

Properties of Oriented Strandboard Produced Using Phenol-Formaldehyde Resin Synthesized with Bio-Oil of Lignocellulosic Wastes

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Abstract: The main objective of the present study was to modify phenol-formaldehyde (PF) resin by using bio-oil obtained by pyrolysis with and without alkali catalyst (potassium carbonate: K_2CO_3) (10 to 50 weight %) and determine technological properties oriented strandboard (OSB) panels produced using the modified PF resin formulations. The pine sawdust was used as a raw material of bio-oil. The chemical characterization of bio-oils was determined by GC-MS analysis. The OSB panels were produced with the bio-based PF resins and then their technological properties were determined. As the amount of potassium carbonate catalyst increased up to 20 wt% in the PF resin, 24-h thickness swelling of OSB panels decreased from 15.4 to 14.3%, but further increment in the potassium carbonate catalyst content increased the thickness swelling (22.8%). The IB strength of the OSB specimens with PF resin with 10 wt% bio-oil produced with catalyst or pyrolysis process was found the same (2.18 N/mm²) and it was higher than the reference value (1.97 N/mm²). As the amount of bio-oil was increased to 20 wt%, the difference in the IB values between treated OSB and reference OSB was negligible. However, above the 20 wt% bio oil, it was observed a decreasing trend in the IB values. The bending strength and bending modulus of the OSB specimens containing 20 wt% bio-oil were also found to be higher than those of the reference OSB specimens. It was concluded that the PF resin synthesized using bio-oil of (20 wt%) produced with and without alkali catalyst could be successfully used in the production of the OSB.

Keywords: bio-oil; phenol-formaldehyde; catalyst; pyrolysis; phenolic-compounds; oriented strandboard.

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1. Introduction

Biomass is one of the renewable sources obtained from lignocellulosics in the world. Due to the environmental concerns caused by petroleum-based energy sources. Many researchers have recently investigated focused on environmentally friendly renewable sources due to the fact that fossil

fuels will finish in a couple of decades. As an alternative to petroleum phenol in the synthesis of bio-oil-phenol-formaldehyde resin, most of countries have focused on the bio-oil derived from biomass using pyrolysis degradation process (fast pyrolysis) technology [1-5]. Bio-oil is one of the



most important natural and sustainable energy sources. Bio-oil can be used in various industries such as fuel (bio-diesel), power generation, coatings, and adhesive [3-11].

The bio-oil contains hundreds of different organic compounds such as aliphatic and aromatic compounds including phenols, aldehydes, benzenes, alcohols, ketones, and organic acids [6-9]. Crude oil is essential chemical in the production of synthetic phenol which is raw material of phenol-formaldehyde (PF) resin. The price and availability of synthetic phenol depend on the fluctuations in oil prices. Molecular weights of the organic compounds of the bio-oil such as furans, ketones, phenols, acids, aldehydes, and alkanes are mostly in the middle and heavy fractions. Heavy fractions limits the use of the bio-oil in the synthesis of formaldehyde-based resins. For this reason, the use of correct catalyst should be used in the catalytic pyrolysis so that the middle and heavy fractions can be decreased to the smaller fractions in the bio-oil.

The main objective of the present study was to examine the effect of the substitution level of the bio-oil on the characteristics of PF resin. Scots pine (*Pinus sylvestris* L.) sawdust was used as biomass. The vacuum pyrolysis process with and without catalyst

was carried out in a reactor at 500 °C. Two different ways were used in the production of bio-oil. In the first way, alkali salt (K_2CO_3) was used as catalyst in a vacuum pyrolysis reactor. In the second way, pyrolysis method was used and compared with the results of alkali salt. The characteristics of bio-oil and modified phenol-formaldehyde resins were investigated. Oriented strandboards (OSBs) are produced from the modified PF resins under laboratory conditions. OSB is a structural wood-based panel that is widely used in construction industry. PF resin is widely used in the production of OSB because the OSB is exposed to humid weather or high humidity when it is used as sheathing component used in the roofs, walls and floors of structures. There are many studies on the characteristics of PF resin modified with bio-oil. However, there is very limited research on the utilization of PF resin modified with different amounts of bio-oil in the production of OSB [12,13].

