

Liquefaction of Oak Wood Using Various Solvents for Bio-oil Production

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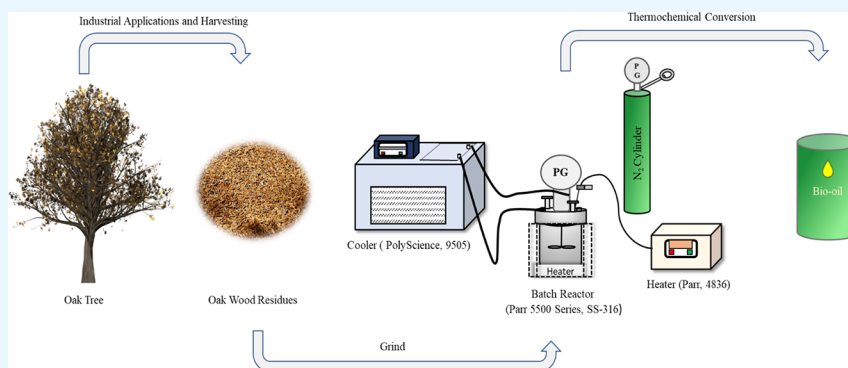
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ABSTRACT: Rapidly increasing global energy demand resulting from the growing population and worldwide development has increased the consumption of limited fossil fuel. The usage causes severe environmental deterioration by CO₂ emission, which has sparked interest in finding green, renewable, and sustainable alternative sources of energy. Bio-oil, derived from several biomasses via liquefaction, is a promising candidate to replace fossil fuels. Turkey's land (27%) is covered with forested areas (consisting of mostly oak trees). Therefore, it has great potential for cheap lignocellulosic feedstock forest residues from industrial applications and harvesting. In the present study, the thermal liquefaction of oak wood particles (OWP) was performed using various solvents in addition to water, namely, ethanol, 1-butanol, and 1,4-dioxane. The experiments were carried out in a batch reactor for 1 and 2 h residence times at different temperatures (210, 240, and 270 °C). Bio-oil samples obtained at 270 °C and a 1 h residence time determined as optimum conditions were analyzed with TGA, CHNS elemental analysis, FTIR, and GC–MS. 1,4-Dioxane showed the best performance in yielding the maximum bio-oil with 51.8% at those conditions. The higher heating values of the bio-oils ranged from 22.1 to 35 MJ/kg. Phenolic groups were the predominant components of bio-oil produced from OWP, while the intensity of alcohols, ketones, and acids varied based on used solvents. Based on energy recovery calculations, the enhancement of pristine OWP's energy efficiency depended on bio-oil yield, and quality was confirmed for all solvent types (1,4-dioxane > 1-butanol > water > ethanol).

1. INTRODUCTION

Rapidly increasing global energy demand resulting from the growing population and worldwide development increased consumption of fossil fuel, which is the primary energy resource in this era. In addition, fossil fuel usage causes serious environmental deterioration such as greenhouse gas emissions and climate change due to the high amount of CO₂ emitted. Concerns about issues caused by fossil fuel use and its limited reserves have sparked interest in finding green, renewable, and sustainable alternative sources for energy and chemical production on a global scale. To provide an environmentally friendly solution about these concerns and a new sustainable energy source, as an inexpensive renewable resource with neutral CO₂ emissions and widespread abundance around the world, biomass is the most promising candidate to replace fossil fuels in producing chemicals and fuels.^{1–3} Conversion of

biomass to platform chemicals thermochemically requires enormous energy consumption. On the other hand, biomass is not an ideal form to use as fuel because it has a natural water content on a dry basis that can reduce the available net heat when directly combusted by up to 20%, so its higher heating value (HHV) varies between only 15 and 20 MJ/kg.^{4,5} However, biomass can be converted into energy sources with environmentally friendly, economically affordable, and rela-

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tively simple technologies. According to the International Energy Agency, in 2019, biofuels fulfilled 9.4% of the total fuel-based energy supply of the world. European countries led by France and Sweden have accelerated their efforts for a carbon-neutral world. The “Multi-Year Plan” and the “Biomass Action Plan,” which were prepared by the European Commission and the US Department of Energy, respectively, demonstrate how politically and economically significant bioenergy is in developing nations. These documents align with the Kyoto Protocol, highlighting the dangers of CO₂ emissions and trying to make a difference, especially in global warming.⁶ In this manner, the utilization of locally abundant biomass sources can enhance energy security and support the development of low-carbon energy systems. Instead of directly using biomass, producing alternative liquid fuels from it, such as bio-oils, can prevent the wastage of huge potential. Also, they have the potential to be renewable and green fuels, which will reduce CO₂ emissions and afford adequate energy in the future. Bio-oils that can replace fossil fuels in many static applications of electricity generation using furnaces, engines, turbines, and boilers are easily transportable and storable and have different properties and several advantages compared with petroleum-derived fuels due to their chemical compositions. As a clean fuel, bio-oils contain negligible amounts of sulfur and a little nitrogen. Therefore, no SO_x generation and also lower than 50% NO_x emissions are observed when used. Upgrading of bio-oil produced with various methods (hydrotreating, hydrocracking, solvent addition, etc.) could be necessary before using it as a transportation fuel. Additionally, bio-oil can be used as an alternative feedstock for producing phenol-formaldehyde-based resins, adhesives, and wood flavors.^{3,7,8} There are two main routes to producing bio-oil: thermal liquefaction and pyrolysis. Although a high-pressure process increases the investment cost, thermal liquefaction has crucial advantages compared to pyrolysis, such as solvent variety, enabling catalyst, and more qualified bio-oil production with a lower oxygen and moisture content, resulting in a higher HHV up to 35 MJ/kg. Biomass is depolymerized during liquefaction, producing bio-oil, using a solvent at elevated temperatures and pressures as a suitable medium and reactant. In addition, contrary to pyrolysis, the drying step is not required before thermochemical liquefaction.^{7,9,10} However, there is no clear market for large-scale bio-oil production as studies are still ongoing at the lab scale.¹¹ In this direction, the temperature, residence time, solvent, catalyst, and biomass/solvent ratio are the main parameters of thermal liquefaction, which are highly investigated to optimize in the literature.^{12–19}

Turkey's land (27%) is covered with forested areas; therefore, it has great potential for cheap feedstock forest residues from industrial applications and harvesting.²⁰ Due to their high holocellulose and relatively low lignin content, they are ready to use and highly suitable for producing bio-oil via the thermal liquefaction process.^{21,22} According to the Atlas of Potential Biomass Energy of Turkey, in 2023, annual residues from forestry and wood industries were over 1.5 million tons, and this number is increasing year by year with growing industrial applications. On the other hand, in Turkey, the largest forestry area, also one of the biggest wood industries, is occupied by oak wood (*Quercus* spp.), which is previously studied as a raw material to produce bio-oil in the literature.²³ First, the thermal liquefaction experiments on oak wood were performed by Ogi et al. for 1 h at a chosen temperature range of 250–300 °C. They used a cosolvent, water/Z-propanol,

resulting in a 10.3–56.7% bio-oil yield with an HHV range of 21.5–28 MJ/kg.²⁴ de Caprariis et al. compared hydrothermal liquefaction performances of different raw materials, namely, natural hay, oak wood, walnut shell, and industrial cellulose, ranging between 240 and 320 °C at subcritical conditions for a 30 min residence time. The maximum bio-oil yield obtained from oak wood was observed at 240 °C with an HHV of 22.7 MJ/kg.²⁵ In another presented article by de Caprariis et al., the hydrothermal liquefaction of oak wood was performed in the range of 260–320 °C for a 15 min residence time in the presence of 10% iron-based catalysts by biomass weight (Fe, Fe₂O₃, and Fe₃O₄) to observe the effect of iron ion addition. Experimental results showed that Fe was the best iron type, yielding nearly 40% bio-oil and the highest HHV of 32.28%.²⁶ Hwang et al. reported the maximum 27.7% bio-oil yield and 31.9 MJ/kg HHV from hydrothermal liquefaction of Mongolian oak in the presence of 0.5 M K₂CO₃ during a 30 min process time at 300 °C.²⁷ de Caprariis et al. also worked with metallic Ni catalysts on the liquefaction of oak wood. Hydrothermal liquefaction of oak wood was carried out in tubular microreactors at different temperatures (280–330 °C), reaction times (10–30 min), and catalyst loads (10–50 wt %) using metallic Ni catalysts. The maximum oil yield was successfully obtained as 38.71% in the presence of 50% nanospiked Ni at 330 °C and 10 min, which are the best conditions, while the highest HHV was calculated to be 28.89 MJ/kg.²⁸ Lastly, Tai et al. investigated the effect of zerovalent metals (Fe and Zn), as hydrogen producers, and hydrodeoxygenation catalysts (Ni and Co) to produce high-yield bio-oil from oak wood via liquefaction. The reaction temperature was set as 330 °C during a 10–30 min residence time, and 48% was the maximum oil yield achieved at the end of the 30 min reaction time with 0.5 g of Fe and 0.1 g of Ni.²⁹

