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Research Article

Investigation of Value-Added Compounds Derived From Oak Wood Using Hydrothermal Processing Techniques and Comprehensive Analytical Approaches (HPLC, GC-MS, FT-IR, and NMR)

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ABSTRACT

In this study, slow pyrolysis of oak woods was carried out in a fixed bed tube reactor at four different temperatures ranging from 100 °C to 400 °C and at 5 °C/min speed time intervals. The compositions of the produced bio-tar and bio-oils were determined in detail using FT-IR, GC-MS, HPLC, and NMR devices. Several pyrolysis parameters were carried out to reveal the distribution of pyrolytic products under different pyrolysis temperatures (100–400 °C) and times (1–4 h). During the slow pyrolysis process, oak wood started to decompose to form organic volatile products at a set temperature of 100 °C and reached a maximum yield of volatile products at around 400 °C. GC-MS analyses revealed that different valuable components such as furans, phenolic compounds, carbonyls, linear, aromatic compounds, acids, and hydrocarbons have been formed. Based on the experimental results of the pyrolysis, it has been detected that the temperature and time interval are very effective parameters in the conversion of oak wood to the amount of liquid product.

Keywords: Biomass, Pyrolysis, Oak Wood, Bio-Tar.

1. INTRODUCTION

Biomass resources are quite high, especially in Asian countries, and the evaluation of biomass as an energy source will play an important role in meeting the energy needs of the future. [1-2] By evaluating biomass sources, energy-side sources such as ethanol, biodiesel, and biogas can be obtained. These energy sources are used to meet energy needs in areas such as housing, transportation, and industry. With the evaluation of biomass, products obtained by refinery techniques such as bio-oil, bio-petrol, and biobutanol are also formed.[2-3] As a renewable carbon source, lignocellulose biomass is the source of many by-products from agricultural and forestry products. As recent studies have shown, lignocellulose-derived by-products will replace fossil resources both in energy and in the production of organic chemical products.[4-5] Oaktree, as a biomass source, is one of the most abundant forest tree species, and oak wood chips, which are used in the furniture and housing industry, are found in large quantities.[6] There are also many oak species, and 120 oak species in the mountainous regions of China alone have been determined.[7-8] Oak wood is used in furniture, shipbuilding, sports equipment, and a wide range of industrial uses.[7] Also, the fruit, branches, bark, and leaves provide medicinal and industrial benefits. Due to these benefits, it is very important to analyze the content of oak wood by-products.

Lignocellulosic biomass consists of three main components: lignin, cellulose, and hemicellulose. These three main components provide organic products such as alcohols, phenols, furans, esters, ketones, organic acids, aldehydes, and phenols.[9-10] The search for new

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and renewable raw materials is very intense for products that can replace fossil resources. For this purpose, products obtained from biomass resources by applying pyrolysis are promising.[11-12] Biooil quality can be improved by applying gradual heating and separate temperature steps to obtain bio-oils obtained by the pyrolysis technique as separate fractions. Pyrolysis is a thermal degradation process applied to separate natural or synthetic polymers into lower molecular weight components in an oxygen-free environment. In the pyrolysis process, experimental parameters such as reactor type, temperature, catalyst, pressure, and amount of substance are applied to obtain economically valuable substances or components.[13-14] In the studies carried out in this field, both bio-oil quality and valuable chemical selectivity have been increased with the application of gradual temperature.[15–17] Three-phase (solid-liquid-gas) products are formed with the pyrolysis of biomass, and the physicochemical properties of these products are affected by conditions such as ambient temperature, reaction conditions, and the type of biomass used.[18]

The liquid phase obtained by the pyrolysis process is called bio-oil. Different from petroleum oils, bio-oil is a mixture of many components such as anhydrous sugar, ester, ketone, and aldehydecarboxylic acid.[19-20] Although these components in bio-oils are very difficult to separate, they can be distinguished by utilizing their differences in molecular weights. However, these components in bio-oil tend to react because they consist of many different functional groups and oxygenated components.[21-22] By separating the components in bio-oil, it can be separated into different compound groups such as phenolics, oxygenates, furans, anhydrous sugars, sugars, and oligomers.[23-24]

Traditionally, three basic methods are used to separate compounds found in bio-oil: distillation, column chromatography, and solvent extraction. By distillation, bio-oil components can be separated according to their volatility[25]. In column chromatography, the mobile phase is separated according to the polarity of the components in the bio-oil with the help of the stationary phase (Al_2O_3 or Silica gel). In solvent extraction, the solvent is used following the component to be separated. [25–27]

As aforementioned, the bio-oil is composed of many different constituents, and identification of these contents is difficult. Hitherto, the studies conducted to detect the constituents of bio-oil showed that many advanced analytical methods such as FTIR, NMR, and GC-MS can be used to detect the composition of bio-oils derived from different biomass sources.[28] Various studies in the literature on the pyrolysis of oak wood by-products have been conducted. In these studies, especially the effective parameters of the pyrolysis process were examined.[29]

In this study, for the first time, in addition to the pyrolysis of oak sawdust, bio-oils obtained from oak wood pyrolysis were separated into their components by solvent extraction method. In addition, several advanced analytical methods such as FT-IR, HPLC, NMR, and GC-MS were applied to obtain quantitative and qualitative analyses of these compounds. As a result, our findings in this study showed that a lot of valuable by-products can be formed after applying the pyrolysis process.

There are a variety of methods, such as high-temperature liquefaction, fixed bed, hydrothermal conversion and permeation through high-pressure/temperature environments, to examine the inside of very hard and difficult-to-degrade structures such as lignin, cellulose, and hemicellulose contained in biomass resources such as oak. Most of these methods are costly and require quite complex processes and devices. Among these, pyrolysis is a very easy and cost-effective method. Therefore, pyrolysis is a highly preferred method because the desired temperature and experimental environment conditions are easily achieved. Our study is related to the elucidation of the liquid tar content obtained from oak wood. The findings obtained in question can be used to make content predictions for other similar biomass resources of products with high added value in the content of oak wood. Additionally, it will prevent loss of time in estimating the content of similar biomass resources and searching for different fields related to the content. In this respect, the findings obtained in the study will be beneficial for further studies.