In this study, technological properties of OSB produced using modified PF resins were determined and the results were compared with the reference OSBs.

2. Materials and Methods

2.1. Lignocellulosic Biomass.

Sawdust of Scots pine was used to produce bio-oil as biomass feedstock. The sawdust was ground by a laboratory mill and then the wood flour was screened by a sieve shaker. The wood flour retained by 1 mm sieve was air dried for 48 h at 20-22 °C before pyrolysis process. The amount of solvent-soluble, non-volatile material in pine wood was determined according to TAPPI standard. The chemical properties of the wood are given in Table 1.

Table 1. Chemical analysis of biomass.

Chemical component	Standard method	% (by weight)
Moisture	ASTM D- 4442-92	8.44
Volatile organic compounds	ASTM E-897-88	78.16
Ash	ASTM D-1102-84	0,44
α -cellulose	Rowell et al., 2005	44.83
Holocellulose	Wise and John,1952	74.41
Lignin	TAPPI T 222 om-02	27.84
Extractives	TAPPI T 204 cm-97	2.79

2.2. Chemicals.

Potassium carbonate (K_2CO_3) catalyst used in the pyrolysis experiments was purchased from

Sigma Aldrich Company. The solubility, melting point, density, and pH of the catalyst were 1120 g/l (20 °C), 891 °C, 2.43 g/cm³ (20 °C), and 11.5 - 12.5 (50 g/l, H₂O, 20 °C), respectively. Phenol (liquid) and formaldehyde solution (37 wt%) used in synthesis of the laboratory made PF resin and modified PF resins were supplied by GENTAŞ chemical company in Izmit district, Turkey.

2.3. Catalytic and Non-Catalytic Vacuum Pyrolysis of Biomass.

The pyrolysis applications were performed in a vacuum pyrolysis reactor (Fig. 1A). The reactor had a stainless-steel cylinder with an inside diameter of 240 mm and a total length of 360 mm, which was externally heated. The pyrolysis temperature and heating rate were controlled with a Proportional-Integral-Derivative. As for the non-catalytic pyrolysis, wood flour of 2000 g was placed into the reactor. In the catalytic pyrolysis, the first the reactor was filled with 200 g (10% weight) of potassium carbonate and 2000 g of wood flour. The reactor was heated up to 500 °C with a heating rate of 15 °C/min and the temperature was kept at a total vacuum pressure of 10 kPa for 60 min. During



pyrolysis process, the bio-oil was evacuated in two condensers by vacuum pump. Bio-oil collection temperature was room temperature.

2.4. Characterization of Bio-Oil and Synthesis of PF Resin.

Gas chromatography mass spectrometry (GC/MS) analysis was carried out to investigate chemical composition of the bio-oil. A capillary column (HP-5.30m by 0.25mm i.d. by 0.25 μm) was used to separate organic compounds. The PF resin resins were prepared in a glass reactor equipped with a stirrer and a water bath for heating. A type K thermocouple was placed inside of the adhesive reactor to measure the reaction temperature. In synthesizing, PF resin without bio-oil (lab. PF resin) was used to produce the control group of the resins. For the lab PF resin synthesis, a 700 g of phenol (F/P molar ratio of 2.0), 1100 g of formaldehyde (37 wt%) and 62.5 g of NaOH solution (50 wt%) (1/3 of total NaOH weight) were charged into the adhesive reactor. The reaction temperature increased to 60°C within 60 min. The mixture was heated to 90 ° C and maintained at 90°C for 60 min. Then the second part NaOH (50 wt%) solution was added into the reactor at the temperature of 60°C. At the end of the reaction, the mixture was allowed to cool to room temperature. BPF resins obtained by the same procedure. The replacement levels of synthetic phenol by the bio-oil were gradually increased from 10 wt% to 50 wt%.

