles	345	840	2.4
Sugars	394	1505	3.8

Fig. 3) to determine reactive sites for the crosslinking reactions with formaldehyde and for the chemical adjustment. For the reaction of lignin with formaldehyde, free ortho positions in aromatic ring are required. Based on the NMR results lignin contained four different phenolic OH's in which the *p*-hydroxyphenyl, catechols and guaiacyl type phenolic OH's contained the important reactive sites. The number of reactive sites in lignin was 3.11 mmol/g.

Table 7

Aliphatic and phenolic OH's (mmol/g lignin) of the water insoluble lignin bio-oil.

	Aliphatic OH	Carboxylic acid	Condensed + syringyl OH	Guaiacyl	Catechols	<i>p</i> -OH-phenyl	Reactive sites
pyrolysis lignin	1.63 ± 0.11	0.62 ± 0.02	1.12 ± 0.06	0.91 ± 0.02	0.96 ± 0.06	0.38 ± 0.03	3.11 *

* Reactive sites calculated from the guaiacyl, catechol and *p*-OH phenyl type units.

3.3. Resin synthesis

The synthesized phenol formaldehyde resins have a formaldehyde: phenol ratio greater than 1. This type of phenol formaldehyde resins is known as resoles. Synthesis of resoles is base-catalyzed. Base (NaOH) deprotonates phenol resulting in the formation of phenoxides, which are the reactive species. Delocalization of the formed negative charge, over the aromatic ring, activates the ortho- and para-sites of the phenolic ring, which react with formaldehyde and form the polymer chain. Water is used as solvent in the synthesis of phenol formaldehyde resin, since the final resin is water soluble. Additionally, under basic conditions the hydration of formaldehyde (which is produced from the depolymerization of paraformaldehyde) takes place, leading to the formation of methylene glycol, a key monomeric species[52]. Lignin bio-oil with water content of 11.5%wt was used as received. The main organic compounds contained at lower concentrations in lignin bio-oil, such as organic acids, alcohols and ketones (e.g., acetic acid, glycolaldehyde) can participate in the polycondensation reaction under the synthesis conditions and be incorporated in the polymer chain (Fig. 6)[53]. The produced PF resins had a light reddish colour. On the other hand, the replacement of phenol with water insoluble lignin fraction, even at the lowest ratio used (10 wt%), resulted in a dark brown and not transparent