Although there have been studies with oak wood in the presence of different catalysts, only water was used as a solvent. Therefore, the effect of the solvent type on conversion of oak wood into bio-oil still has a gap. In this work, the thermal liquefaction of oak wood, which is the tree species that covers the most area in Turkey, was performed using various solvents in addition to water, such as ethanol, 1-butanol, and 1,4-dioxane to investigate the effects of the solvent type for the first time in the literature at different experimental conditions. Solvent selections were made mainly based on different important properties (dielectric constant, density, etc.) of solvents effective on bio-oil yielding, which are listed in Table 5. Especially, remarkable differences were carefully considered between the dielectric constants of solvents in addition to their specific features when choosing solvents. Among the selected solvents, water, ethanol, and 1-butanol are members of polar protic solvents that are Lewis bases and superior donors and acceptors of H-bonds, while 1,4-dioxane is a dipolar aprotic solvent without the –OH group. Water is the cheapest, harmless, and most used solvent to decompose lignocellulosic biomass. Even though the hydrothermal liquefaction of oak wood was extensively studied, with this work, water was used as the solvent again to check and compare with published previous results. On the other hand, alcohols can lead to higher lignin solubility because of their unique properties such as high dispersion capacity, heat transfer, and inhibiting char formation. Ethanol is the cheapest and most environmentally friendly low-boiling-point alcohol that reaches the supercritical stage easily with providing high solubility, ease of separation, and low corrosivity.³⁰ In addition, compared to the other

alcohols, there is not enough study in the literature of 1-butanol as a liquefaction solvent. The main reason for this is that unaided 1-butanol is found to be appropriate as one of the future biofuels. Also, it can be used to upgrade bio-oil alongside a catalyst instead of producing it under protecting the catalyst and enhancing H₂ dissolution.³¹ However, 1-butanol is a biorenewable solvent, and it is stable during liquefaction reactions and not consumed, which means that it can be recycled after liquefaction experiments and used for more than one cycle.³² 1,4-Dioxane, the only solvent belonging to a different group with great potential, is a highly suitable solvent for conversion of biomass. However, the available studies in the literature are limited.

The key objective of the study is to produce green fuel bio-oil in the absence of a catalyst from OWP via thermal liquefaction in high yield while showing the effect of the solvent type for the first time at determined operation conditions. In this respect, the experiments were carried out in a batch reactor at different temperatures (210, 240, and 270 °C) for 1 and 2 h residence times with a constant biomass/solvent ratio. Ethanol, 1-butanol, and 1,4-dioxane, selected according to their specific properties mentioned above, with potential were used as solvents for the first time in the thermal liquefaction of OWP. Before starting the experiments, the characterization of the oak wood was made. Bio-oil samples obtained under optimum conditions were analyzed with thermogravimetric analysis (TGA), CHNS elemental analysis, Fourier transform infrared spectrometry (FTIR), and gas chromatography–mass spectrometry (GC–MS). FTIR analysis was also employed for solid residues formed at optimum conditions as well as scanning electron microscopy (SEM).

2. MATERIALS AND METHODS

2.1. Materials. Oak wood samples were supplied from a wood industry region in İzmir and were ground to particles between 250 and 500 μm after washing and overnight drying at 60 °C. Obtained particles were called oak wood particles (OWP) for this study. Solvents (ACS grade) and other chemicals such as ethanol, 1-butanol, 1,4-dioxane, dichloromethane (DCM), acetone, toluene, sulfuric acid, acetic acid, and sodium chlorite (NaClO₂) were purchased from Merck.

2.2. Biomass Characterization. According to the procedure developed by Teramoto et al., the content of cellulose, hemicellulose, and lignin in OWP was found as follows.³³

To obtain defatted particles, the Soxhlet extraction method was performed with a mixture of EtOH and toluene (1:2 v/v) for 6 h. Defatted particles (2.5 g) were treated four times for 1 h at 75 °C with 2 g of NaClO₂ in 150 mL of diluted acetic acid to determine the amount of holocellulose. The particles were washed after treatment with acetone and distilled water. Following a 24 h, 105 °C, vacuum-drying process, the remaining parts of the delignified (holocellulose) components were weighed. Twenty-five mL of a 17.5% NaOH aqueous solution was used to dissolve 1 g of extracted holocellulose. This mixture was then agitated for 40 min at room temperature before the addition of 25 mL of distilled water. The solution was filtered 5 min after the water addition, and the filtrate was blended with 40 mL of a 10% acetic acid solution before the second filtration. To wash the residue, 1 L of boiling water was used. The remaining part weighed after drying in a vacuum for 48 h at 105 °C was α-cellulose, which was accepted as the cellulose content for this study. In addition, the hemicellulose

content was determined by subtracting α-cellulose from holocellulose. As the last step, to calculate the klason lignin content, 15 mL of a solution containing 72% sulfuric acid was added to 1 g of defatted OWP. The mixture was agitated for 4 h at room temperature before the addition of 560 mL of distillate water. Following filtration, the residue was washed with cold and hot water before drying for 24 h at 105 °C in a vacuum dryer and weighing.

The ash content of OWP was found using a muffle furnace operated in static air for 4 h at 600 °C. Also, the proximate and ultimate analyses of OWP were determined by TGA and elemental analysis, respectively.

2.3. Experimental Setup and Operating Conditions for Thermal Liquefaction. Thermal liquefaction experiments were performed in a 300 mL pressurized and stirred batch reactor (Parr 5500 series, SS-316, USA) that was equipped with an adjusted cooler (PolyScience, 9505) and heater (Parr, 4836) to retain the desired operating temperature. Before all experiments, pure N₂ was used to purge the inside of the reactor from gases (Figure 1). For each run, 4 g of OWP was

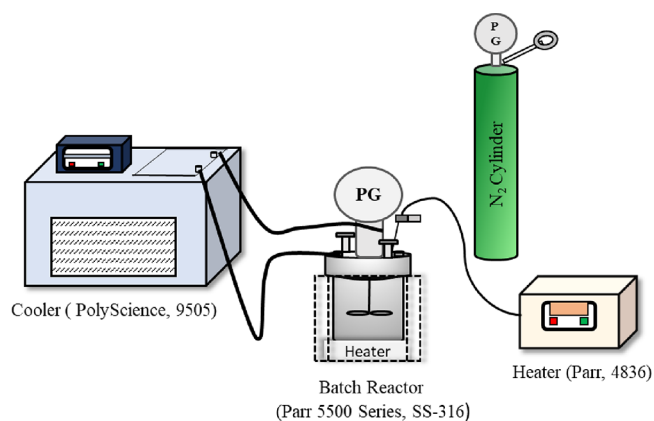


Figure 1. Experimental setup for the thermal liquefaction experiments.

loaded with 100 mL of a pure solvent (water, ethanol, 1-butanol, and 1,4-dioxane). The reactor was sealed, and then, the inside of the reactor was purged with N₂ 10 times before being heated to the desired temperature (210, 240, or 270 °C) with a 7 °C/min heating rate using a magnetic stirrer. To investigate the time effect, the residence time was set at 1 and 2 h when the temperature reached the desired level. At the termination of each run, the heater was turned off in order to reduce the reactor to room temperature at a 6 °C/min cooling rate.

2.4. Separation of Products. Filter paper (Whatman grade 307) was used to separate the liquid and solid mixtures. Solid parts were washed and dried overnight at 60 °C to get solid residues. In a separatory funnel, the liquid parts produced by using water as the solvent were extensively mixed with DCM (1:1 volume ratio), and we waited for an adequate time to obtain phases that were both DCM-soluble (bio-oil content) and water-soluble. Contrary to the water solvent, the ethanol-, 1-butanol-, and 1,4-dioxane-based liquid products were first evaporated by using a rotary evaporator (Heidolph Laborota 4001 efficient) to remove the solvent. Afterward, to extract the bio-oil content, the solvent-free portions were blended with DCM. The remaining parts were collected with the same solvent to recover the solvent-soluble products. To

purify the bio-oil, DCM-soluble phases were evaporated again with the rotary evaporator (Figure 2).^{34,35} At the end of the

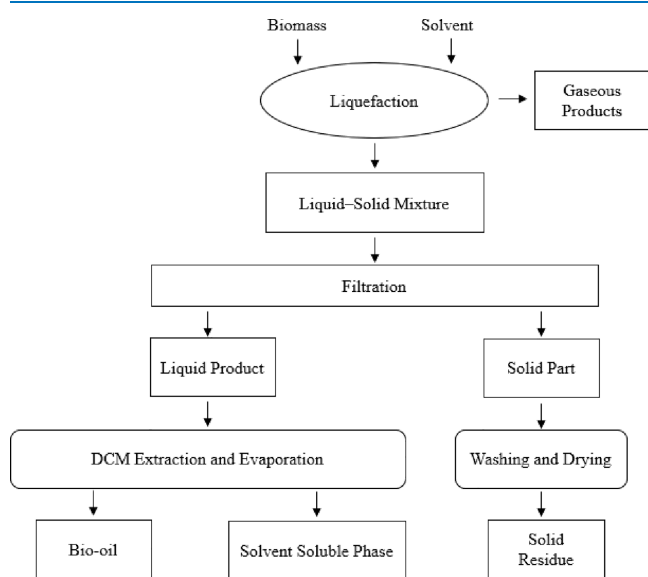


Figure 2. Separation procedure of products.