2. EXPERIMENTAL

2.1. Materials

Oakwood was collected at a biomass collection center in Kahramanmaraş, Turkey. The chemical reagents of methanol, acetone, ethyl acetate, ether, and hexane used in this study were of analytical grade. All chemicals were purchased from Sigma Aldrich Company and used without further processing. ^1H NMR spectra was recorded in a $CDCl_3$ solution on a Bruker Avance™ 600 MHz spectrometer (Bruker, Billerica, MA, USA). Organic volatile chemical compounds were analyzed by gas chromatography-mass spectrometry (GC-MS). High-yield liquid chromatography (HPLC) with model 1260 Infinity II LC System coupled with mass spectrometry was preferred to test organic acid fractions qualitatively. The peaks containing the bond structure of the compound in the sample were determined using a Fourier transform infrared (FT-IR) device.

2.2. Methods

The tar was obtained from the gasification of pine sawdust for 5 hours at 100, 200, 300 and 400 °C in a fixed bed pyrolysis reactor device. Since the best tar formation was achieved at 400 ^{o}C (as seen in Table 1 and Table 2), only the tar composition at this temperature was examined. The oak wood used in this study was pyrolyzed at 400°C for about four hours at one-hour intervals. At the end of the 1st hour, the sample was named compound 1h, after two hours of exposure the sample was named compound 2h, after the third hour the sample was named compound 3h and finally the fourth hour of exposure was labeled 4h. The last remaining tar fraction after the fourth hour at 400°C was labeled as croissant and prepared for analysis. The final analysis of the tar is shown in Table 1. Oak tree branches were used in pyrolysis studies. Dry oak tree branches were ground and sieved to prepare samples with a grain size of -60+80 mesh. 10 g of sifted oak wood sample was placed in the pyrolysis device. It was allowed to burn for 1 hour at the appropriate temperature and the liquid sample was taken by passing the burning sample part through the cold arm.

HPLC analyses of oak tar were performed with the Infinitely Better 1200 Series Agilent brand device. The method properties used in HPLC analysis; mobile phase is 0.02 N H_2SO_4, injection 10 µL volume, 0.6 ml/min flow rate, 50 ^{o}C column temperature, HI-PlexH, 300X7.7 column type. GC-MS analyses were performed with Agilent brand 7000 GC/MS Triple Quad 7890. Column specifications: 30m X 0.25 mm X 0.25 µm. MS features; 280 °C, 35/550 amu scan range, -70 eV electron energy, and 100 ms scan time.

3.RESULTS and DISCUSSION

Characterization of tar and bio-oils obtained from oak wood was performed by FT-IR, HPLC, GCMS, and NMR analysis. HPLC analysis results of the samples were taken for different hours of pyrolysis products. As seen in Figure 1 and Table 1, 5 organic acids of quinic acid, lactic acid, formic acid, acetic acid, and propionic acid were formed. The most abundant organic acid-valued components are given in Table 1.