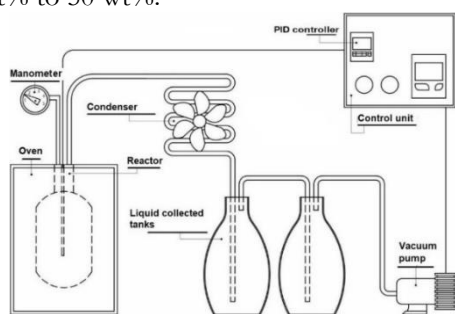


Figure 1. Scheme of the bench-scale vacuum pyrolysis experimental setup.

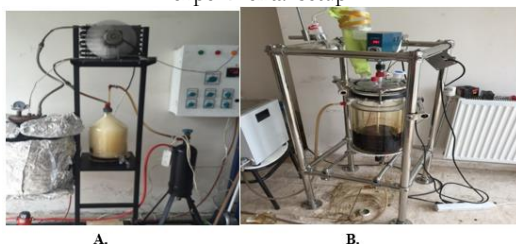


Figure 2. A: Laboratory scale vacuum pyrolysis reactor. B: Laboratory scale resin synthesis reactor.

2.5. Characteristics of Bio-Oil Modified Phenol-Formaldehyde (MPF) Resins.

The physical properties of the MPF resins were determined at the laboratory. For this aim, all the pH measurements were performed with digital pH meter. The dynamic viscosity of resins was measured using a rotational viscometer specified in ASTM D1084-08. The solids content of the resin was determined according to ASTM D 3529-03. The gel time of the MPF resins was determined through the addition of 5 g of the prepared resin samples to a test tube and heating in an oil bath having 100 °C.

Table 2. The standard number and number of samples.

Test type	Standard number	Number of samples
Density	EN 323	20
Thickness swelling	EN 317	20
Bending strength (parallel)	EN 310	8
Bending strength (perpendicular)	EN 310	8
Bending modulus (parallel)	EN 310	8
Bending modulus (perpendicular)	EN 310	8
Internal bond strength	EN 319	10
Screw withdrawal resistance (surface)	EN 320	10

2.6. Manufacture of OSB Panels and Laboratory Performance Tests.

Three-layer OSBs were produced under laboratory conditions. Commercial poplar wood strands were supplied by Kronospan OSB Plant located in Kastamonu city, Turkey. The OSB strands (thickness: 0.6-0.7 mm, width: 20-30 mm, length: 90-110 mm) were dried to the moisture content of 2-3% in an oven with a fan. The strands were mixed with reference and modified PF resins in a rotary drum blender. The resin content was kept constant at 10 wt% based on the oven-dry weight of strand. The hot-press temperature, maximum pressure, and press time were 190 °C, 3.5 N/mm², and 8 min, respectively. Three OSBs were produced for each type of resin. The OSBs were conditioned in a climate room having 20 °C and 65% relative humidity. The test type and sample details are given in Table 2.

3. Results and Discussion

3.1. Characterizations of the Bio-Oil.

The amounts of organic compounds in the bio-oil samples were given in Table 3. The GC-MS analysis results showed that the major compounds in the bio-oil were aromatic compounds including phenol, 2-Metoksi-4- metilfenol, 4-Metil 1,2-benzendiol, Naftalin, etc. In all of the bio-oils from these sawdust samples, phenol was the most abundant compound found. As expected, the potassium carbonate increased the total phenol compounds in the bio-oil. According to the results of GC-MS analysis, the total phenolic compounds of bio-oil (94.4%) produced with alkali catalyst (potassium carbonate) was found to be higher than the bio-oil (72.2%) produced with pyrolysis process (Table 3).

3.2. Characterization of the Reference and Modified PF (MPF) Resins.

The results of the reference and MPF resins are given in Table 3. The MPF resins produced with non-catalytic bio-oil had higher acidity than the reference PF resins and MPF resins synthesized with catalytic bio-oil. Moreover, the acidity of the MPF resins significantly increased with increasing bio-oil content. Bio-oil contains organic acids which may increase the acidity of the MPF resins. The gel times of MPF resins at 100 °C were found to be lower than the reference resin (165 s). In particular, the increase in the bio-oil content in PF resin resulted in an increase in the gel time.