separation processes, the conversion of OWP, solid residue yield, liquid product yield, bio-oil yield, gaseous product yield, and energy recovery were calculated using the following equations, respectively:

$$\begin{aligned} \text{solid conversion of OWP (wt \%)} \\ = \frac{\text{mass of initial OWP} - \text{mass of solid residues}}{\text{mass of initial OWP}} \times 100 \end{aligned} \quad (1)$$

$$\text{solid residue yield (wt \%)} = 100 - \text{conversion (wt \%)} \quad (2)$$

$$\begin{aligned} \text{liquid product yield (wt \%)} \\ = \frac{\text{mass of liquid products}}{\text{mass of initial biomass}} \times 100 \end{aligned} \quad (3)$$

$$\text{bio-oilyield (wt \%)} = \frac{\text{mass of bio - oil}}{\text{mass of initial biomass}} \times 100 \quad (4)$$

$$\begin{aligned} \text{gaseous product yield (wt \%)} \\ = \text{conversion (wt \%)} - \text{liquid product yield (wt \%)} \end{aligned} \quad (5)$$

$$\begin{aligned} \text{energy recovery (\%)} \\ = \left(\frac{\text{HHV of bio-oil}}{\text{HHV of pristine OWP}} \right) \times \text{bio-oil yield} \end{aligned} \quad (6)$$

2.5. Analysis Methods of Products. To find the weight percentages of volatile materials (VM), fixed carbon (FC), and

moisture of OWP and bio-oil samples, TGA (Shimadzu, TGA-51) analysis with a heating rate of 10 °C/min under N₂ flow at 10 mL/min between 20 and 1000 °C was performed. For the same samples, elemental analysis (LECO 932 CHNS Determinator) was carried out in the presence of a CuSO₄ catalyst with helium gas at 1050 °C in an oxidation furnace, while the reduction furnace was set at 650 °C. The oxygen composition was calculated by the percentage difference between the remainder of the elements (eq 7). Sulfur was considered negligible because of its insignificant amount.³ Calculation of higher heating values (HHV) of all samples was made based on Dulong's formula (eq 8).³⁶

$$\text{O\%} = 100\% - \text{C\%} - \text{H\%} - \text{N\%} - \text{ash\%} \quad (7)$$

$$\text{HHV} = 0.3383\text{C\%} + 1.422(\text{H\%} - \text{O\%/8}) \quad (8)$$

OWP, solid residues, and bio-oil samples were analyzed with FTIR (ATR-FTIR, PerkinElmer-Spectra Two, USA) within the 4000 and 400 cm⁻¹ wavenumber range and with an average of 20 scans per 4 cm⁻¹ resolution to examine functional groups. Also, SEM (250 Fei Quanta 250 FEG, USA) analysis was employed for morphological analysis of the solid samples and OWP.

Major components of bio-oils were determined by GC-MS (Agilent 6890/5973 N Network, USA). Helium (1 mL/min) was used as the carrier gas in an HP-5MS column (0.25 mm × 30 m × 0.25 μm). Using a 10:1 split ratio, the injection volume was 1 μL. The temperature of the oven was initially set at 40 °C and maintained for 3 min. Then, it was heated to 190 °C at a rate of 12 °C/min and held for 1 min. Finally, the temperature was kept constant for 20 min after being raised from 190 to 300 °C at 8 °C/min. On the basis of the NIST 05 Library, the main components were identified. Water-soluble phases were also analyzed via TOC (Shimadzu TOC-Vcph TNM-1/SSM-5000 A).

3. RESULTS AND DISCUSSION

3.1. The Characterization Results of OWP. All characterization results of OWP found by the analysis methods described previously are given in Table 1. Cellulose, hemicellulose, and lignin contents were calculated to be 41, 23.7, and 28.3%, respectively, while extractives comprised 7% OWP. According to the proximate analysis results, the moisture percentage of OWP was 5.3, and the ash content was found to be 0.73%. On the other hand, the VM content of OWP was determined with TGA, and subtracting from 100% of VM and ash content gave an FC amount of OWP of 0. Also, using the ultimate analysis results of OWP, the HHV of pristine OWP was calculated based on Dulong's formula to be 18.05 MJ/kg. The results are compatible with the literature.^{37,38}

3.2. The Effect of Changing the Residence Time. The residence time (without counting heating and cooling intervals at a desired temperature) is one of the essential process parameters for biomass liquefaction, which affects biomass conversion, product yields, and compositions. Generally,

Table 1. OWP Characterization Results

chemical compositions (wt %)				proximate (wt %)				ultimate (wt %)				HHV (MJ/kg)
cellulose	hemicellulose	lignin	extractives	moisture ^a	ash ^b	VM ^a	FC ^{a,c}	C	H	O ^d	N	
41.0	23.7	28.3	7.0	5.3	0.73	99.27	0	49.5	6.3	42.7	0.8	18.05

^aDetermined by TGA. ^bDetermined using a muffle furnace at 600 °C for 4 h in static air. ^cFC = 100% - VM% - ash%. ^dDetermined by eq 7.

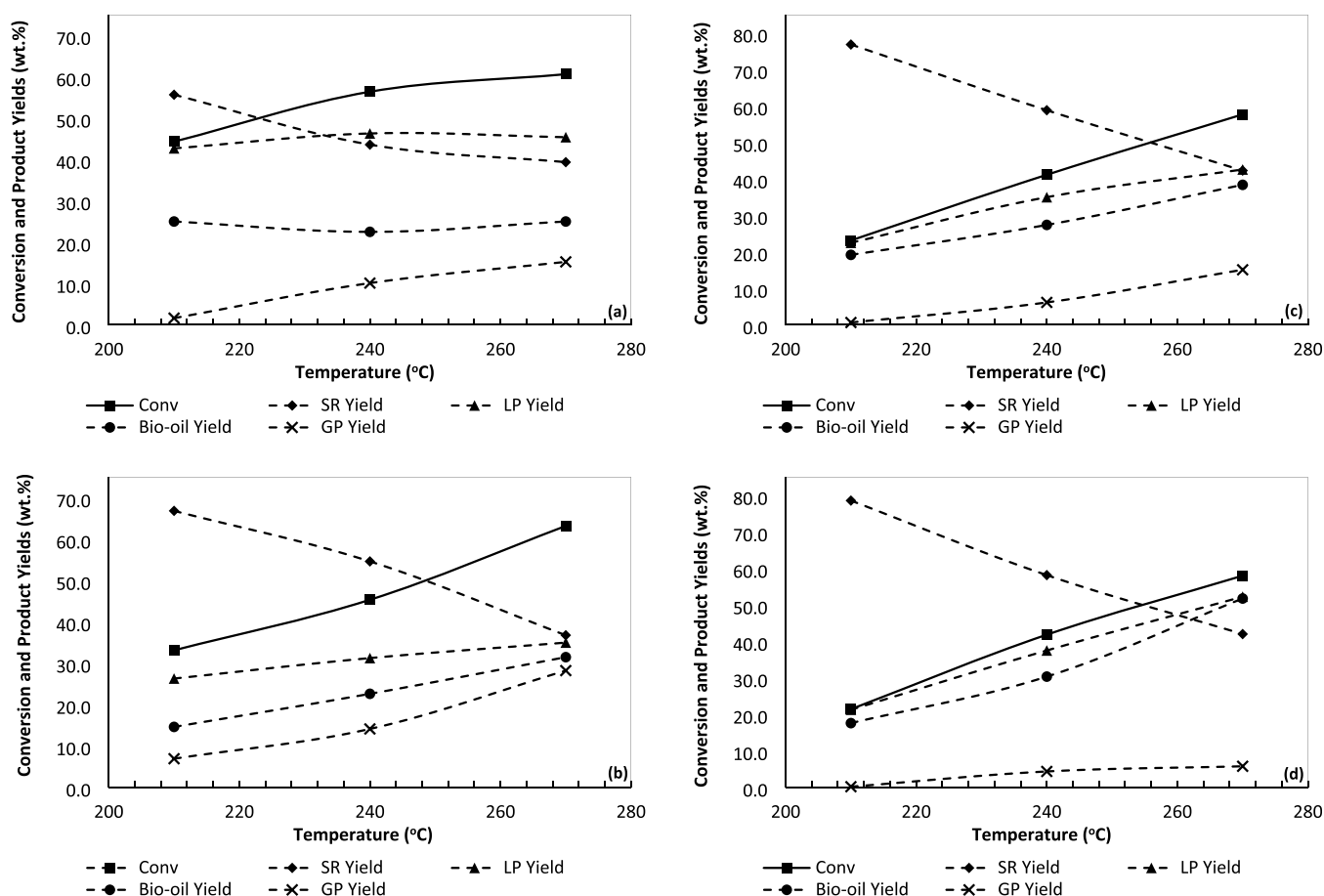


Figure 3. Conversion of OWP and product yields (solid residue, liquid, bio-oil, and gaseous) obtained in (a) water, (b) ethanol, (c) 1-butanol, and (d) 1,4-dioxane reaction media at different temperatures (210, 240, and 270 °C) for 1 h.

increases in the residence time improve biomass decomposition and product yields. However, depending on operating conditions and the type of biomass, solvent, and catalyst, further increases may have a negligible or negative effect after a certain point.

