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APPLICATION OF DES (DEEP EUTECTIC SOLVENTS) TO WOOD EXTRACTIVES

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Abstract

Deep eutectic solvents (DES), known as environmentally friendly, recyclable, nonpoisonous, low volatility, non-flammability and harmless are first found by Abbott et al. in 2003. In the last decade, scientists are working with DES in different areas. Mainly, they focus on isolation of cellulose and lignin. Regard to extractives, to the best of our knowledge DES was not studied before. In this study, it was aimed to determine the extractive composition of Scotch pine with deep eutectic solvents.

Pinus *sylvestris* L. was used as wood material. As deep eutectic solvent (DES) Choline chloride (Merck 5.00117), ethylene glycol (Merck 1.00949) and urea (Merck 1.08487) were used with molar ratio of choline chloride; ethylene glycol (1:2 m/m), and choline chloride: urea (1:2 m/m). Sequential soxhlet extraction was performed first with n-hexane and then acetone-water with 5 g wood sample for 6 hours. With DES two extractions were performed in an ultrasonic (UB) and hot-water bath (HWB) at 60°C for 30 min. 0.05 g wood samples were used for these extractions. Identification and quantification were done with Shimadzu GCMS-QP2010 GC-MS and Shimadzu GC 2010 FID-GC.

Similar results were obtained with DES and organic solvents. Fatty acids, resin acids and stilbenes are the main chemical groups. Oleic acid (1.4-9%), linoleic acid (1.6-8%) and levopimaric acid (0.6-17.7%) are dominant compounds, found in all extracts. Also, monomethyl pinosylvin (51.5%) was found in acetone:water mixture. DES can be an alternative to organic solvents in wood extraction.

Keywords: Deep Eutectic Solvents (DES), Extractives, Scots pine

1. Introduction

Deep eutectic solvents (DES) are the mixtures of two or more compounds with a low melting point then preliminary compounds (Soares et al., 2017). They composed of hydrogen bond donor and hydrogen bond acceptor which support the dissolution (Li and Row, 2016). Hydrogen bond acceptors are generally quaternary ammonium salts while hydrogen bond donors involves amines, carboxylic acids, alcohol, polyoses or carbohydrates (Shishov, 2017). DES has some advantages compared to organic solvents; easy to prepare high purity compounds with low cost and biocompatibility (Hayyan et al.2013). Studies point out that DES are environmentally friendly, recyclable, nonpoisonous, low volatility, non-flammability and harmless solvents (Abbott et al., 2004; Jhong et al., 2009; Hayyan et al., 2012; Singh et al., 2012; Wu et al., 2012 Lynam et al. 2017).

DES were used in the following processes: the determination of bioactive compounds (Gu et al., 2014), the extraction of anthocyanins (Bosiljkov et al., 2017),the removal of aromatic hydrocarbons from aliphatic compositions (Hou et al., 2015), the analysis of volatile substances (Nie et al., 2017), the analysis of sugar amount in the corncob (Procentese et al., 2015), the increment of the cellulose derivation from the corn stoves for the butanol fermentation (Xu et al., 2016), the fractionation of lignocellulosic biomass (van Osch et al., 2017).

DES are mainly applied on cellulose and lignin (Lynam et al., 2017; Liu et al., 2017). To the best of our knowledge, isolation of low molecular compounds (fatty-resin acids) from wood with DES was not studied before. In this study, it was aimed to determine the extractive composition of Scotch pine with deep eutectic solvents.

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2. Materials and Methods

2.1. Material

Pinus sylvestris L (Scots pine), a widely studied wood species, was used as a wood material. Samples were taken from 630 m altitude of Hasankadi-Bartin province of Turkey and prepared according to TAPPI T 257- cm-02. After debarking and cutting in to matchstick size, samples were dried in a freeze dryer and grounded in the Wiley mill.

Choline chloride (Merck 5.00117), ethylene glycol (Merck 1.00949), glycerin (Merck 1.04092) and urea (Merck 1.08487) were used as deep eutectic solvent (DES). Eutectic mixtures molar ratio was as; choline chloride; ethylene glycol (1:2 m/m), choline chloride:glycerol (1:2 m/m) and choline chloride: urea (1:2 m/m). Also organic solvents n-hexane and acetone were used.