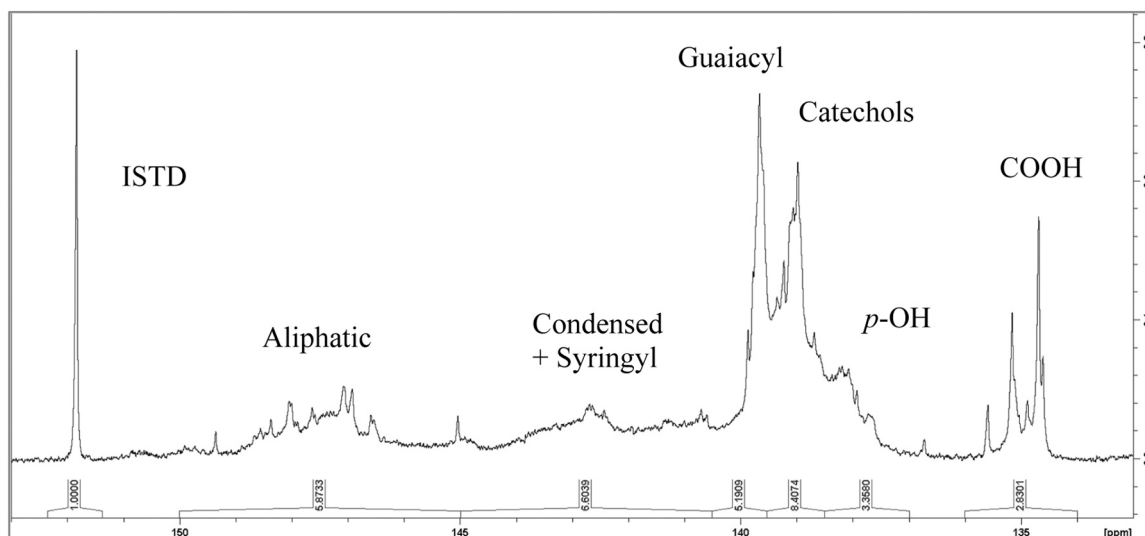


Fig. 3. NMR spectra of water insoluble lignin bio-oil.

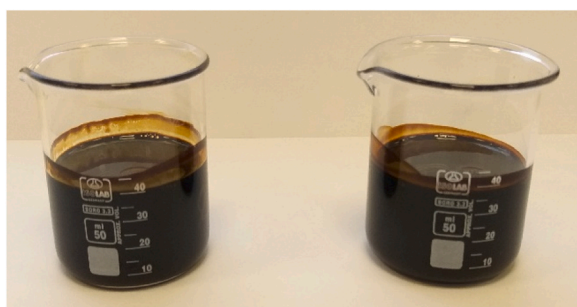


Fig. 4. Examples of PF-lignin bio-oil resins with 50% replacement of phenol with lignin bio-oil.

resin, similar to the lignin fraction (Fig. 4). Initial experiments (Table 8, trials 1–6) were focused on the optimization of the synthesis conditions (e.g., reaction time, reagents' ratio) of the PF resin. Having determined the optimal experimental conditions, phenol was gradually replaced by lignin bio-oil, and PF resins containing lignin bio-oil at 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% (in relation to the mass of phenol), were successfully produced. The molar ratio of formaldehyde to phenol varied from 1.7:1 up to 2.8:1 and the molar ratio of phenol to sodium hydroxide varied from 2.8:1 up to 3.3:1. The results obtained from the characterization of the produced resins are presented in Table 8.

Both formaldehyde sources (paraformaldehyde and formaldehyde solution) were effective under the tested synthetic conditions. The addition of NaOH solution of lower concentration (10%) in three stages, resulted in a resin of higher free formaldehyde content and lower viscosity (trials 1 and 2), compared to the addition of NaOH solution 50% in two stages (trials 3 and 4). The addition of urea can reduce the free formaldehyde content (comparison of trials 3 and 4 with trials 5 and 6), while the addition of boric acid did not prevent the red colour formation (trials 5 and 6).

All produced PF resins, except trials 4 and 6, exhibited sufficiently low viscosity and low free formaldehyde values. The pH of all resins was alkaline, around 9.5–10.9. The non-volatile content of the obtained resins was close to 50%. In the trials 7–11 where a fraction of phenol is replaced by lignin bio-oil the higher lignin bio-oil ratio in the PF resin was correlated with higher viscosity of the final resin. Resins produced with 40% and 50% lignin bio-oil fraction (as replacement of phenol) exhibited very high viscosity (almost in the form of a paste) and were diluted to obtain a resin of acceptable viscosity. Thus, further

Table 8

Characterization results of produced PF resins and lignin bio-oil based PF resins. Solvent used is H₂O.

Trial	Lignin wt% (as replacement of phenol)	Solid content (wt%)	Free Formaldehyde (%)	Viscosity ^h (cP @ 25°C)	pH
1 ^a	0	44.17	1.68	71	SP01 9.7
2 ^b	0	42.47	1.68	41	SP01 9.5
3 ^c	0	50.15	0.39	75	SP01 10.4
4 ^d	0	52.20	0.41	229	SP01 10.5
5 ^e	0	50.95	0.02	103	SP01 10.5
6 ^f	0	51.48	0.18	136	SP01 10.6
7	10	48.80	0.32	542	SP02 10.9
8	20	48.70	0.36	142	SP01 10.4
9	30	48.76	0.27	6820	SP05 10.2
10 ^g	40	24.38	0.14	194	SP01 10.2
11 ^g	50	24.18	0.18	110	SP01 9.8