All the conversions and other product yields resulting from the liquefaction of OWP at different temperatures for 1 and 2 h residence times using various solvents are presented in Table 3. Increasing the residence time increased the conversion of OWP and product yields slightly at different temperatures for all solvents except the water medium. The highest increases in the conversion of OWP and bio-oil yield that resulted from the change of residence time from 1 to 2 h were observed to be 6.7 and 5.6% at 270 and 210 °C using ethanol, respectively. For 1-butanol, a 1 h time difference resulted in increases in the OWP conversion and bio-oil yield being 5.3 and 3.4%, respectively, while the increase in the gaseous product yield was only 0.3% at 270 °C. The slightest effect of increasing time was observed in experiments with 1,4-dioxane at 210 °C. The increments in the conversion of OWP, liquid, bio-oil, and gaseous products provided under the stated conditions are only 0.5, 0.3, 0.8, and 0.1%, respectively. Interestingly, the time-dependent decrease in the bio-oil yield (5%) and the most significant rise in gaseous product yields (8.4%) were only experienced using water as a solvent at 270 °C when the residence time changed from 1 to 2 h. The different reaction behaviors at low and high temperatures depend on residence time since it is always possible for secondary and tertiary reactions to occur in a

liquefaction medium. Due to the long residence times of heavy intermediates, several species of liquids, gases, or residues can be formed. After biomass conversion reaches the saturation stage, a decrease in bio-oil production becomes more likely.¹ Xu and Etcheverry proposed two possible reasons for the decrease in bio-oil yield at higher residence times: (1) the cracking of the liquid products to gases and (2) the formation of char by condensation, crystallization, and repolymerization of the liquid products.³⁹ In the present case, the large bio-oil molecules were cracked into light and small molecules like solvent-soluble gases by the time effect, and no extra char formation was observed. It explains the sharp increase in the gaseous product yield.

Under the present article scope, it can be said that increasing the residence time from 1 to 2 h has a negligible effect, especially on the bio-oil yield. For that reason, also considering from an economic point of view, 1 h was accepted as the optimum residence time for this study. Hence, the effects of the temperature and solvent type were investigated based on a 1 h residence time.

3.3. The Effect of an Increasing Reaction Temperature. The temperature, accepted as the critical parameter for the liquefaction process, significantly affects the conversion, product yields, and distribution. Generally, increasing the temperature improves bio-oil yields, as was observed in this work. According to Behrendt et al., the enhancement that is welded by increasing temperature results from the repolymerization of fragments, solid depolymerization, and aggregation

Table 2. Conversions of OWP and Product Yields (Solid Residue, Liquid, Bio-oil, and Gaseous) Obtained at Different Temperatures for 1 and 2 h Using Various Solvents via Thermal Liquefaction

solvent type	time (h)	temperature (°C)	weight (%)				
			conv. ^a	SR ^b yield	LP ^c yield	bio-oil yield	GP ^d yield
water	1	210	44.3	55.7	42.5	25.0	1.8
		240	56.4	43.6	46.3	22.5	10.1
		270	60.6	39.4	45.4	25.0	15.2
	2	210	45.4	54.6	42.3	25.0	3.1
		240	60.4	39.7	47.5	22.5	12.9
		270	63.9	36.1	40.3	20.0	23.6
ethanol	1	210	33.1	66.9	26.3	14.6	6.9
		240	45.4	54.6	31.3	22.6	14.1
		270	63.2	36.8	35.0	31.5	28.2
	2	210	35.1	64.9	27.6	20.2	7.5
		240	48.3	51.7	31.3	25.6	17.1
		270	69.9	30.1	40.0	33.4	29.9
1-butanol	1	210	23.1	76.9	22.5	19.2	0.6
		240	41.2	58.9	35.0	27.4	6.2
		270	57.7	42.3	42.6	38.4	15.2
	2	210	26.8	73.2	22.5	19.6	4.3
		240	44.5	55.5	35.0	29.9	9.5
		270	63.0	37.0	47.5	41.8	15.5
1,4-dioxane	1	210	21.4	78.6	21.2	17.6	0.2
		240	41.8	58.2	37.5	30.3	4.3
		270	58.0	42.0	52.2	51.8	5.8
	2	210	21.9	78.2	21.5	18.4	0.3
		240	45.6	54.4	40.0	32.5	5.6
		270	64.4	35.6	57.8	53.3	6.6

^aConversion. ^bSolid residue. ^cLiquid product. ^dGaseous product.

of gases.⁴⁰ However, producing bio-oils at high temperatures is not economically feasible, and decreasing oil yields are reported in the literature.^{41,42} This situation can be explained with increasing gas products depending on the activation of Boudouard gas reactions, the formation of charcoal due to the recombination of free radical reactions, and the transformation of large molecules into lighter molecules that dissolve in the solvent. An alternative explanation about the leveling-off is that the degradation of hemicellulose and lignin is endothermic at low temperatures and exothermic at high temperatures. Furthermore, biomass decomposition cannot be completed at low temperatures, and large amounts of unreacted biomass can suppress product formations.⁴³

In the present study, thermal liquefaction experiments were carried out to find the optimum reaction temperature at three different temperatures, namely, 210, 240, and 270 °C. Figure 3a–d depicts the effect of temperatures on the conversion of OWP and product yields for a 1 h residence time using various solvents, namely, water, ethanol, 1-butanol, and 1,4-dioxane. As expected, increasing the temperature generally increased the conversion of OWP and product yields for all types of solvents. The increments ranged from 4.2 to 20.4%, 2.5 to 21.5%, 2.9 to 16.3%, and 1.5 to 14.1% in the conversion of OWP, bio-oil, liquid, and gaseous product yields per 30 °C temperature difference, respectively. In thermochemical processes, increasing temperature leads to an increase in pressure (approaching the critical points), which means to observe decreasing pressure-dependent variables such as the dielectric constant and polarity; thus, reducing these properties of solvents forces organic compounds to be more soluble. Additionally, higher pressures also increase the density of solvents upon which solvent dissolving capability increases; as a result of this, a

better breakdown is achieved by high-density solvents since they can more readily enter the molecules of the biomass components.⁴⁴ However, temperature-independent pressure increases in the supercritical stage might trigger the cage effect as a consequence of inhibiting C–C bond breakage with increasing local solvent density.⁴² On the other hand, like other lignocellulosic biomasses, OWP mainly consists of cellulose, hemicellulose, and lignin (Table 1). Lignin, linked with the hemicellulose fraction, becomes a free state due to the more straightforward decomposition of hemicelluloses by the interaction between the temperature and woody biomass. The degradation of free lignin is facilitated by increasing reaction temperature and can also be accelerated by autohydrolysis interactions with acids produced by the degradation of hemicelluloses.⁴⁵ Because of its amorphous structure, hemicellulose decomposes faster than cellulose and lignin at low temperatures.¹⁷ It is almost wholly converted up to 265 °C,⁴⁶ while the degradation rate of lignin and cellulose under hydrothermal conditions increases after 250 °C.⁴⁷ It explains that the rise in bio-oil yield when the temperature increased from 240 to 270 °C is higher than when increasing from 210 to 240 °C. In addition, it is known that cellulose and lignin show similar TGA results up to 350 °C, even if lignin is more difficult to decompose than cellulose and hemicellulose. Therefore, it suggests that similar amounts of bio-oil came from lignin and cellulose.

