THE HYDROPHILIC PINE BARK EXTRACTIVES AS A RENEWABLE PRECURSOR FOR SYNTHESIS OF BIO-POLYOLS BY ‘’GREEN” OXYPROPYLATION METHOD

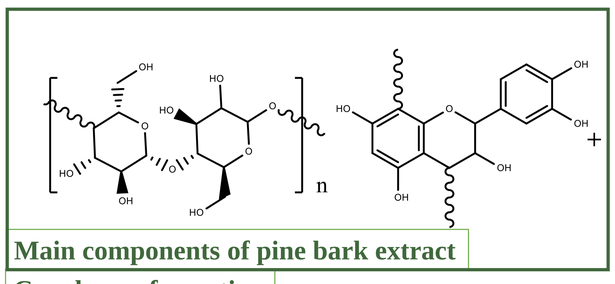
Matiss Pals, A. Vjalikova, O.Bikoven, L.Jashina, A. Arshanitsa

Laboratory of Lignin chemistry. Latvian State Institute of Wood Chemistry. Dzerbenes street 27, Riga. Latvia
+371 28330283
matiss.pals@kki.lv

Introduction

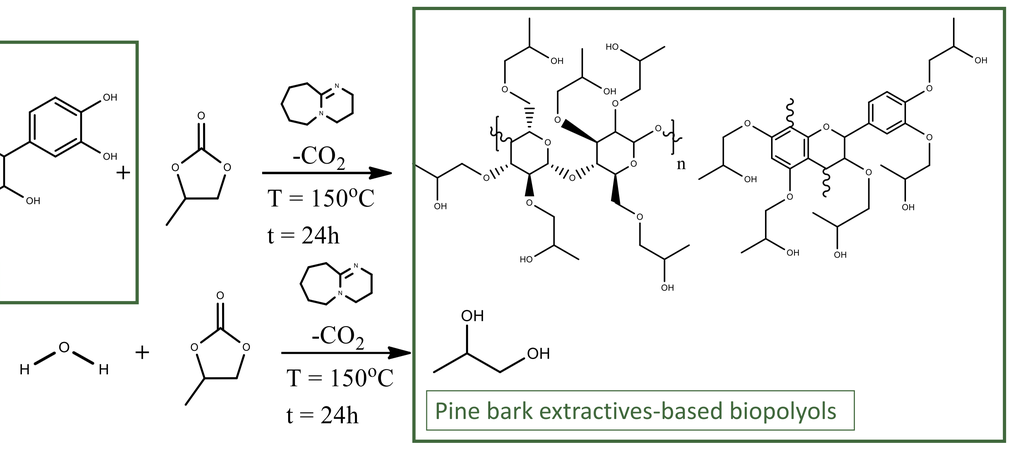
Pine bark is a widely available, low-value biomass resource from which hydroxyl-group enriched extractives can be separated via high-temperature water extraction.
Pine bark extractives are a promising renewable precursor for bio-polyol synthesis. This study investigates the high-temperature water extraction of hydrophilic components from *Pinus sylvestris* bark, focusing on how extraction temperature affects extraction yield and the obtained extract composition, particularly carbohydrate and total polyphenol content. Obtained extracts were oxypropylated using “green" oxypropylation with propylene carbonate to synthesize bio-polyols suitable for polyurethane material production.