a = addition of NaOH solution in three stages and use of paraformaldehyde, b = addition of NaOH solution in three stages and use of formaldehyde solution, c = addition of NaOH solution in two stages and use of paraformaldehyde, d = addition of NaOH solution in two stages and use of formaldehyde solution, e = addition of NaOH solution in two stages, use of formaldehyde solution, boric acid and urea, f = addition of NaOH solution in two stages, use of paraformaldehyde, boric acid and urea, g = resins diluted to 50%, due to the high viscosity of the produced resin. Initial solid content 49.66% for resin 10% and 49.76% for resin 11, h = The viscosity was measured using the suitable spindle, depending on the sample viscosity (Spindle 1 to Spindle 5), at 20 or 50 rpm.

optimization was carried out to reduce the viscosity of these resins.

A known undesirable feature of PF resins is the low or medium storage stability. Additionally, high non-volatile content of the PF resins leads to better adhesion properties. Working in this regard, the first option was to slightly increase the solvent content, without significantly decreasing the non-volatile content, aiming to achieve lower viscosities values. After the resin's synthesis (trials 13 and 14, Table 9) the non-

Table 9

Characterization results of produced PF-lignin bio-oil resins. Solvent used H₂O and H₂O/n-Butanol (70:30 wt/wt).

Trial	Solvent	Lignin fraction wt% (as replacement of phenol)	Free formaldehyde (%)	N.V. %	Viscosity (cP)
12 ^a	H ₂ O	40	0.23	39.02	1100
13 ^b	H ₂ O	50	0.18	38.18	1440
14 ^c	H ₂ O/n-Butanol	50	0.76	41.50	82.5
15 ^d	H ₂ O/n-Butanol	50	0.50	46.71	119
16 ^e	H ₂ O/n-Butanol	50	0.45	50.47	4280

a = diluted resin with 40 wt% lignin bio-oil (solvent H₂O), b = diluted resin with 50 wt% lignin bio-oil (solvent H₂O), c = use of H₂O/n-Butanol at ratio 70:30 combined with lower N.V.% content, d = use of H₂O/n-Butanol at ratio 70:30, e = use of H₂O/n-Butanol at ratio 95:5.

volatile content was determined and adjusted close to 40% by adding the appropriate amount of deionized water (~50% of the initial amount). Moreover, the experimental study of the effect of the solvent type used in the synthesis of PF-lignin resins resulted in the selection of the optimum type and ratio of solvents. When a mixture of H₂O/n-butanol (ratio 70:30 wt/wt) was used in the synthesis, resins with the desirable viscosity, improved storage stability and low free formaldehyde content were obtained. The viscosity of produced resins using as solvent H₂O and H₂O/n-butanol mixture was examined regularly and revealed the positive effect of n-butanol on the storage stability of the resins. As indicated in the Fig. 5, the viscosity of the resins produced with H₂O as solvent increases exponentially, especially after a storage period of 12 days. In contrary, resins produced with the solvent mixture

H₂O/n-butanol show a linear viscosity increase for the same storage period. Additionally, viscosity increases at a lower rate, suggesting that the mixture H₂O/n-butanol can successfully prolong the storage stability of PF-lignin resin with non-volatile content of 47%.