As shown in Figure 3, the conversion of OWP and gaseous product yields increased consistently with increasing temperature; the solid residue yield decreased typically due to conversion for all solvents. The obtained product yields and the decomposition of OWP were substantially higher with water compared to other solvents at 210 °C. Nevertheless,

since its critical points ($T_c = 374\text{ }^\circ\text{C}$ and $P_c = 220.6\text{ bar}$) were much higher than other solvents, it was less affected by the temperature increase. Although the constant increase can be seen in the bio-oil and liquid product yields obtained with solvents other than water, in experiments using water, one liquid product and bio-oil yields increased, while the other decreased. This situation is also reflected in the TOC analysis results of the water-soluble phase, which will be discussed later. 1-Butanol and 1,4-dioxane showed similar trends in the conversion of OWP. Also, produced bio-oil amounts were nearly the same at 210 and 240 $^\circ\text{C}$ for these two solvents; the differences were merely 1.6 and 2.9%, respectively. However, the highest conversion and liquid product yield rises were obtained to be 20.4 and 16.3% with 1,4-dioxane when the temperature increased from 210 to 240 $^\circ\text{C}$. Despite conversion increasing by 18.1% using 1-butanol in the same range, the increase in the liquid product yield remained at 12.5%. A value of 21.5% was observed as the highest rise in the bio-oil yield when the temperature increased from 240 to 270 $^\circ\text{C}$ again using 1,4-dioxane, while the gaseous product yield was just increased by 1.5%. It can be related to the fact that 1,4-dioxane has the lowest dielectric constant (2.21) and polarity (16.4). The increment in bio-oil was 11% for 1-butanol from 240 to 270 $^\circ\text{C}$, but the gaseous product yield reached 15.2% as it got closer to its critical points ($T_c = 288.5\text{ }^\circ\text{C}$ and $P_c = 49.6\text{ bar}$). In addition, the highest gaseous product yield (28.2%) and conversion of OWP rate (63.2%) were acquired at 270 $^\circ\text{C}$ using ethanol. This is probably because ethanol ($T_c = 241\text{ }^\circ\text{C}$ and $P_c = 61.4\text{ bar}$) exhibits supercritical properties at 270 $^\circ\text{C}$, and even a 1 h residence time became long enough to produce bio-oil. Because the rate of fragmentation and degradation is higher in supercritical processes, the longer residence time causes a rise in the gaseous product yield by breaking down large molecules into lighter and smaller molecules. Therefore, it can be assumed that much more bio-oil can be obtained using ethanol at 270 $^\circ\text{C}$ with a shorter residence time than with OWP. Nevertheless, at the highest temperature for this study, 270 $^\circ\text{C}$, all conversions of OWP, bio-oil, liquid, and gaseous product yields reached the highest level regardless of the solvent type (Table 2). The results are consistent with previous studies, including the thermal liquefaction of various lignocellulosic biomasses in terms of the effect of temperature on conversion and product yield.^{48–51} Thus, 270 $^\circ\text{C}$ was determined as the best temperature under experimental conditions of this study.

3.4. The Effect of the Solvent Used. During the liquefaction process, the solvent acts as a catalyst and reactant, directly determining the content of product formations, in addition to conversion and product yields.⁵² Water is commonly used in studies since it is environmentally friendly and the least expensive solvent. Because of its relatively high polarity properties, critical temperature, and pressure, using water as a solvent could not increase the bio-oil yield to the desired levels; also, the bio-oils with a high oxygen content were obtained, prompting the researchers to try organic solvents instead of water.^{2,3} In this direction, organic solvents such as methanol,⁵³ ethanol,⁴⁸ propanol,¹³ butanol,³² hexanol,⁵⁴ acetone,⁵⁵ and 1,4-dioxane¹⁷ were utilized to produce more qualified bio-oil with a higher yield from various biomasses.

The effect of the solvent type on conversion and product yields via thermal liquefaction of OWP at determined conditions (1 h and 270 $^\circ\text{C}$) using water, ethanol, 1-butanol,

and 1,4-dioxane is illustrated in Figure 4. OWP was subjected to subcritical water, 1-butanol, and 1,4-dioxane but super-

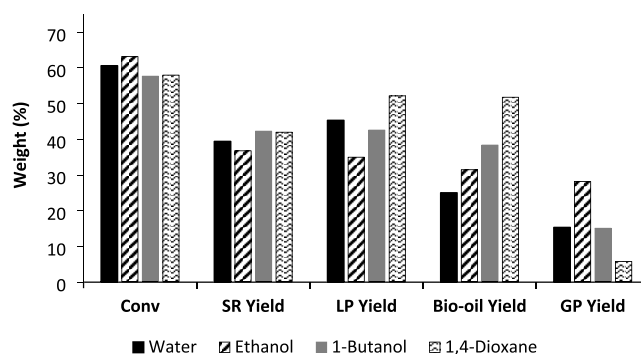


Figure 4. Conversion of OWP and product yields (solid residue, liquid, bio-oil, and gaseous) obtained at the optimum conditions (270 $^\circ\text{C}$ and 1 h) in water, ethanol, 1-butanol, and 1,4-dioxane reaction media.

critical ethanol treatments according to their critical points for a 1 h optimum residence time at the determined best reaction temperature, 270 $^\circ\text{C}$ (Table 3). The conversion of OWP was nearly the same at the end of the thermal liquefaction process, with a range of 57.7–63.2%. The highest difference in the conversion of OWP was 5.5%, which was observed between ethanol and 1-butanol. The solid residue yield, which depends on conversion, varied between 36.8 and 42.3%. Liquid product yields were in the order 1,4-dioxane > water > 1-butanol > ethanol at 52.2, 45.4, 42.6, and 35%, respectively. This is probably because of the density of solvents; as shown in Figure 4, in the subcritical region, the solvent with the highest density, 1,4-dioxane, provided the highest liquid product formation; however, as the density decreased, the yield of the liquid product was reduced. The lowest liquid product yield was obtained with the solvent ethanol providing the highest gaseous product yield. Ethanol was the most effective solvent for converting OWP (63.2%) and producing gaseous products (28.2%) because it showed supercritical properties at that temperature. The decomposition of biomass is higher in supercritical processes and occurs faster. As discussed in the previous sections, the residence time of 1 h might be too long for supercritical treatment of OWP via ethanol, so lighter and smaller molecules generated from the larger molecules that composed bio-oils and liquid products increased the production of gaseous products. The significant rise in gaseous product yields during liquefaction experiments using ethanol as a solvent above its critical points was reported previously in the literature. Yang et al. obtained similar findings from supercritical liquefaction of rice straw with ethanol for a 30 min residence time at 270 $^\circ\text{C}$ and found a 22.8% gaseous yield, and the gaseous yield increased to 43.36% at 345 $^\circ\text{C}$.⁵⁶ Wu et al. observed an increase in the yield of gas and other volatile components from 17.3 to 43%, in addition to a decrease in bio-oil yield from 27.6 to 14.6% when the temperature increased from 260 to 320 $^\circ\text{C}$ with respect to liquefaction in ethanol.⁵⁷

Water showed superior performance to 1,4-dioxane and 1-butanol in the decomposition of OWP as well as alcohols in the formation of liquid products, even though it produced the lowest bio-oil yield. Because water becomes an acid/base precursor, it can catalyze several ionic processes when heated to a temperature above the boiling point but below the critical point. Subcritical water, which can be used for many synthesis

Table 3. Properties of Selected Solvents^{61,62}

solvent	formula	BP ^a (°C)	T _c ^b (°C)	P _c ^c (bar)	κ ^d	polarity	ρ _c ^e
water	H ₂ O	100	374	220.6	79.7	100	0.3320
ethanol	C ₂ H ₆ O	78.37	241	61.4	32.6	76.2	0.2760
1-butanol	C ₄ H ₁₀ O	117.7	288.5	49.6	17.8	58.6	0.2700
1,4-dioxane	C ₄ H ₈ O ₂	101	315	52.1	2.21	16.4	0.3702

^aBoiling point. ^bCritical temperature. ^cCritical pressure. ^dDielectric constant. ^eCritical density.

reactions, counting some degradation reactions such as liquefaction of biomass, accelerates depolymerization by hydrolyzing the biomass. The polar glycosidic link between cellulose and hemicellulose hydrolyzes quickly in water in the subcritical region. Eventually, the entire biomass structure starts to convert into the smaller sugar units produced by the cellulose and hemicellulose molecule breakdown. For instance, in this situation, Liu and Zhang obtained the highest conversion rates with water compared to ethanol and acetone due to the liquefaction of pinewood at 250 and 270 °C for a 20 min residence time in their study.⁵⁸

Bio-oil yields fulfilled expectations, showing an increasing trend with a decreasing dielectric constant. As shown in Table 3, dielectric constants of used solvents are 79.7, 32.6, 17.8, and 2.21 for water, ethanol, 1-butanol, and 1,4 dioxane, though observed bio-oil yields are as ordered 1,4-dioxane (51.8%) > 1-butanol (38.4%) > ethanol (31.5%) > water (25%). The dissolving power of solvents is related to the dielectric constant. As in the expression “like dissolves like”, the polar solvents with a higher dielectric constant have a higher capability to dissolve polar molecules like salts. The decrease in the dielectric constant induces lower polarity, which increases the soluble power of solvents on nonpolar organic molecules such as biomass resulting in higher bio-oil yields.⁵⁹ Among all solvents used, due to its lower dielectric constant polarity and higher density, 1,4-dioxane was the best solvent in producing bio-oil and liquid products. It yielded the highest bio-oil and liquid products, at 51.8 and 52.2%, respectively. Nevertheless, it can be seen that almost all of the liquid products (>99%) produced with 1,4-dioxane were obtained as bio-oil. On the other hand, compared to other solvents used, gaseous products generated with 1,4-dioxane are much lower, at only 5.8%. For the same purpose, Mazaheri et al. performed subcritical liquefaction experiments on oil palm fruit press fiber using 1,4-dioxane at 250 °C, and they achieved 37.8% bio-oil yield, while the conversion rate, liquid, and gaseous product yields were 55.1, 44.2, and 10%, respectively.¹⁷ On the contrary, Yuan et al. reported lower bio-oil yield with 1,4-dioxane compared to methanol and ethanol at 300 °C as a result of thermochemical liquefaction of microalgae.⁶⁰ These results suggest that 1,4-dioxane may give better results in bio-oil production with lignocellulosic biomass than with algal biomass.