2.2. Extraction Methods

Three different extraction procedures, was applied. Traditional successive soxhlet extraction was performed with n-hexane and acetone-water respectively. 5 g wood sample was extracted 6 hours with each organic solvent. The other two extractions were performed in an ultrasonic (UB) and hot-water bath (HWB) at 60°C for 30 min. with deep eutectic solvents. 0.05 g wood samples were used for these extractions. 500 µl of aliquot from each extract was taken to a test tube and 1 ml of acetone has added. 700 µl of acetone phase was evaporated under nitrogen and was silylated.

2.3. Identification

Identification of compounds were performed with Shimadzu GCMS-QP2010 GC-MS equipped with TRB-5MS column (30 m x 0.25mm (0.25 µm thickness). Temperature program was started at 120 °C set for 1 min. then rised to 310 °C with a 6 °C/min. waiting for 20 minutes. The injection temperature was set to 260 °C, with 1:25 split mode, ion source was 200 °C and ionization energy 70eV. Wiley and NIST libraries were used. For quantitative analysis, Shimadzu GC 2010 FID-GC was used with TRB-5 column (30 m x 0.25 mm (0.25 µm thickness). Temperature program was set as above.

3. Results and Discussion

Extractive composition of Scots pine wood was analyzed with organic solvents applied classically (soxhlet) and by new biodegradable deep eutectic solvent (DES). The results are represented in Table 1. Fatty acids, resin acids and stilbenes (pinosylvin monomethyl ether) are the main chemical groups identified.

Total amount of fatty acids concerning palmitic acid, oleic acid and linoleic acid were found 19% in hexane extract. Except ChCl-Gly with HWB (19.6 %) the amount of total fatty acids was low (13.9-17%) with other solvents and extraction method. Oleic acid was found to be the major fatty acid in hexane. The results are in agreement with literature (Yildirim and Holmbom, 1978). Thus the ratio of this acid was 5.5%, 4.9% and 5.4% in ChCl-EG, ChCl-Gly, ChCl-Urea respectively in UB. With HWB, amount of oleic acid was low.

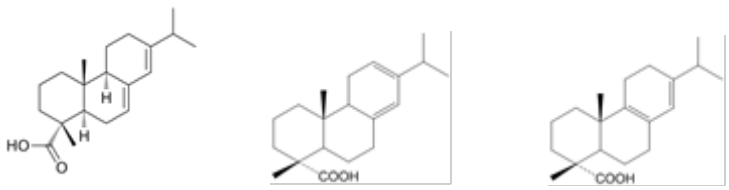
Table 1. Extractives of P. *sylvestris* wood obtained by organic and DES solvents (%)

	RT	Compound	H	A-W	ChCl-EG (1:2 molar)		ChCl-Glycol (1:2 molar)		ChCl-Urea (1:2 molar)	
					UB	HWB	UB	HWB	UB	HWB
1	15,12	Palmitic acid	0.1	-	0.4	0.9	1.0	3.8	0.7	2.2
2	16,54	Heptadecanoic acid	-	-	0.3	0.5	0.8	0.8	1.9	1.4
3	17,86	α-Linolenic acid	2.0	0.8	2.1	2.1	2.0	1.9	2.1	1.9
4	18,14	Linoleic acid	8.0	1.6	5.9	6.4	5.2	6.7	5.5	6.7
5	18,22	Oleic acid	9.0	1.4	5.5	4.7	4.9	6.4	5.4	4.8
6	19,48	Monomethyl pinosylvin	3.2	**51.5**	**12.0**	**15.5**	**16.4**	**16.1**	5.9	10.9
7	19,72	Pimaric acid	7.1	0.3	6.3	5.3	4.9	4.5	7.7	4.9
8	19,97	Sandracopimaric acid	1.1	-	1.3	0.8	1.0	1.5	1.3	0.9
9	20,14	Isopimaric acid	3.3	**-**	5.6	6.1	**10.2**	7.5	5.7	7.5
10	20,16	n.i.	-	**41.0**	-	-	**-**	-	-	-
11	20,45	Palustric acid	**14.3**	0.5	**12.4**	**11.6**	**11.0**	9.3	**12.5**	**13.9**
12	20,76	Levopimaric acid	**16.5**	0.6	**12.7**	**11.3**	**10.7**	**9.5**	**17.7**	**11.5**
13	20,88	Dehydroxyabietic acid	7.1	0.9	**10.4**	9.0	8.6	8.5	6.1	9.5
14	21,30	Abietic acid	**15.0**	0.8	**14.5**	**14.8**	**13.1**	**14.1**	**13.0**	**14.7**
15	22,63	Neoabietic acid	**13.0**	0.5	**10.7**	**10.9**	**10.1**	**9.5**	**14.5**	9.3