A comparison of the viscosities between the first and the last measurement for the produced resins shows an extreme viscosity increase in trials 12 and 13 where H₂O was used as the sole solvent. More specifically, on the first day of measurement trial 12 (40 wt% lignin bio-oil as replacement of phenol) had a viscosity of 1100 cP and after 19 days it reached a viscosity of 224000 cP, corresponding to an increase of 2000%. Similarly, resin 13 (50 wt% lignin bio-oil as replacement of phenol) had a viscosity of 1440 cP on the first day and reached a viscosity of 180000 cP after 16 days, which corresponds to an increase of 1250%. In contrary, resins prepared using the mixture H₂O/n-butanol, exhibited lower viscosity increase during storage. Resin corresponding to the trial 14 (50 wt% lignin, 41.5 N.V.%) had a viscosity of 83 cP on the first day and it reached 209 cP after 15 days. Finally, resin corresponding to the trial 15 (50 wt% lignin, 46.7 N.V.%) had a viscosity of 119 cP on the first day and 400 cP after 13 days, allowing storage for 2 weeks before its use in the targeted application.

Curing of all produced resins was assessed by assessing their gel time. Sodium hydroxide that is used as catalyst during the synthesis reaction acts additionally as curing catalyst. Having a basic pH, resins can be cured by heating over 100 °C. At such temperature, the water is removed resulting in curing of the resin. Basic pH and contained NaOH favor the crosslinking reactions between the polymer chains, resulting in the final curing. The produced bio resins need 3 min for a total cure when heated at 150 °C (gel time at 150 °C). The gel time was determined by transferring 1.50 g of resin in a 250 mL glass beaker and subsequent heating under constant stirring with a spoon spatula at 150 °C in an oil bath. The time when a sudden increase in viscosity was observed is defined as the gel time. [54].

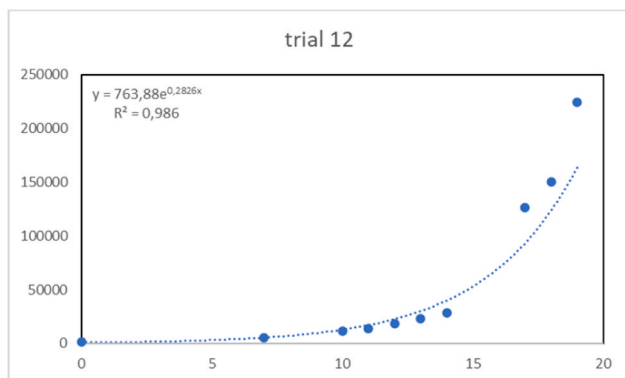
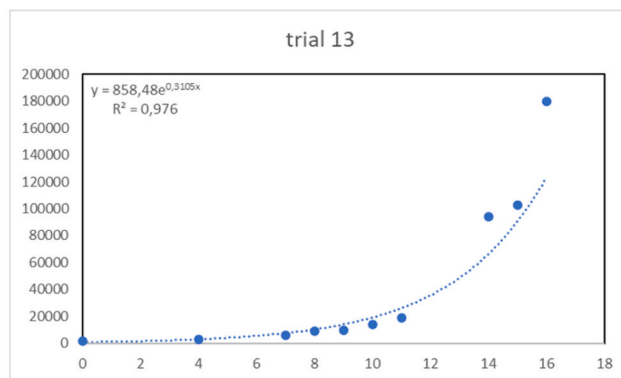
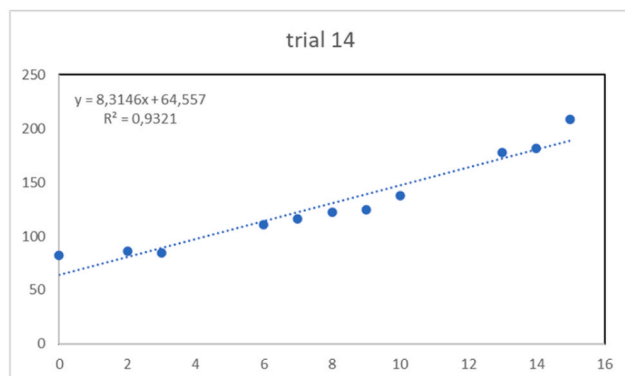
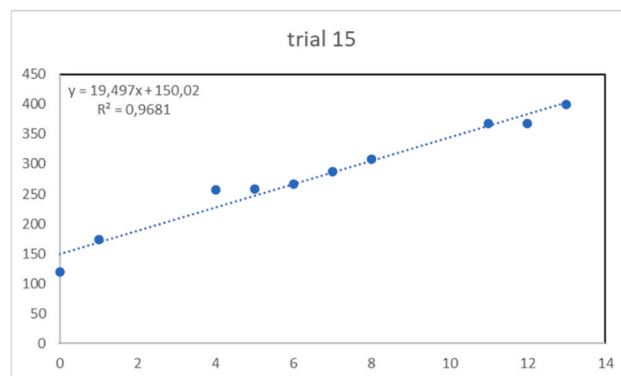
i. Trial 12, 40wt% lignin, solvent H₂O.ii. Trial 13, 50wt% lignin, solvent H₂O.iii. Trial 14, 50wt% lignin, solvent H₂O/n-butanol.iv. Trial 15, 50wt% lignin, solvent H₂O/n-butanol.