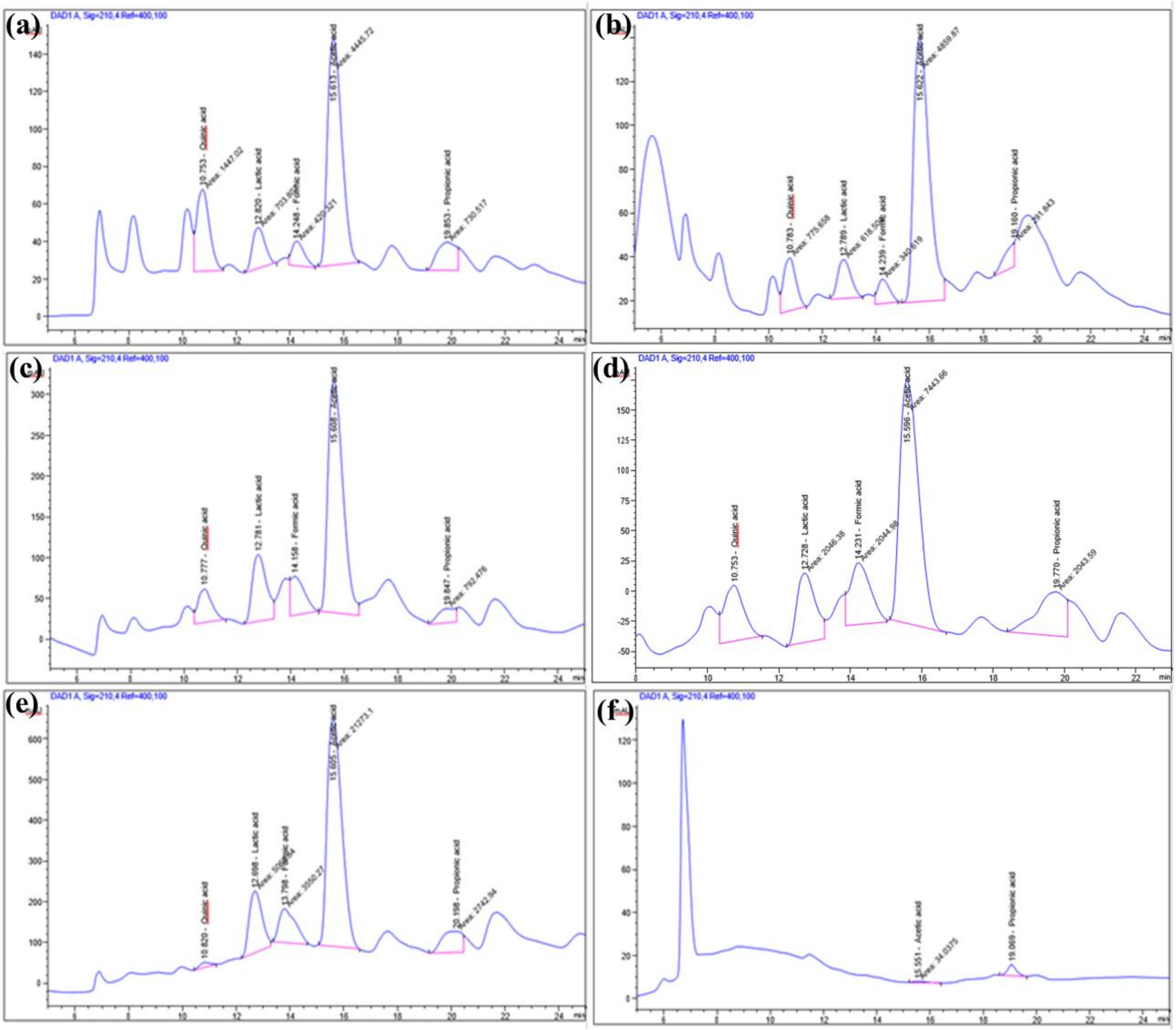

Figure 1. HPLC chromatograms of pyrolysis products at 400 °C for a certain time interval (a: 1h, b: 1h-2, c: 2h, d: 3h, e: 4h, f: tar, h: hour).

Table 1. Organic acid characterization of tar and bio-oils obtained from oak wood by HPLC.

	Organic acids (ng/ul)				
Pyrolysis Extracts	**Quinic acid**	**Lactic acid**	**Formic acid**	**Acetic acid**	**Propionic acid**
1 h	2946.58	663.20	533.03	14797.80	1005.96
2 h	3001.81	2840.17	2160.24	36748.90	1091.33
3 h	3622.03	1922.74	2601.08	24776.70	2815.25
4 h	314.02	2375.39	2258.57	35406.04	1889.44
Tar	-	-	-	56.56	78.33

* **h**: hour

Data for HPLC, GC-MS, and FTIR analyses for one tar and 4 bio-oils were given in Tables 1 and 2, respectively. Tables 1 and 2 show that both tar and bio-oils contained higher carbon and lower oxygen depending on the increase in heating time. The list of compounds obtained by GC-MS is plotted in Figure 2, and given in Table 2. As predicted, bio-fatty acids produced by the breakdown of oak wood into compounds containing hemicellulose, cellulose, and lignin contain many types of group compounds with different structures and molecular structures. Biooils identified by GC-MS were found to constitute many different classes of organic compounds, such as monoaromatics, aliphatic, oxygenated compounds, nitrogenous compounds, aromatic compounds, and derivatives.

Table 2: The main chemical compounds formed in bio-oil products and tar matter obtained at 400 °C and at different times by GC-MS.