H: Hexane; A-W: Acetone-water; UB:ultrason bath; HWB: Hotwater bath; n.i: not identified.

Resin acids, more than 70% of total extracts composed of pimaral and abietal type of acids (Fig.1). The most abundant compounds were levopimaric acid (16.5%) and abietic acid (15%) in hexane. With DES solvents amount of levopimaric acid varied between 9.5-17.7% and abietic acid 13-14.8%. UB method showed better result than HWB at 60°C. As known resin acids have antiviral, antibacterial and antifungal effects (Savluchinske-Feio et al, 2006) and used in pharmacy and food industry. Specially for food industry residue of organic solvent is a big problem. With DES more secure extracts can be obtained. The amounts of total resin acids are almost compatible with hexane.

Pinosylvin and pinosylvin monomethyl ether which have an inhibition factor against some fungus and effect the decay resistance of wood (Venäläinen et al. 2004, Vainio-Kaila et al.2015) was found 51.5% in acetone:water extract. Sequential extraction was applied with organic solvents to recover first fatty and resin acids and then to extract pinosylvin monomethyl ether (Fang et al, 2013). With DES, the best results were obtained with ChCl:Glycol treated samples. The amount of pinosylvin monomethyl ether with ChCl:Glycol was 14.4% and 13.2% in ultrasonic and hot water bath respectively. In other DES applications hot-water bath give better results.



Abietic acid Levopimaric acid Palustric acid

Figure 1. Some resin acids found in the P. *sylvestris* wood.

Ultrasonic (UB) and hot-water bath (HWB) two different method applied to DES. As seen in Fig.2 total amount of resin acids were 5% more with UB compared to HWB at 60°C. However, with fatty acids the situation was reverse. Fatty acids gave better results with HWB. The structure of fatty acid is, linear long

chains and HWB application seems to be enough. Resin acids forms from ring structures with one or more double bonds. UB was more effective for these structures.

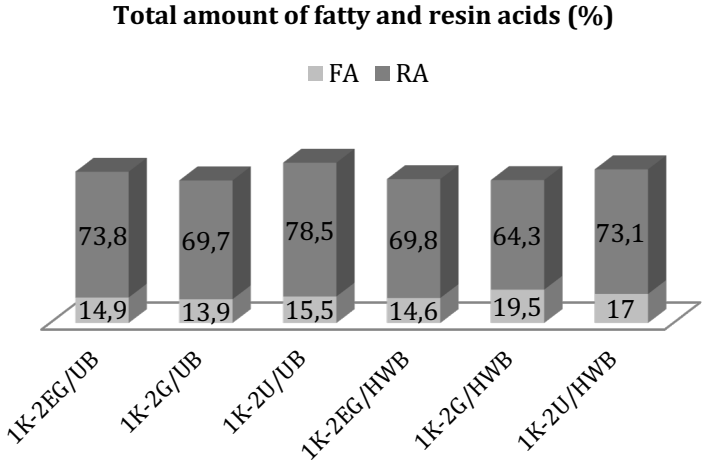


Figure 2. Total amount of fatty and resin acids with DES (%)

4. Conclusion

Organic solvents (hexane, acetone, ethanol, toluene etc.) are used in the extraction procedures. These are petroleum-based solvents and have some environmental problems with high-cost. Deep Eutectic Solvents (DES) are cheap and eco-friendly green chemicals used since 2003. This study showed that, DES can be used for the wood extraction. For fatty and resin acids, DES can be an alternative for organic solvents. Also, extraction procedure decreased to 30 min. with ultrasonic bath. Choline chloride: urea combination gave better results for P. *sylvestris* wood.

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