Fig. 5. Plots of resin viscosities (cP @ 25 °C) vs storage time (days). Resins were stored at room temperature.

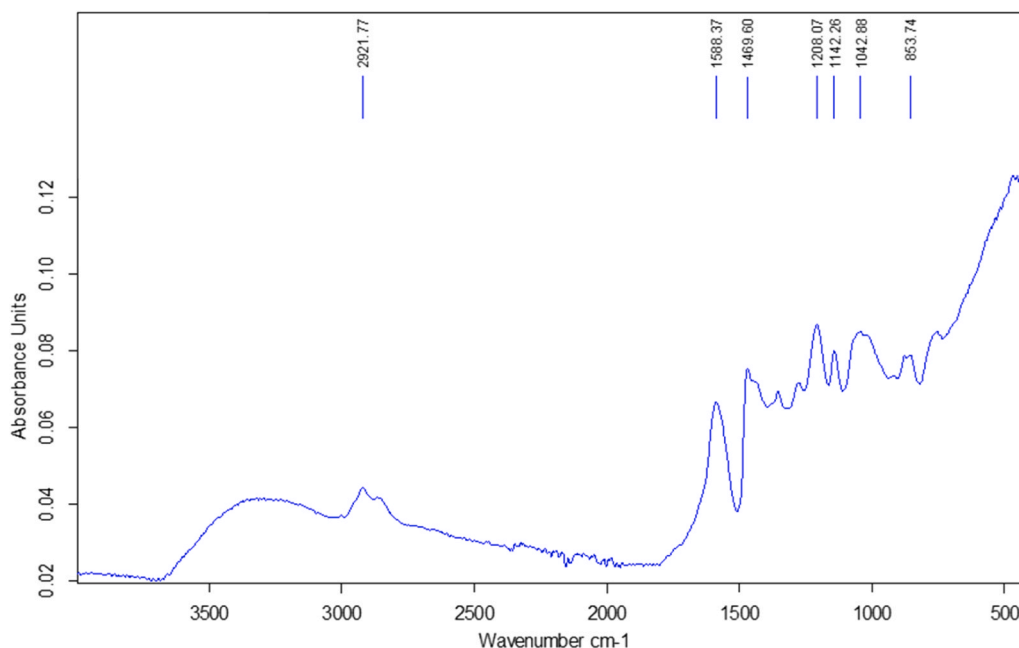


Fig. 6. FT-IR spectra of phenol formaldehyde resin with 50% replacement of phenol with lignin bio-oil.

Table 10

Tensile strength of dry/wet sample 14 and sample 15 resins. Average values of 5 samples.