The gel times of both MPF resins showed similar trends. The gel time of PF resin synthesized with bio-oil produced using pyrolysis process decreased from 158 to 119. Similarly, gel time of the PF resin synthesized with bio-oil produced using potassium carbonate catalyst decreased from 158 to 124 s. The solids content of the MPF resins was slightly higher than that of the reference resin (Table 4). This can be explained by the increased bio-oil content in the PF resin. Similar results were reported in previous studies [14-16]. The bio-based PF resins had higher molecular weights, higher polydispersity indices, shorter gel times, and faster curing rates than the lab synthesized control PF resin [17].

3.3. Technological Properties of OSB Boards.

Technological properties of OSBs produced with the PF resins modified with

different contents of catalytic pyrolysis oil are presented in Table 5. The PF resins containing catalytic bio-oils improved the thickness swelling and bond strength between the strands of OSB boards although the effect sizes were different from each other. The IB strength of OSB specimens with 10 wt% bio-oil was higher than that (1.97 N/mm²) of the reference OSB (Table 5). The IB strength of the OSB specimens with PF resin with 10 wt% bio-oil produced with catalyst or pyrolysis process was found the same (2.18 N/mm²) and it was higher than the reference value (1.97 N/mm²). As the amount of bio-oil was increased to 20 wt%, the difference in the IB values between treated OSB and reference OSB was negligible. However, above the addition of the 20 wt% bio oil, it was a considerable decrease in the IB values. The IB strength of the specimens was lower than that of the reference OSB specimen. The IB strength of OSB specimens containing bio-oil (to 20 wt%) produced by pyrolysis process was higher than that of the specimens with bio-oil produced by potassium carbonate. Further increment (above 20 wt%) in the bio-oil content from pyrolysis process decreased the IB strength of the OSB specimen more than the pyrolysis without catalyst (Table 5).

The results showed that pyrolysis process had better performance up to 20 w% of bio-oil than the potassium carbonate catalyst. A similar trend was observed for the screw withdrawal resistance. This could be mainly explained by the fact that the MPF resins with bio-oil (up to 20 wt%) had similar curing characteristics of reference PF resin. Lui et al. [20] reported that modified PF resins with relatively high bio-oil addition such as (30% and 40% wt% bio-oil) required much more energy to cure completely than those having low bio-oil addition. They determined that the optimum bond performance was found in the PF resins modified with 20 wt% content of bio-oil from lignocellulosic biomass.

All the OSB specimens, except for the 50 wt% bio-oil of pyrolysis method, showed higher screw withdrawal resistance than the reference specimen. Wan et al. [16] investigated bond strength of PF resin modified with bio-oil. They reported that the optimum content of the crude bio-oil was 25 wt% for the PF resins. In their study, a further increase in the amount of the crude

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bio-oil decreased the bond strength of both modified and blended PF resins. They concluded that this was mainly due to increased viscosity and acidity of blended PF resins at high crude bio-oil addition percentage and a shortage of reactive phenolic compounds in modified PF resins at high phenol substitution percentage. Similar results were reported in previous studies [11,18,20-25].

For example, Shahid et al. [14] reported that the gel time of the modified PF resins increased as the addition of bio-oil was above 45 wt% while the bond strength decreased. In another study, Ren et al. [19] reported that bond strength of resorcinol-formaldehyde (RF) resin modified with bio-oil of 10 and 20 wt% bio-oil was slightly lower than that of the reference RF resin.

Table 3. GC-MS analysis results of bio-oil.