Despite having a conversion rate that is only 2.3% lower than that of 1,4-dioxane, 1-butanol has a 13.4% lower bio-oil yield. The main reason for this is that 1-butanol has a nearly three times higher gas product yield (15.2%) than 1,4-dioxane. Nevertheless, the yield is also the same for the gaseous product yielded by water, 15.2%. However, then, due to its lower dielectric constant, while more bio-oil yields were obtained with 1-butanol, the most solvent-soluble phase was observed in the experiments using water because of its higher density. The experimental results showed that the residence time effect was negligible on the conversion of OWP and product yields compared to the effects of the reaction temperature and

solvent type. The reaction temperature and solvent type were highly influential on conversions of OWP and product yields, so remarkable differences were observed at that temperature range and also solvent behaviors during the thermal liquefaction of OWP. The results obtained at optimum conditions are compatible and competitive with previous studies in the literature that yielded bio-oil by 1,4-dioxane over 50%. Under the scope of the present article, product distribution and quality were also examined to understand the effect of the solvent type on the formed bio-oil samples.

3.5. The Properties of Bio-oils Obtained at the Optimum Conditions. 3.5.1. Thermal Stability of Bio-oils.

The weight loss as a function of the temperature of the bio-oil samples obtained at the best reaction temperature and optimum residence time (270 °C for 1 h) with water, ethanol, 1-butanol, and 1,4-dioxane was measured by TGA. Figure 5a,b presents the weight percentage curve (TG) and the first

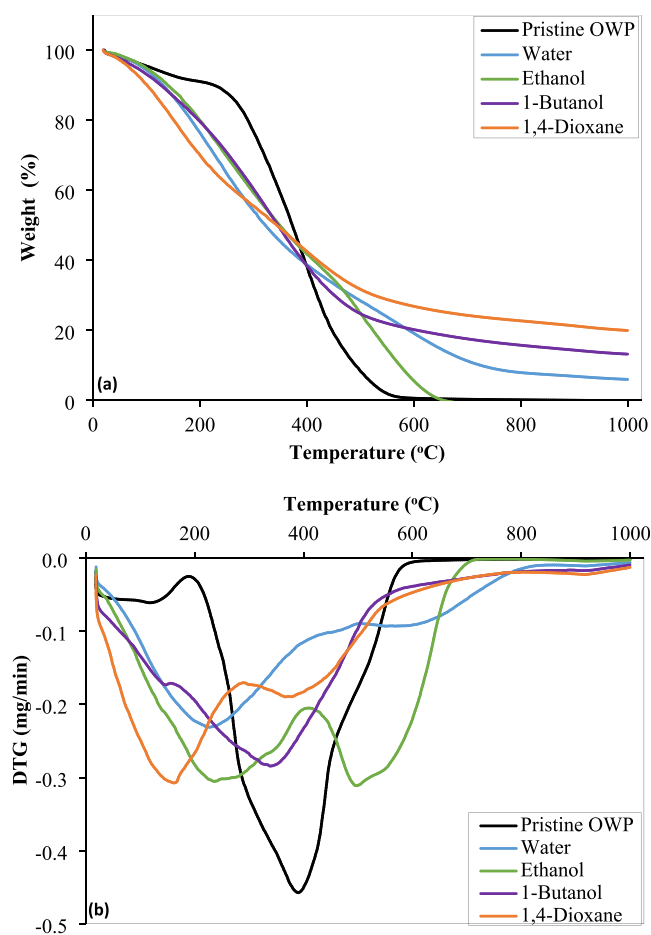


Figure 5. TGA (a) and DTG (b) curves for OWP and bio-oils obtained at the optimum conditions (270 °C and 1 h) in water, ethanol, 1-butanol, and 1,4-dioxane reaction media.

derivative of the weight loss curve (DTG) of the samples. The key parameters (VM and FC) of bio-oils obtained by TG/DTG curves are listed in Table 5. The composition of VM for untreated OWP was 99.27 (Table 1). At the same time, the VM contents for all derived bio-oils using water, ethanol, 1-butanol, and 1,4-dioxane were 93.98, 100, 86.77, and 80.03%, respectively, indicating that (1) not all the VM contents of the original biomass were transformed into bio-oils, in addition to solid residues and solvent-soluble and gaseous products; (2) also, bio-oils are not only composed of only VM, but they also contain FC (0–19.97%). Except for ethanol, other solvents reduced the amount of VM in untreated biomass VM. However, with ethanol, the VM amount slightly increased to 100%, and FC was the same with pristine OWP with 0% in that bio-oil, while interestingly, other bio-oils have higher FC amounts than natural OWP. It could be related to the region of thermal liquefaction; producing more volatile components may be caused by the supercritical region. Additionally, it can be asserted that the bio-oils, a complex mixture, might be converting with self-polymerizing into resins and other condensed materials when heated.⁵ On the other hand, FC amounts of the bio-oils produced from OWP that were subjected to the subcritical region with water, 1-butanol, and 1,4-dioxane showed a reverse trend with a decreasing dielectric constant and polarity of the used solvent. As observed in bio-oil yields, FC percentages are ordered as 1,4-dioxane (19.97%) > 1-butanol (13.23) > water (6.02). It suggests a relationship between the dielectric constant and polarity of solvents and FC formation.

Boiling points of bio-oils can vary, and TGA can also be used in estimating boiling point distributions. The estimated boiling point distributions of bio-oils obtained at 270 °C and a 1 h residence time using different solvents are presented in Table 4. The weight loss of the bio-oils before 110 °C is the

Table 4. Estimated Boiling Point Distribution of Bio-oils (wt %) Obtained at the Optimum Conditions (270 °C and 1 h) Based on TGA

distillate range (°C)	reaction medium (wt %)			
	water	ethanol	1-butanol	1,4-dioxane
20–110	6.97	6.25	7.98	11.60
110–200	16.65	13.83	12.46	18.36
200–300	22.26	20.61	19.20	14.51
300–400	15.40	17.52	21.97	13.01
400–500	10.27	16.90	13.60	10.78
500–600	9.29	19.30	4.56	4.85
600–700	7.84	5.57	2.64	2.57
700–800	3.34		1.80	1.57
800–900	1.05		1.39	1.42
900–1000	0.89		1.14	1.32

measure of moisture. Above 110 °C, when the water content was effectively separated, bio-oils contained a substantial amount of high-boiling-point components. As shown in Table 5, between 39 and 46% of bio-oils are components with boiling points below <300 °C. It means that less than half of the bio-oil composition can be detected by GC/MS; moreover, the remaining oil fractions have larger molecular weights (54–61%). The boiling point distribution completed between 600 and 700 °C because the bio-oil produced with ethanol is wholly formed from VM, while the separation of the VM of other oils reached 1000 °C. It is also indicated that

ethanol produced a milder bio-oil than other solvents. Nevertheless, according to other researchers, the resulting bio-oils are much heavier than ordinary petroleum crude oil, with a boiling point of less than 250 °C in about 45% of its composition.^{63,64}

3.5.2. Elemental Analysis of Bio-oils. The elemental analysis of bio-oils obtained under optimum conditions (270 °C and 1 h) in different reaction media (water, ethanol, 1-butanol, and 1,4-dioxane) and their HHV values and energy recoveries are presented in Table 5. As a result of the liquefaction process performed with different solvents, compared to pristine OWP (C: 49.5%, O: 42.7%), the carbon content of obtained bio-oils (62.7–75.6%) was much higher, whereas their oxygen contents (13.6–30.9%) were much lower. While the HHV of pristine OWP was 18.05 MJ/kg, the increase in the carbon content and the decrease in the oxygen content enabled higher HHV values in bio-oils regardless of the solvent type. Although the lowest HHV value was expected to be observed in the bio-oil obtained in the aqueous medium, water was the solvent producing the bio-oil with the highest HHV value of 35 MJ/kg; 1-butanol, 1,4-dioxane, and ethanol followed water with 33.3, 26.3, and 22.1 MJ/kg, respectively. The O/C molar ratios of bio-oils were much lower than that of untreated OWP (0.65) and ranged between 0.14 and 0.36. It is hypothesized that, during thermal liquefaction, deoxygenation reactions, such as dehydration and decarboxylation, occur, producing a nonbio-oil liquid part and CO₂ in the gaseous products.⁶⁵ On the other hand, compared to raw OWP (1.58), the H/C ratios for water and 1,4-dioxane were lower, also almost the same as 1.33 and 1.38, respectively, while the H/C ratio of ethanol (0.78) was much lower than that of raw OWP. Lower H/C ratios can be related to the predominance of aromatic compounds. In addition, the H/C ratio of 1-butanol was surprisingly much higher (1.93), even though the bio-oil produced from it had the highest HHV value compared to other solvents except water, proving the importance of a lower O/C molar ratio to obtain a higher HHV.