Resin sample	Tensile shear strength, dry (N/mm ²)	Tensile shear strength, wet (N/mm ²)
14	10.9	4.3
15	10.8	6.0

The structure of the lignin bio-oil phenol formaldehyde resins was analyzed with FT-IR spectroscopy. As illustrated at the recorded spectra (Fig. 6), the width of the 1600 cm⁻¹ band can be related to the presence of conjugated carbonyl groups (focused at 1590 cm⁻¹) in the polymer structure. The broad peak at 3268 cm⁻¹ is assigned to the stretching vibration of hydroxyl while the peaks at 1209 cm⁻¹ and 1142 cm⁻¹ are assigned to the stretching vibration of phenol C–O and benzyl hydroxyl C–O, respectively. The benzene or its derivatives are identified by the peaks around 877 cm⁻¹, 854 cm⁻¹ which are associated with the bending vibration of C–H in the aromatic rings. The molecular chain of hydrocarbons may be inferred from the stretching vibration of aliphatic C–H at 2928 cm⁻¹ and 2863 cm⁻¹ or the bending vibration of aliphatic –CH₂ at 1438 cm⁻¹ and –CH₃ at 1354 cm⁻¹. [55].

3.4. Resin gluing validation

The results showed that in the first round of resins produced with pyrolysis derived lignin fraction (trials 7–11), a dry strength limit of ≥ 10 N/mm² was fulfilled by all those resins and a wet strength limit of ≥ 7 N/mm² was reached by resins 7–10 (EN 12765: 2001). With the highest content of lignin oil tested (50 wt% substitution in trial 11) the wet strength was somewhat reduced (6 N/mm²) but showed a good dry strength over 14 N/mm². Similar good results were also found with the n-butanol optimized resins 14 and 15, both with 50 wt% phenol substitution by lignin fraction (Table 10). The dry strength was just over 10, but the wet strength was below 7 for both samples. It should be added that, in average, resin 14 showed 100% and resin 15 70% detached wood failure in dry conditions and respectively 80% and 70% wood failure at wet conditions. This confirms a promising potential of pyrolysis derived lignin bio-oil in phenolic wood adhesives.

4. Conclusions

Recycling of waste wood, collected from building demolition site, into resol type phenol-formaldehyde resins via fast pyrolysis was demonstrated. Waste wood was pyrolyzed with 20 kg/h circulating fluidized bed pyrolysis pilot unit with high organic liquid yield (60 wt% on average). The produced fast pyrolysis bio-oil was fractionated by water addition into aqueous phase and water insoluble phase: 31.7 wt% of organics were captured within the water insoluble lignin bio-oil fraction, meaning that 67.1 wt% of the organics were deposited on the aqueous fraction. Small quantity of lignin derived products could be determined from the water-soluble fraction due to the hydrophilicity of certain phenolic compounds, whereas small quantity of anhydrosugars were determined from the water insoluble lignin fraction indicating the incomplete separation of the water soluble and water insoluble fragments. Further washing of water insoluble fraction with water would probably improve the purity.

Separated water insoluble lignin fraction was successfully incorporated in phenol formaldehyde resins. Phenol was successfully replaced by lignin bio-oil at 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% producing resins of low free formaldehyde content. Resins with high replacement ratio of phenol with lignin bio-oil exhibited higher viscosities. The use of H₂O/n-butanol mixture as solvent at a ratio 70:30 wt/wt% proved capable to prolong the storage time of lignin PF resins, and additionally contribute to maintain the viscosity at acceptable values for at least 2 weeks before their use in the targeted application.

The gluing performance of the resins was evaluated by measuring the tensile shear strength of lap joints formed by gluing 5 mm thick beech wood veneers (EN 205:2003). All the produced resins fulfilled a dry strength limit of ≥ 10 N/mm². Wet strength limit ≥ 7 N/mm² was fulfilled by the resins with the replacement ratio up 40 wt%, but resins with replacement ratio of 50 wt% had somewhat reduced wet strength. These results confirm a promising protentional application of pyrolysis derived lignin fraction in phenolic wood adhesives, at least in dry conditions. However, stable quality of the pyrolysis oil, as well as pyrolytic lignin fraction derived from demolition and waste wood feeds should be confirmed by further experiments.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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