RT (min)	Name of compounds	Area (%)		Category
		Termaal	K ₂ CO ₃	
14.65	5-Methyl-2-furankarboksialdehit	2.00	1.09	Aldehyde
15.86	Phenol	7.33	4.01	Phenol
18.81	3,5-Dimethyl-siklopentan	-	0.20	Alkane
18.92	2-Methyl-phenol	4.15	2.91	Phenol
19.75	4-Methyl-phenol	9.82	8.43	Phenol
20.10	2-Metoksi-phenoll	3.40	4.71	Phenol
20.72	1-Metoksi-3-methyl-benzene	0.16	-	Benzene
22.25	2,5-Dimethyl-phenol	3.16	3.35	Phenol
22.95	2,3-Dimethyl-phenol	-	4.12	Phenol
23.22	Naphthalene	4.09	-	Benzene
23.67	2-Metoksi-4- methyl-fenole	6.66	6.21	Phenol
23.83	1-cyclo hexane-1- carboxy aldehide	-	1.19	Aldehyde
23.88	1,2-Benzendiol	4.34	1.30	Phenol
23.89	1,3-Benzendiol	-	1.21	Phenol
25.73	4-Metil 1,2-benzendiol	5.91	2.06	Phenol
25.85	2-Furan carboxy aldehide	-	-	Aldehyde
26.29	4-Ethyl-2-metoksi-fenol	-	3.35	Phenol
26.30	Pyrazine	2.93	-	PAH
26.63	1-Methyl-naphthalene	1.18	-	Benzene
28.77	2-Methoxy-4-propenil-fenol	0.78	-	Phenol
29.15	4-Ethyl-1,3-benzediol	2.74	-	Phenol
30.79	2,4-Dimethyl-phenol	-	-	Phenol
30.80	2,5-Dimethyl-phenol	-	-	Phenol
30.81	Biphenylene	2.04	-	Benzene
32.41	3,4-Dimethyl-phenol	-	-	Phenol
32.96	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	0.52	-	Ketone
33.74	2-Methoxy-4- methyl-phenol	-	-	Phenol
34.07	1,4-Benzenediol	-	-	Phenol
34.08	2,6-Dimethyl-phenol	-	-	Phenol
34.11	Fluorene	1.96	-	Benzene
38.50	Sikloproponon	2.70	-	Keton
39.85	2-Methoxy-4-ethyl-phenol	-	-	Phenol
40.98	2-Methyl 1,3-benzene-diol	-	-	Phenol
40.99	3-Methyl-phenanthrene	0.99	-	Benzene
45.75	2,5-Dihydroxypropiofeno	-	-	Ketone
68.40	Anthracen	-	-	Benzene

Table 4. Technical properties of PF resins.

Resin type	Bio-oil substitution level (% wt)	pH (20 °C)	Viscosity (cPs)	Solid content (% wt)	Gel time (s)
Lab made PF	0	11.98	265	46.65	165
	10	11.88	326	47.37	158
	20	11.84	342	48.24	150

Resin type	Bio-oil substitution level (% wt)	pH (20 °C)	Viscosity (cPs)	Solid content (% wt)	Gel time (s)
Pyrolysis without catalyst	30	11.84	355	49.51	143
	40	11.76	359	51.58	135
	50	11.71	371	53.19	119
Pyrolysis with catalyst (potassium carbonate)	10	11.92	321	47.19	158
	20	11.90	320	48.04	150
	30	11.90	327	48.89	147
	40	11.87	345	51.15	136
	50	11.83	351	51.91	124

Table 5. Technological properties of OSB panels produced with PF resin modified with bio-oil from pyrolysis with and without potassium carbonate.