Experimental



Copolymer formation

Homopolymer formation

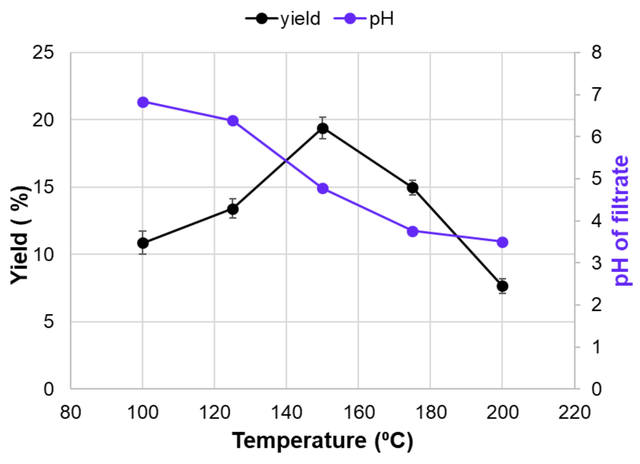


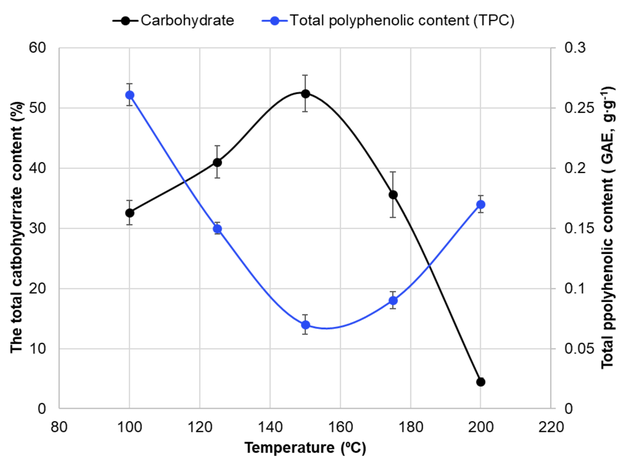
Pine bark was extracted with water using a laboratory-scale Parr reactor. The extraction was carried out with isothermal period in range from 0h to 1.5h with mechanical stirring of a 15% suspension in the temperature range of 100–200°C, number of cycles from 1 to 3

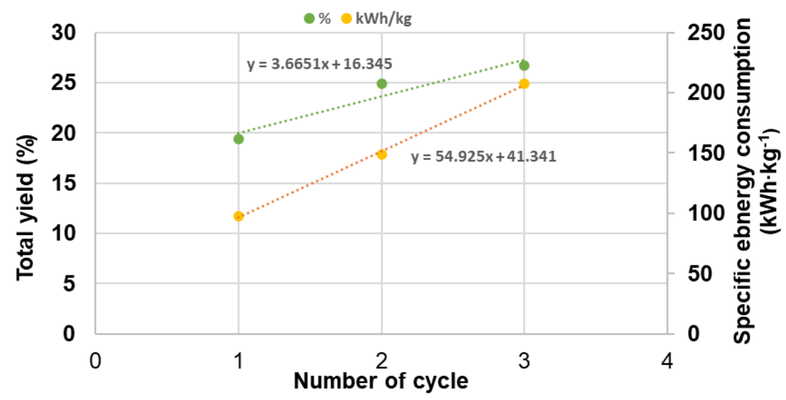
The oxyalkylation of isolated extractives with propylene carbonate was investigated in the presence of tertiary amine (DBU) as a catalyst. Synthesis was done with propylene carbonate to a hydroxyl group molar ratio from 1 to 5 at 150 and 170C. The synthesized polyols, derived from bark extractives, were characterized in terms of composition, viscosity, and hydroxyl value, focusing on their suitability for polyurethane material production.