			Hexane					**Ether**					**Tar**
NO	**RT**	**Name**	**1S1-H**	**1S-2H**	**2S-H**	**3S-H**	**4S-H**	**1S1-E**	**1S2-E**	**2S-E**	**3S-E**	**4S-E**	**Krezol**
1	6.19	3-furfural-isomer	-	0.13	-	-	-	-	0.42	-	-	-	-
2	6.61	3-furfural	0.31	0.33	-	0.15	-	0.34	0.40	-	0.13	-	-
3	7.31	Furfural	21.22	20.53	6.65	13.19	5.75	35.53	31.87	27.21	13.61	3.21	-
4	7.32	2.5-Dimethylfuran	-	-	-	-	-	-	-	-	-	-	0.62
5	7.56	*α*-methylcyclopentanone	0.18	0.48	-	0.24	-	-	-	-	-	-	-
6	7.79	3-methylcyclopentanone	0.14	0.15	nd	nd	nd	nd	nd	nd	nd	nd	-
7	8.12	Furfuralcohol	0.34	0.23	0.33	0.33	0.75	6.08	5.83	14.75	4.03	nd	-
8	8.27	3-furylmethanol	-	-	-	-	-	-	-	-	-	2.78	-
9	8.65	Hexyl acetate	0.52	0.50	0.27	0.34	0.36	1.42	1.13	3.07	0.78	0.47	-
10	8.69	Ethylbenzene	-	-	-	-	-	-	-	-	-	-	0.23
11	9.73	Cyclohexanone	0.18	0.11	-	-	-	-	-	-	-	-	-
12	10.28	2-methyl-2-cyclopentenone	1.50	1.44	0.67	0.87	1.16	1.33	1.27	1.35	0.45	0.37	0.22
13	10.53	Acetylfuran	1.48	1.30	0.63	0.92	0.99	1.32	1.27	1.12	0.56	0.28	0.19
14	10.73	5-methylfurfural-isomer	0.31	0.30	0.07	0.16	-	-	-	-	-	0.24	-
15	11.14	5-methylfurfural-isomer	0.08	-	-	-	-	-	-	-	-	-	-
16	11.24	2-hydroxycyclopent-2-en-1-one	-	-	-	-	-	-	-	2.24	0.29	0.55	-
17	11.58	2-cyclohexenone	0.10	-	-	-	-	-	-	-	-	-	-
18	11.89	2-cyclopenten-1-one. 3.4-dimethyl-	0.49	0.52	0.09	0.21	0.17	-	-	0.53	-	-	-
19	12.28	2-cyclopenten-1-one. 2.3-dimethyl-isomer	0.26	0.20	-	-	-	-	-	-	-	-	-
20	13.08	Benzaldehyde	0.30	0.34	-	0.16	-	-	-	-	-	-	-
21	13.28	5-methylfurfural	8.00	7.41	3.43	5.66	3.65	7.78	6.86	9.41	3.52	1.33	0.39
22	13.46	2-oxobutyl acetate	0.17	0.14	0.09	0.23	0.18	0.47	0.39	0.89	-	-	0.23
23	13.99	Furoylhydrazide	1.20	1.22	0.27	0.64	0.35	0.31	0.29	0.64	-	-	-
24	14.60	Phenol	0.69	0.58	0.60	0.68	1.56	3.84	3.47	9.82	2.60	2.94	0.62
25	14.73	Phenyl hexanoate	-	-	-	-	-	-	-	-	0.17	-	-
26	14.94	2-cyclopenten-1-one. 2.3-dimethyl-isomer	0.27	0.26	0.14	0.17	0.37	-	-	-	-	-	-
27	15.13	Unknown	0.11	-	-	-	-	-	-	-	-	-	-
28	15.24	2-cyclopenten-1-one. 2.3-dimethyl-isomer	0.52	0.48	0.18	0.32	0.31	-	0.16	-	-	-	-
29	15.47	3.5-dimethyl-2(5H)-furanone	0.13	0.11	0.18	0.12	0.23	0.48	0.45	1.85	0.33	0.20	-
30	15.67	1-methyl-2-formylpyrrole	0.11	0.12	-	-	-	-	0.76	-	-	-	-
31	15.80	Isobutyric anhydride	0.44	0.37	0.70	0.38	1.18	0.93	-	2.67	0.45	0.62	-
32	15.91	2-propionylfuran	0.25	0.13	-	0.16	-	-	-	-	-	-	0.39
33	16.29	2-formylpyrrole	-	-	-	-	-	-	-	1.12	0.47	-	-
34	16.62	1.5-cyclooctadiene. 3-t-butyl-	0.11	-	0.11	-	0.20	-	-	0.33	-	-	-
35	17.04	Cycloten	-	-	0.45	0.57	1.39	3.00	2.22	16.89	3.07	-	0.53
36	17.62	2-acetyl-5-methylfuran	0.20	-	0.12	0.12	0.18	-	0.65	0.36	0.34	3.10	-
37	17.70	2-cyclopenten-1-one. 2.3-dimethyl	0.93	0.84	0.72	0.67	1.22	-	-	1.44	-	0.19	0.32
38	18.86	Benzylethanolamine	-	-	-	0.14	0.25	0.72	-	1.55	0.29	-	-
39	18.86	1.3-cyclopentanedione. 2.4-dimethyl-	-	-	0.14	-	-	0.42	0.31	-	-	-	-
40	19.06	*o*-cresol	1.49	1.31	1.23	-	2.65	1.45	1.16	2.74	0.66	1.02	0.39
41	19.26	2-cyclopenten-1-one. 3.4.4-trimethyl-	0.37	0.22	0.11	1.05	-	-	0.26	-	0.20	-	-
42	19.46	Acetophenone	0.18	-	-	0.36	-	-	-	-	-	-	-
43	20.07	2-cyclopenten-1-one. 3-ethyl-isomer	-	0.11	0.20	0.20	0.53	-	-	-	0.18	0.23	-
44	20.40	*p*-cresol	0.91	0.73	0.83	0.14	1.65	1.41	1.31	-	1.32	1.07	-
45	20.47	*m*-cresol	1.00	0.83	1.30	0.80	2.87	2.04	1.83	-	1.00	1.64	1.03
46	21.05	*o*-guaiacol	13.89	12.9	8.92	0.65	10.3	6.55	5.68	-	3.58	1.79	1.58
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47	21.16	3-ethyl-2-hydroxy-2-cyclopenten-1-one	-	0.24	-	12.08	0.25	-	-	-	0.13	-	-
48	21.38	4-hepten-3-one. 4-methyl-	0.29	0.26	0.24	0.40	0.22	-	-	-	-	-	-
49	21.83	4.4-dimethylcyclohexenone	0.50	0.51	0.24	0.22	0.30	-	-	-	-	-	-
50	22.22	*o*-xylenol	0.27	0.25	0.09	0.35	0.28	-	-	-	-	-	0.18
51	22.46	Larixic acid	-	-	-	-	-	-	-	-	0.24	-	-
52	22.95	2-cyclopenten-1-one. 3-ethyl-2-hydroxy	-	-	0.60	0.19	0.94	1.00	0.94	-	0.96	0.70	0.13
53	23.75	2-cyclopenten-1-one. 3.4.4-trimethyl-isomer	0.36	0.35	0.19	0.35	0.14	-	-	-	-	0.29	-
54	24.53	*o*-ethylphenol	0.27	0.26	0.31	0.24	0.55	-	-	-	-	-	-
55	24.83	2-oxaadamantane	0.17	0.12	0.19	0.29	0.26	-	-	-	-	-	-
56	25.14	*o*-xylenol-isomer	-	-	-	0.50	0.79	-	-	-	-	-	0.24
57	25.23	*o*-xylenol-isomer	-	-	-	0.15	0.72	-	-	-	-	-	0.29
58	26.41	*p*-ethylphenol	0.24	0.22	0.22	0.37	0.40	-	-	-	-	-	-
59	26.58	*m*-ethylphenol	0.38	0.33	0.58	0.47	1.26	-	0.35	-	0.30	0.25	-
60	26.88	Isocreosol-isomer	0.51	0.51	0.16	0.32	0.39	-	-	-	-	-	-
61	27.38	Phenol. 2-methoxy-3-methyl-	0.55	0.50	0.39	0.46	0.49	-	-	-	-	-	-
62	27.87	Isocreosol	9.24	8.84	6.01	8.69	6.46	1.83	1.61	-	0.89	0.39	1.79
63	28.14	3.4-xylenol	-	-	0.27	-	-	-	-	-	-	-	-
64	28.84	*α*-acetylcyclohexanone	-	0.14	0.33	0.17	0.39	-	3.84	-	-	-	-
65	28.89	Catechol	-	-	-	-	-	-	-	-	13.77	20.91	
66	29.21	4.7-Dimethylbenzofuran	-	-	-	-	-	-	-	-	-	-	0.22
67	30.49	5-(hydroxymethyl)furfural	-	-	-	-	-	-	-	-	0.79	-	-
68	30.99	3.4-dimethoxytoluene	0.39	0.38	-	0.23	0.24	-	-	-	-	-	-
69	31.05	4-ethyl-o-cresol	-	-	-	-	-	-	-	-	-	-	0.36
70	32.32	4-methoxybenzene-1.2-diol	-	-	0.21	-	0.53	-	1.57	-	4.90	-	-
71	32.52	???	-	-	-	-	-	-	-	-	-	-	0.14
72	32.92	3-methylcatechol	-	-	-	-	0.50	-	0.97	-	2.59	8.29	-
73	33.12	Acetylhydroquinone	-	-	0.59	0.51	0.94	-	-	-	0.23	5.32	-
74	33.15	*α*-iunknownanone	-	-	-	-	0.76	-	-	-	-	-	0.21
75	33.51	*p*-ethylguaiacol	6.38	6.41	3.74	-	3.99	0.59	0.39	-	0.23	-	4.13
76	33.90	*α*-resorcinol	-	-	-	-	-	-	-	-	0.23	2.40	-
77	34.18	*α*-methylnaphthalene	-	-	-	-	-	-	-	-	-	-	0.33
78	34.82	3-methylcatechol-isomer	-	-	-	-	-	-	-	-	4.48	10.11	-
79	35.23	1-ethylidene-1*H*-indene	-	-	-	-	-	-	-	-	-	-	0.22
80	35.43	1.8-dimethyltetralin	-	-	-	-	-	-	-	-	-	-	0.15
81	35.55	(5-formyl-2-furyl)methyl acetate	-	-	-	-	-	-	-	-	0.21	0.41	-
82	35.72	4-hydroxy-3-methylacetophenone	-	-	-	-	-	-	-	-	-	-	0.59
83	35.74	*o*-veratryl alcohol	-	0.49	0.20	6.26	0.44	-	-	-	-	-	-
84	36.08	(2-methyl-cyclohex-2-enylidene)-acetaldehyde	-	-	-	-	0.24	-	-	-	-	-	-
85	37.58	Chavicol	-	-	-	-	0.26	-	-	-	0.13	2.00	-
86	38.15	Syringol	5.63	5.44	13.11	0.55	13.22	10.91	10.57	-	12.07	9.16	5.15
87	38.51	Eugenol	0.72	0.67	0.31	9.28	0.19	-	-	-	1.75	-	0.13
88	38.66	Anisole. *o*-(methylthio)-	-	-	-	-	0.78	-	-	-	-	-	0.14
89	39.04	2.6-dimethoxy-3-pyridinamine	-	-	-	-	-	-	-	-	-	2.26	-
90	39.11	Cerulignol	0.68	0.68	0.44	0.65	0.27	-	-	-	-	-	1.63
91	40.64	4-ethylcatechol	-	-	-	-	-	-	-	-	1.12	0.42	-
92	41.04	Lioxin	-	-	-	0.13	-	0.65	0.36	-	0.89	3.19	-
93	41.16	1.3-Dimethylnaphthalene	-	-	-	-	-	-	-	-	-	-	0.28
94	41.53	3.4.5-trimethoxytoluene	0.20	0.22	0.27	0.57	0.22	-	-	-	-	-	0.29
95	41.63	*cis*-isoeugenol	0.17	0.35	0.27	-	-	-	-	-	-	-	-
96	41.99	1.8-dimethylnaphthalene	-	-	-	-	-	-	-	-	-	-	0.17
97	42.18	1.8-Dimethylnaphthalene-isomer	-	-	-	-	-	0.43	0.30	-	0.18	-	0.21
98	44.06	3.5-dimethoxy-4-hydroxytoluene	5.59	5.77	12.20	0.38	10.94	4.30	4.47	-	5.06	4.85	5.15
99	44.19	Isoeugenol	-	1.32	-	8.82	-	-	-	-	-	-	2.33
100	46.31	1.4-dimethoxy-2.3-dimethylbenzene	-	-	0.13	1.19	0.16	0.42	0.33	-	0.95	0.22	0.72
101	46.54	Acetovanillone acetate	-	-	-	-	-	-	-	-	-	0.42	-
102	47.16	Geranyl isovalerate	-	-	-	-	-	-	-	-	-	-	0.16
103	47.89	BHT	-	-	-	-	-	0.43	0.30	-	0.18	-	-
104	48.03	6-hydroxy-3.4-dihydrocoumarin	-	-	-	-	-	-	-	-	0.15	0.61	-
105	48.71	4-*o*-methylphloracetophenone	6.36	6.56	11.92	0.20	8.40	1.67	1.61	-	1.42	0.99	8.43
106	48.92	Guaiacylacetone	-	-	11.92	8.08	0.47	0.93	1.50	-	3.29	1.65	0.56
107	49.23	5-*sec*-butylpyrogallol	-	-	0.21	0.45	0.36	-	-	-	-	0.24	
108	50.18	2.3.5-Trimethylnaphthalene	-	-	-	-	-	-	-	-	-	-	1.08
109	50.70	Unknown	-	-	-	-	-	-	-	-	-	-	0.56
110	51.12	1'-hydroxyeugenol	-	-	-	-	-	-	-	-	0.13	-	0.32
111	51.45	*α*-acetonaphthone	-	-	-	-	-	-	-	-	-	-	0.81
112	52.38	Unknown	-	-	-	-	-	-	-	-	-	-	0.24
113	52.58	Methoxyeugenol	0.91	1.09	1.54	1.49	0.86	-	0.21	-	0.21	-	0.71
114	52.91	Homosyringic acid	1.44	1.53	2.55	1.66	1.58	-	-	-	-	-	5.00
115	54.58	1-propanol. 3-(4-hydroxy-3-methoxyphenyl)-	-	-	-	-	-	-	-	-	0.58	0.30	-
116	54.80	*trans*-4-Propenylsyringol	-	0.53	0.68	0.83	0.58	-	-	-	-	-	0.73
117	55.13	Trimethoxyamphetamine. 2.3.5-	-	-	-	-	-	-	0.19	-	0.36	0.22	-
118	55.63	Unknown	-	-	-	-	-	-	-	-	-	-	0.16
119	56.48	Unknown	-	-	-	-	-	-	-	-	-	-	0.16