Resin type	Bio-oil substitution level	Density (g/cm ³)	Thickness swelling (%)	Internal bond strength (N/mm ²)	Screw withdrawal resistance			Modulus of rupture		Modulus of elasticity	
					Surface	Parallel	Perpendicular	Parallel	Perpendicular		
										(N)	(N/m ²)
Lab made PF	0	0.812 (0.013)	19.3 (1.6)*	1.97 (0.21)	82.6 (2.8)	32.6 (3.1)	29.2 (2.6)	4860.4 (135.4)	4885.3 (152.7)		
Pyrolysis without catalyst	10	0.810 (0.05)	14.1 (3.1)	2.18 (0.18)	114.6 (4.3)	42.2 (4.6)	33.6 (3.5)	5585.7 (182.3)	4864.5 (113.9)		
	20	0.824 (0.09)	16.5 (4.0)	1.95 (0.22)	95.9 (4.8)	34.8 (3.7)	31.2 (2.8)	6012.4 (168.6)	5322.9 (195.4)		
	30	0.816 (0.013)	16.7 (3.5)	1.42 (0.19)	91.7 (3.7)	31.5 (2.8)	24.5 (2.4)	5306.7 (103.9)	5117.1 (203.6)		
	40	0.813 (0.015)	17.1 (4.1)	1.19 (0.14)	84.1 (4.2)	30.0 (4.2)	24.5 (3.6)	4615.1 (121.6)	4459.3 (134.7)		
	50	0.828 (0.016)	19.8 (3.1)	1.02 (0.11)	80.3 (3.6)	25.8 (2.6)	23.8 (3.1)	4245.5 (138.4)	4278.6 (162.8)		
Pyrolysis with catalyst (potassium carbonate)	10	0.826 (0.015)	15.4 (4.4)	2.18 (0.15)	117.5 (5.3)	36.2 (4.3)	37.9 (4.1)	6326.2 (172.7)	5650.4 (185.4)		
	20	0.813 (0.016)	14.3 (1.4)	1.91 (0.18)	106.4 (4.8)	42.5 (3.7)	35.5 (3.7)	5883.8 (128.7)	5268.3 (216.8)		
	30	0.819 (0.015)	19.4 (3.6)	1.81 (0.10)	98.9 (4.2)	30.8 (2.6)	34.3 (2.6)	5625.7 (154.9)	5035.2 (169.3)		
	40	0.811 (0.01)	21.7 (2.6)	1.73 (0.12)	93.7 (3.7)	25.6 (2.3)	28.4 (3.7)	5189.2 (129.4)	4618.9 (148.4)		
	50	0.825 (0.013)	22.8 (2.1)	1.68 (0.15)	84.5 (2.8)	22.3 (3.4)	25.9 (3.0)	4769.1 (155.6)	4436.4 (175.6)		
Standard value**			12	0.50	-	30	16	4800	1800		

The improvement in the mechanical properties of the OSB panels produced with MPF containing bio-oil of 20 wt% can be explained by the fact that the resin will have a higher amount of hydroxyl methyl and hydrocarbons, which was beneficial to form the crosslinking structure and improved the bonding performance of between the strands [26]. This improves the mechanical properties of the OSB panel. Above the 20 wt% of bio-oil, the internal bond strength of the MPF resin began to drop sharply, as the inert and less active compounds hindered the synthetic reactions between resorcinol and formaldehyde, or, when more bio-oil was used as reactant, caused resorcinol to drop to insufficient amounts [27]. The IB strength is important to

evaluate the bond performance of the resin. The IB strength of all the OSB specimens was significantly higher (3 to 4 times) than minimum property requirement of EN 300 OSB-4 which is 0.50 N/mm² (IS EN 300, 1997). Moreover, bending modulus values of all the OSB groups, except for 40 and 50 wt% of bio-oil from pyrolysis process and 50 wt% bio-oil from potassium carbonate catalyst, met the minimum requirements for OSB-4 (outdoor applications) (Table 5). As for the bending strength, the OSB specimens, except for the 50 bio-oil from pyrolysis process and IB50 wt% bio-oil from potassium carbonate catalyst, met the the minimum requirements for OSB-4.



4. Conclusions

The results showed the amount of the phenolic compounds in the bio-oil increased with the pyrolysis process and catalyst. Functional groups were found to be considerably higher in the bio-oil. The viscosity and solids content of the modified PF resins increased with increasing bio-oil content. Its viscosity was found to be higher than that of the laboratory PF resin. This was mainly due to the compounds having high molecular weight compounds in bio-oil. The addition of 10 wt% bio-oil into the PF resin resulted in higher IB strength as compared to reference OSB. The

difference in the IB strength values of reference OSB and treated OSB having 20 wt% bio-oil was negligible. However, further increment in the bio-oil content decreased the bond performance of the OSB specimens. Particularly, screw withdrawal resistance of the specimens was considerably higher than that of the reference group. Based on the findings obtained from the present study, it was concluded that PF resin synthesized using bio-oil produced with and without alkali catalysts could be successfully used in the production of the OSB.

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Conflicts of Interest

The authors declare no conflict of interest.

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