Results

Extraction



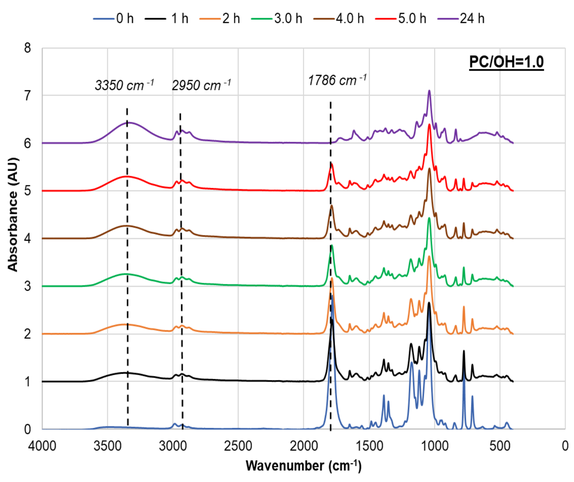


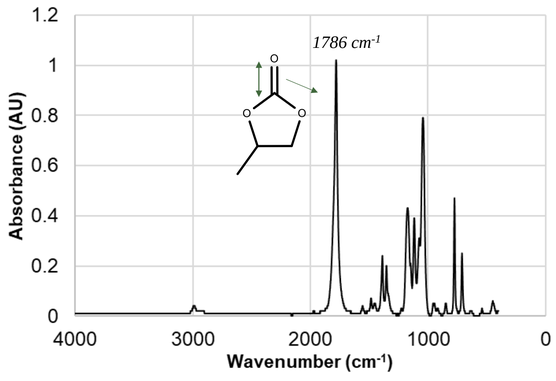


The maximum yield of extractives (23%) was achieved at 150°C, with carbohydrates comprising more than 50% of the total extract. Increasing or decreasing the extraction temperature led to a significant reduction in both extractive yield and carbohydrate content. Conversely, the polyphenolic content in extractives obtained at 150°C, measured as total polyphenols according to the Folin-Ciocalteu method, was at its lowest (0.07 GAE, $g \cdot g^{-1}$), but increased to 0.2–0.25 GAE, $g \cdot g^{-1}$ in extracts obtained at other temperatures. This suggests that, unlike carbohydrates the non-lignin polyphenolics exhibited higher thermal stability.

Regarding extraction efficiency, temperature was the main parameter that influenced the obtained extract composition and yield. The isothermal period did not affect the extraction yield. An increase in extraction cycles slightly increases total extraction yield, but also increases specific energy consumption.

Oxypropylation of extractives





No	PC/OH	Content. %			Hydroxyl value mgKOH/g	Acid value mgKOH/g	Viscosity (25ºC) at 50 s^{-1} . Pa·s
		Biomass	DBU	H_2O (K.F)			
0	Initial extract	100	-	0.1	848±12	n.d	-
1	1	50.2	5.8	0.26	471±19	n.d	>10^3
2	2	34.9	4.0	0.20	664±24	n.d	85.1
3	**3**	**26.7**	**3.1**	**0.16**	**604±18**	**n.d**	**26.6**
4	4	21.6	2.5	0.13	624±27	n.d	22.9
5	5	18.2	2.1	0.05	584±39	n.d	8.6
6	3	26.7	3.1	0.11	592±21	n.d	210.0
7	3	26.7	3.1	0.04	730±41	n.d	9.5

Polyols suitable for the production of PU foam: viscosity < 300 Pa · s, OHV = 300-800 mgKOH/g

Nr 1-5, 7: temperature 150ºC, Nr 1-6: PC equivalents added in one step,
Nr 6: temperature 170ºC Nr 7: PC equivalents added step-wise (after full conversion)

The oxyalkylation process was monitored using FTIR spectroscopy of the reaction mixture. A decrease at 1786 cm^{-1} (corresponds to the carbonyl group in PC), shows that all PC has completely reacted by 24h, while an increase at 3350 cm^{-1} and 2950 cm^{-1} shows an increase in hydroxyl group content and increased aliphatic chain length.

At stoichiometric conditions, polyols with the highest biomass content (~50%) were synthesized, but they exhibited a viscosity that was too high for use in rigid PU foam compositions. Taking into account the OHV and viscosity characteristics, all other polyols synthesized with an excess of PC meet the requirements for polyols suitable for rigid PU foam production.It was concluded that polyols synthesized at 150 °C with a molar PC/OH ratio of 3 exhibit a suitable compromise between biomass content and viscosity.

An optimal extraction temperature of 150°C yielded the maximum extractives (23%), with carbohydrates comprising over 50%. While carbohydrate degradation increased above 150°C, polyphenolic content was lowest at this optimal temperature. These extractives were effectively converted to liquid polyols using a greener oxyalkylation reaction with propylene carbonate. Based on their viscous characteristics, functional composition and water content oxypropylated pine bark extractives exhibited potential for polyurethane material production. The synthesized polyols will be tested in rigid PU foam formulations, offering a viable route to transform a renewable resource into valuable bio-based materials

Project No. VPP-ZM-VRIIILA-2024/2-0002 "Innovation in Forest Management and Value Chain for Latvia's Growth: New Forest Services, Products and Technologies (Forest4LV)"

This research is supported by project: Innovation in Forest Management and Value Chain for Latvia's Growth: New Forest Services. Products and Technologies (Forest4LV) – Project Nr. VPP-ZM-VRIIILA-2024/2-0002.