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120	56.86	*trans*-4-propenylsyringol-isomer	0.19	1.51	1.09	3.43	1.83	-	0.25	-	-	0.19	4.69
121	58.18	Acetosyringone	-	-	-	-	-	0.92	0.83	-	1.32	0.54	0.44
122	59.68	*trans*-sinapyl alcohol	0.18	0.19	0.39	0.43	0.15	0.94	1.72	-	2.23	1.63	0.80
123	59.99	1-octadecene	-	-	-	-	-	-	-	-	-	-	0.14
124	60.42	1-Hexadecanol. 2-methyl-	-	-	-	-	-	-	-	-	-	-	0.50
125	60.68	Octadecane	-	-	-	-	-	-	-	-	-	-	0.64
126	60.87	2-Phenyldodecane	-	-	-	-	-	-	-	-	-	-	1.07
127	61.71	Benzene. (1-pentyloctyl)-	-	-	-	-	-	-	-	-	-	-	1.75
128	61.72	3.4.5-trimethoxyphenyl-2-propanone	-	-	-	-	-	-	-	-	0.14	-	-
129	62.39	Benzene. (1-propyldecyl)-	-	-	-	-	-	-	-	-	-	-	1.61
130	63.19	Benzene. (1-ethylundecyl)-	-	-	-	-	-	-	-	-	-	-	2.25
131	64.01	9-nonadecene	-	-	-	-	-	-	-	-	-	-	0.28
132	64.24	9-nonadecane-isomer	-	-	-	-	-	-	-	-	-	-	0.76
133	64.55	Benzene. (1-methyldodecyl)-	-	-	-	-	-	-	-	-	-	-	13.3
134	65.14	Palmitic acid. methyl ester	-	-	-	-	-	-	-	-	-	-	2.90
135	67.34	1-eicosene	-	-	-	-	-	-	-	-	-	-	1.45
136	67.55	Eicosane	-	-	-	-	-	-	-	-	-	-	1.30
137	70.48	Henicos-1-ene	-	-	-	-	-	-	-	-	-	-	0.75
138	70.67	Heneicosane	-	-	-	-	-	-	-	-	-	-	1.31
139	71.50	Stearic acid. methyl ester	-	-	-	-	-	-	-	-	-	-	0.28
140	71.63	Linoleic acid	-	-	-	-	-	-	-	-	-	-	0.17
141	71.69	???	-	-	-	-	-	-	-	-	-	-	0.14
142	71.76	???	-	-	-	-	-	-	-	-	-	-	0.21
143	72.04	Linoleic acid ethyl ester	-	-	-	-	-	-	-	-	-	-	0.37
144	73.45	1-docosene	-	-	-	-	-	-	-	-	-	-	2.50
145	73.62	Docosane	-	-	-	-	-	-	-	-	-	-	1.47
146	76.64	1-tricosanol	-	-	-	-	-	-	-	-	-	-	0.44
147	76.84	Hexacosane	-	-	-	-	-	-	-	-	-	-	0.77
148	80.73	Octacosanol	-	-	-	-	-	-	-	-	-	-	0.83
149	80.97	???	-	-	-	-	-	-	-	-	-	-	0.25
150	85.78	9-hexadecenoic acid. 9-octadecenyl ester	-	-	-	-	-	-	-	-	-	-	1.10
151	89.00	???	-	-	-	-	-	-	-	-	-	-	1.20
152	89.15	???	-	-	-	-	-	-	-	-	-	-	0.40
153	90.84	???	-	-	-	-	-	-	-	-	-	-	1.71