According to energy recovery calculations, the enhancement of OWP's energy efficiency depends on bio-oil yield, and quality was confirmed for all solvent types. In comparison with water and 1-butanol, although it produced bio-oil with a lower HHV value because the highest yield (51.8%) was achieved using 1,4-dioxane, it was the best solvent with 75.4% for thermal liquefaction of OWP at optimum conditions (270 °C and 1 h) in the present study. 1-Butanol followed it as the second-best solvent, with only a difference of 4.5% by forming a much higher-HHV bio-oil. The energy recovery of the water, which produced the bio-oil with the lowest yield and the highest HHV value, was less than 50%, 48.2%. Contrary to expectations, the energy recovery of ethanol (38.5%) was the minimum among all solvents because the bio-oil obtained using it has the lowest HHV.

3.5.3. Functional Groups of Bio-oils. FTIR analysis of the pristine OWP and obtained bio-oils at optimum conditions was performed in the range of 4000–400 cm⁻¹ to examine functional groups. The wide band between 3600 and 3250 cm⁻¹ represents the typical characteristic of OH stretching depending on the presence of water impurities and polymeric molecules, such as phenolics, alcohols, and carboxylic acids. The presence of hydrocarbons is indicated by the absorption between 3000 and 2840 cm⁻¹, which corresponds to the C–H stretching vibrations, which are usually observed in bio-oils. The peaks around 1730 cm⁻¹ are attributed to the C=O

Table 5. Properties of Bio-oils Obtained at the Optimum Conditions (270 °C and 1 h) in Water, Ethanol, 1-Butanol, and 1,4-Dioxane Reaction Media

solvent type	weight percentages (wt %)				elemental				H/C	O/C	HHV (MJ/kg)	energy rec. (%)
	moisture	ash	VM	FC	C	H	O	N				
water	6.98	NG ^a	93.98	6.02	75.6	8.4	13.6	2.4	1.33	0.14	35.0	48.5
ethanol	6.25	NG ^a	100.0	0.00	64.3	4.2	30.9	0.6	0.78	0.36	22.1	38.5
1-butanol	7.99	NG ^a	86.77	13.23	66.0	10.6	23.0	0.4	1.93	0.26	33.3	70.9
1,4-dioxane	11.60	NG ^a	80.03	19.97	62.7	7.2	29.4	0.7	1.38	0.35	26.3	75.4

^aNegligible.

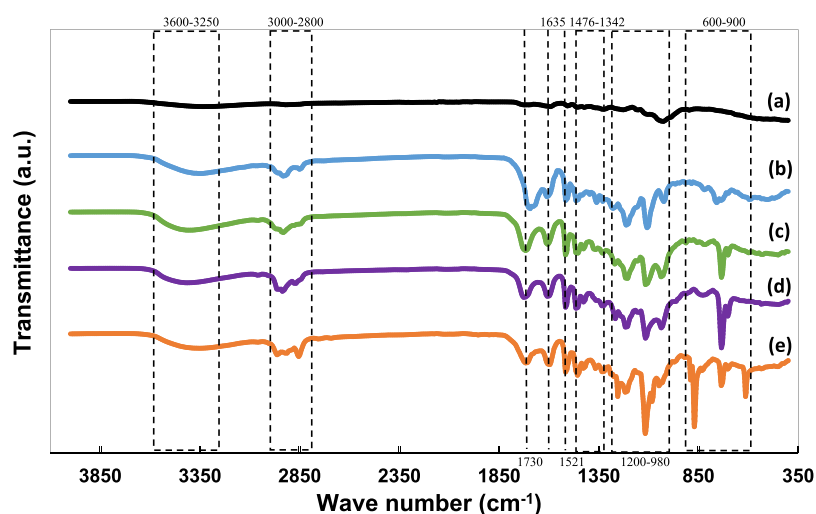


Figure 6. FTIR spectra of (a) pristine OWP and bio-oils obtained at optimum conditions (270 °C and 1 h) in (b) water, (c) ethanol, (d) 1-butanol, and (e) 1,4-dioxane reaction media.

stretching vibration of carbonyl groups and suggest the presence of aldehydes, ketones, and carboxylic acids. The existence of esters, which are carboxylic acid derivatives, can be explained by the presence of both C=O and –OH stretching vibrations. The vibrations of aromatic C=C bending and its derivatives are observed at 1635, 1521, and 1476 cm⁻¹. The peak at 1342 cm⁻¹ and the peak at 1476 cm⁻¹ can also be identified as the –CH₂ and –CH₃ stretching, respectively. The absorptions between 1200 and 980 cm⁻¹ can be attributed to the C–O vibrations, which may indicate the presence of phenols, alcohols, acids, and esters in the bio-oil products.^{66–68}

As shown in Figure 6, all bio-oils showed nearly similar peaks between 4000 and 900 cm⁻¹, regardless of the solvent type. The peak at 1117 cm⁻¹ was remarkably intense in the bio-oil produced using 1,4-dioxane, although observed in all oils. In addition, compared to the other bio-oils, the bio-oil showed main differences in the peaks between 600 and 900 cm⁻¹ (especially at 870 and 620 cm⁻¹), which correspond to the single, polycyclic, and substituted aromatic groups.⁶⁹ It demonstrates that 1,4-dioxane is more effective than other solvents in the formation of phenolic and aromatic compounds in bio-oils.

Solid residues obtained under optimum conditions in water, ethanol, 1-butanol, and 1,4-dioxane reaction media were also analyzed with FTIR (Figure 7). The peaks between 3600 and 3250 cm⁻¹, 3000 and 2800 cm⁻¹, 1240 and 1160 cm⁻¹, and 1056 and 1033 cm⁻¹ represent the OH, C–H, C–O–C, and C–O stretching in cellulose, hemicellulose, and lignin, respectively, while OH functional group peaks can be observed between 850 and 605 cm⁻¹. The peaks at 1730, 1635, 1521,

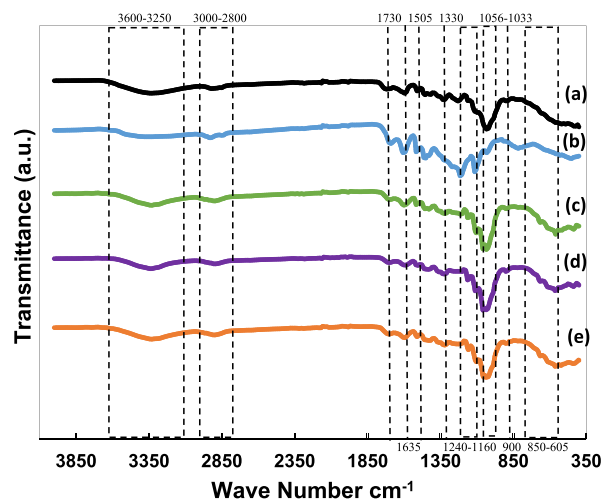


Figure 7. FTIR spectra of (a) pristine OWP and solid residues obtained at optimum conditions (270 °C and 1 h) in (b) water, (c) ethanol, (d) 1-butanol, and (e) 1,4-dioxane reaction media.

and 900 cm⁻¹ are related to the C=O stretching vibration of carbonyl groups, C=C stretching (in lignin), benzene ring stretching, and anomeric carbon vibration (in cellulose and hemicellulose), respectively.⁷⁰ As shown in Figure 7, the solid residues resulting from the liquefaction of OWP using ethanol, 1-butanol, and 1,4-dioxane were similar. The solid residue generated with water has main differences in peaks between 1240 and 1033 cm⁻¹. SEM was performed to analyze the