***H:** hour

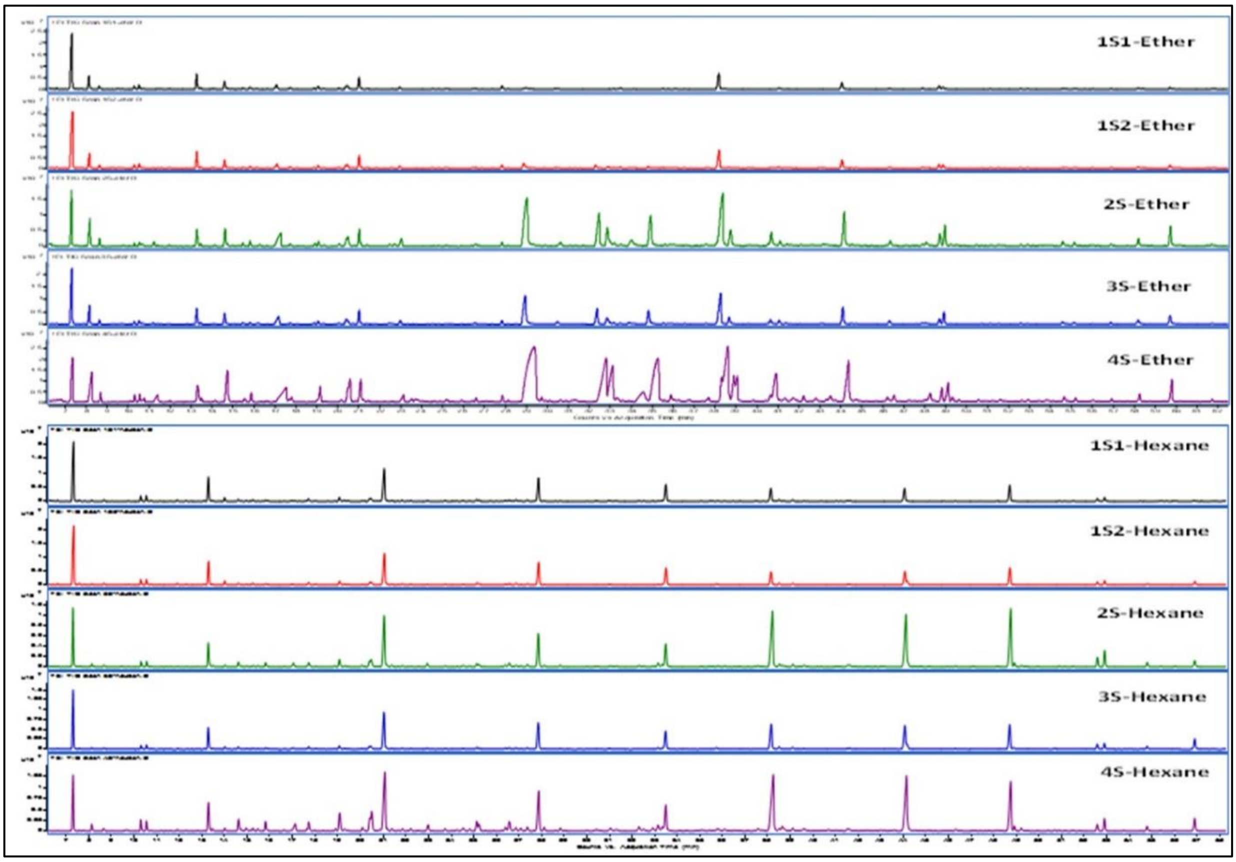

Figure 2. GC-MS spectrums of tar obtained at 400 ºC.

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We can classify benzene and its derivatives, toluene substances, furan compounds, phenols, and their derivatives as monoaromatic compounds. However, alkanes, alkenes, and alkynes form the aliphatic class, while aldehydes, esters, carboxylic, and ketones form oxygenated compounds.

In addition, amines and amides are compounds in the nitrogen class. As can be understood from previous literature studies, most of the bio-oil product compounds are phenolic and their derivatives are products obtained due to the degradation of lignin raw material.[31] The bio-oil products formed by the heating process are valuable not only as a fuel in motor vehicles or boiler machines but also as an organic chemical, for example, phenols used with commercial value. Bio-oil products are mainly composed of aldehydes, ketones, and phenolic-containing oxygen-containing compounds. These classes of compounds are formed from the degradation of most lignin substances, and the other classes of compounds are from cellulos.

As a result of the heating process, compounds containing the most acetic acid, 2,6 dimethoxy phenol, furfural, and furan derivatives are formed in bio-oils. When woody materials are exposed to the heating process, hemicelluloses first decompose (200-280 °C), resulting in acidic compound products such as acetic acid. Celluloses decomposed when it exposed to 240-350°C heat treatment. Anhydro glucoses, furan, and furan derivatives are also formed together with the first levoglucosan as the primary degradation product due to cellulose decomposition. Finally, the primary products of the degradation of lignin, the majority of which are 2,6-dimethoxy phenol and its derivatives, were obtained by heat treatment at 280-400 °C.

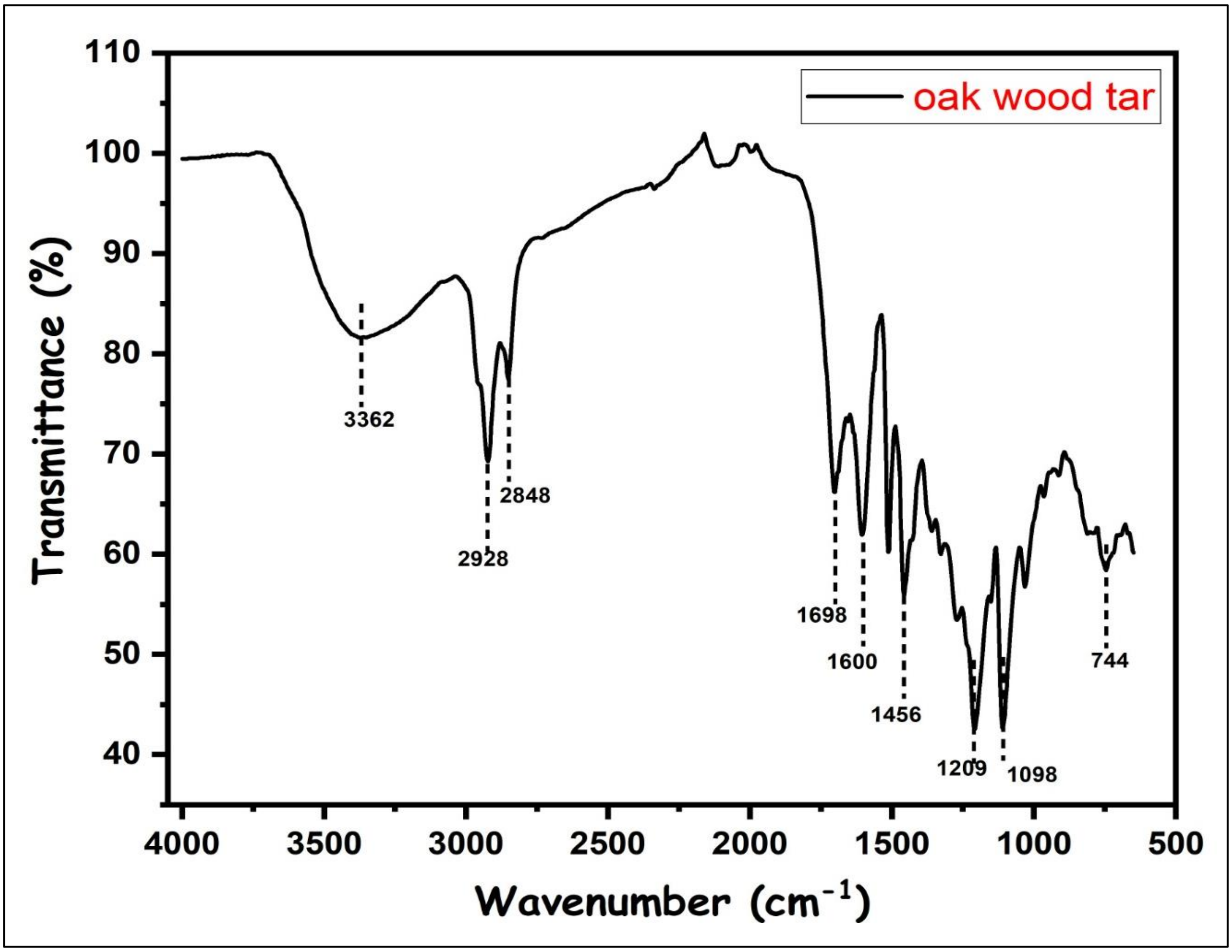

Figure 3. FT-IR spectrums of bio-oils and tar obtained at 400 °C.

The degradation of biomass occurs in 3 stages depending on the pyrolysis temperature.[32] Between 100 -200 °C, the moisture in the biomass content decomposes. In the second stage, the depolymerization reaction (200-400 °C) called primary pyrolysis takes place. In this temperature range, biomass condensable and non-condensable products begin to form. Secondary tar formation processes continue with the formation of primary coals, secondary coals and permanent gases. In other words, various reactions take place such as the breakdown, shaping and re-polymerization of the tar.

However, there is no clear distinction between primary and secondary transformations.

FT-IR spectrum data of tar obtained at 400°C are given in Figure 3. It found that significant changes formed as seen in the FT-IR spectrum as a result of the pyrolysis process. The weak peak of O-H stretching vibration band at 3362 cm^{-1} shows that the amount of biochar was significantly absent because oxygen was removed from the raw material during pyrolysis, causing it to break down into phenol and aromatic parts, resulting in carbon-based solid products. FT-IR spectra of bio-oils exposed to different heating times show very similar characteristics. Weak peak bands observed between 2550 cm^{-1} and 2650 cm^{-1} indicate aliphatic C-H stretching. The bands of C-C stretching vibrations observed between 1350 and 1700 cm^{-1} indicate the formation of aromatic and alkane groups. C-O stretch absorption peak values observed between 950 and 1350 cm^{-1} prove that primary, secondary, and tertiary alcohol compounds, phenol groups, ethers, and ester compounds are formed. The FT-IR spectrum analysis results showed that the aromatic and aliphatic groups of the bio-oils obtained by the pyrolysis process were more intense.

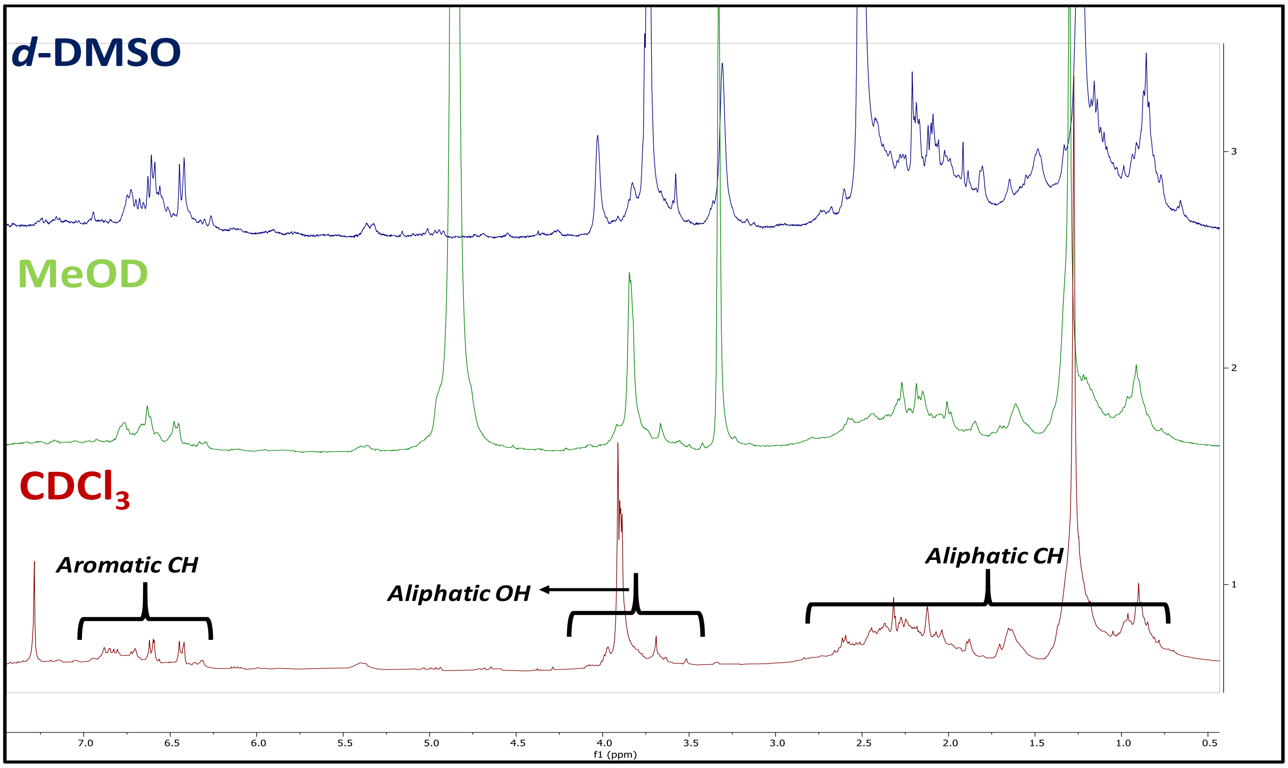

Figure 4. NMR spectrums of bio-oils and tar obtained at 400 ºC.

NNR analyses were carried out to detailed results of the experimental analyses of pyrolysis products. The NMR spectrum results are given in Figure 4. The peaks from O-H or N-H vibrations indicated between 3100 and 3370 cm^{-1} that show the presence of phenol and alcohol compound groups, and absorption peaks from C-H and =C-H vibrations detected between 2800 and 2950 cm^{-1} indicate the presence of alkane and alkene group compounds. Group (C=O) stretching vibrations of carbonyl compounds at their peaks at approximately 1698 cm^{-1} of bio-oil products prove that aldehyde, ketone, or carboxylic acid group members are produced due to raw material degradation. However, peaks from C=C stretching vibrations at about 1600 cm^{-1} confirm the presence of alkene compounds. In addition, the indicated C=C stretch vibration peaks between 1450 and 1570 cm^{-1} confirm the presence of aromatic compounds. The formation of benzene derivatives and phenol compound products is thought to result from the decomposition of lignin.[30]

4.CONCLUSION

In this current study, the heating process of oak wood was carried out to obtain tar and liquid (bio-oil) products at 400 °C without a catalyst at different heating times. It was found at 400 °C after 4 hours as the most suitable parameter for bio-oil formation without using catalytic. The composition of bio-oil products obtained by the pyrolysis process of oak wood was characterized using advanced chromatographic and spectroscopic techniques. It was determined that the heating process oil is a very complex organic mixture containing aromatic, oxygenated, and nitrogenous. FT-IR, HPLC, NMR, and GC-MS results of bio-oil products can be evaluated as a chemical raw material for the pyrolysis of oak wood both in production as fuel and for different purposes such as fertilizer in agriculture.

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Conflict of Interest

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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