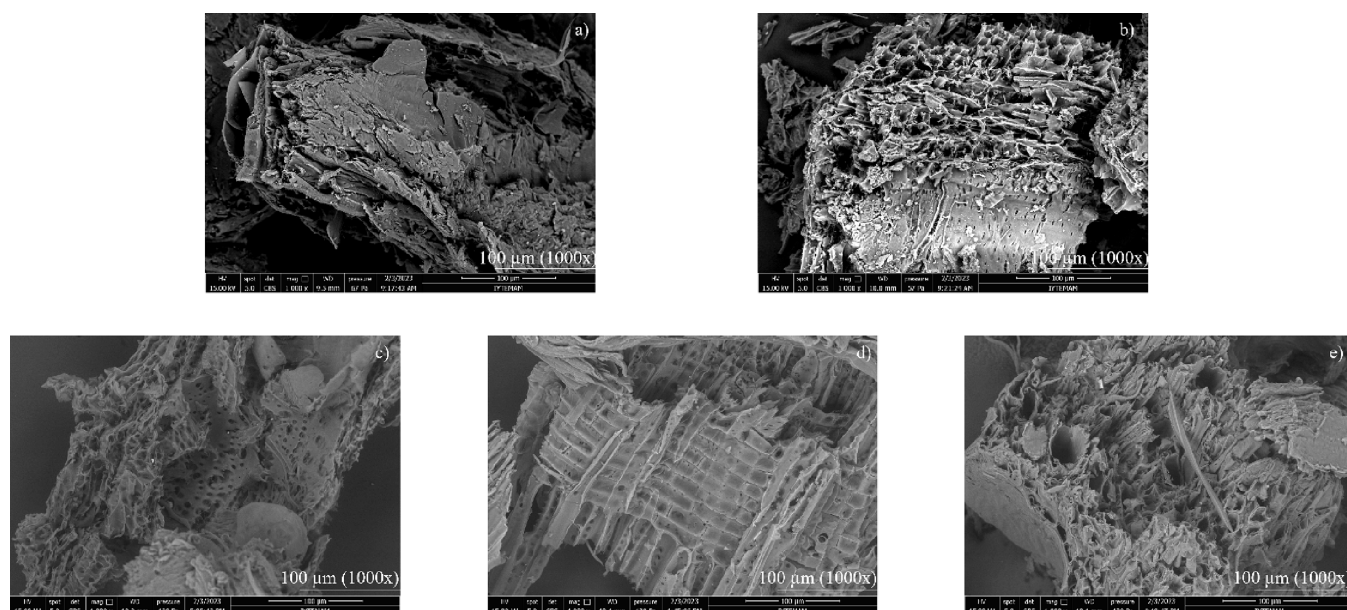


Figure 8. SEM images of (a) pristine OWP and solid residues obtained at optimum conditions (270 °C and 1h) in (b) water, (c) ethanol, (d) 1-butanol, and (e) 1,4-dioxane reaction media.

morphologies of pristine OWP and solid residues, shown in Figure 8. It can be clearly seen that the rough surface of the feedstock with thick cell walls was degraded successfully by all solvents during thermal liquefaction; thus, the fibrous structure of the lignocellulosic biomass has become evident. Regardless of the solvent type, cavities and pores were formed on the lignocellulosic biomass surface, which did not exist before, and became visible after the volatile matters such as solvents were removed. On the other hand, the characteristics of the generated solid residue are significantly influenced by the level of devolatilization. It is generally recognized that characteristics with lower density, increased porosity, and noticeably altered pore structures result from a greater release of volatile compounds. Higher temperatures powerfully break down biomass, exposing its primary layers and enlarging pores by eliminating the neighbors and improving porosity.^{44,71}

3.5.4. Major Components of Bio-oils. The major components of bio-oils produced at the optimum residence time (1 h) and best temperature (270 °C) at which maximum bio-oil yields were obtained using water, ethanol, 1-butanol, and 1,4-dioxane as reaction medium were identified by GC–MS analysis (Table 6), which were consistent with FTIR results. The results were in accordance with the FTIR analysis discussed in the previous section. Because the maximum temperature reached by GC–MS is 300 °C, as seen in the estimated boiling point distribution of bio-oils prepared according to TGA results (Table 5), GC–MS could determine 39–46% of the compositions of the obtained bio-oils. Due to unidentified peaks and the omission of peaks only observed in one bio-oil sample with very little proportion, the total area did not reach 100%. As a complex combination of hundreds of different organic molecules, a bio-oil mostly includes alcohols, acids, esters, ketones and aldehydes, lignin-derived oligomers, and phenols (Figure 9). Aromatic compounds such as benzene and its derivatives are mainly generated from lignin degradation. Also, the existence of phenolic groups in a bio-oil indicates the degradation of low-molecular-weight lignin, so the absence of phenolics demonstrates the delignification. Degradation of cellulose and hemicellulose is another possible

way to observe the generation of aromatics and phenolics. Holocellulose is first fragmented into the smallest unit, sugars, and then condensed to furfural-like intermediates, which can join the aromatic and phenolic compounds. Degradation of lignin and sugars also indicates formation of acids. In addition, ketones can be included in the structure of aromatic carbons as a result of condensation reactions. On the other hand, the breakdown of hemicellulose and cellulose in the raw material is principally attributed to the formation of alkanes, aldehydes, alcohols, carboxylic acids, furan, and its derivatives. Additionally, generation of esters is probably because of esterification reactions between alcohols and acids.^{39,42,72}

Based on the analysis results, the major components of bio-oils varied depending on used solvents except for the predominance of phenolic groups such as phenol, 2-methoxyphenol, 2,6-dimethoxy-4-(2-propenyl)-. Significantly, the highest yielded bio-oil obtained with 1,4-dioxane had a maximum phenolic compound area of 40.17%. Ketones, also furan groups, were dominant in bio-oil produced with water; for example, one of the furan derivatives, furfural, was another major component of it with a 14.59% area. Acid groups, mainly butanoic acid derivatives, were primarily observed in bio-oil formed by using alcohols as a solvent. The formation of the highest number of compounds with low area percentages was caused by 1-butanol. Moreover, the highest area was detected for phenol, 2,6-dimethoxy-4-(2-propenyl)- with 10.68% among phenolic compounds and for pentanoic acid with 5.11% in acids. Additionally, ethyl, α -D-glucopyranoside had a maximum area of 10.45% and was seen only after liquefaction of OWP with ethanol.

Unlike other solvents, water did not show a gradual increasing trend in liquid product and bio-oil yields during experiments for the 1 h retention time. When the temperature increased from 210 to 240 °C, liquid product yield increased from 42.5 to 46.3%, but interestingly, the bio-oil yield decreased from 25 to 22.5%. On the other hand, when the temperature reached 270 °C, the liquid product yield decreased from 46.3 to 45.4%, while the bio-oil yield once more was obtained to be 25%. In

Table 6. GC–MS Analysis Results of Bio-oils Obtained at the Optimum Conditions (270 °C and 1 h) in Water, Ethanol, 1-Butanol, and 1,4-Dioxane Reaction Media

no.	retention time	compound	area (%)			
			water	ethanol	1-butanol	1,4-dioxane
1	4.057	acetic acid, hydroxy-, ethyl ester		2.03		
2	5.537	furfural	14.59	0.59		2.54
3	6.359	2-furanmethanol		4.07	0.73	2.26
4	6.887	1-hexanol				2.66
5	8.384	2-cyclopenten-1-one, 2-methyl-	0.93			
6	8.433	butanoic acid, 2-hydroxy-, ethyl ester		1.29		
7	9.151	2-cyclopenten-1-one, 2-hydroxy-		0.17	0.18	1.17
8	9.413	2,5-hexanedione	2.07			
9	11.028	2-furancarboxaldehyde, 5-methyl-	2.87	0.15		0.17
10	14.106	2-cyclopenten-1-one, 2-hydroxy-3-methyl-	4.73	0.75	0.31	0.91
11	14.652	2-acetyl-5-methylfuran	0.95			
12	17.239	phenol, 2-methoxy-	6.32	1.53	0.39	0.51
13	17.374	L-alanine, methyl ester		1.48		3.82
14	17.807	2,3-butanediol, 2,3-dimethyl-			2.89	
15	22.689	1,2-benzenediol	0.66	0.85	0.53	1.09
16	23.838	2,5-piperazinedione		1.21		0.52
17	23.994	2-furancarboxaldehyde, 5-(hydroxymethyl)-	1.32	0.48	0.24	1.51
18	25.417	1,2-benzenediol, 3-methoxy-	0.83	0.31		0.54
19	25.551	1,2-benzenediol, 3-methyl-	0.36			0.72
20	25.844	butanoic acid, propyl ester		7.45		
21	26.623	phenol, 4-ethyl-2-methoxy-	1.1	1.63	0.49	0.39
22	27.877	2-methoxy-4-vinylphenol		1.04	1.11	1.81
23	29.293	ethyl, α -D-glucopyranoside		10.49		
24	29.561	phenol, 2,6-dimethoxy-	16	4.67	1.72	1.22
25	30.593	1,2,3-benzenetriol	1.25			
26	30.868	heptanoic acid		1.34		
27	31.524	benzaldehyde, 3-hydroxy-4-methoxy-	3.72	0.99	0.58	0.75
28	32.154	thiophene, tetrahydro-		0.91		
29	32.679	cyclopentanecarboxylic acid, 3,3-dimethyl-4-oxo-, methyl ester			2.23	
30	33.133	butanedioic acid, dipropyl ester			1.79	
31	33.637	benzoic acid, 4-hydroxy-3-methoxy-	1.11			
32	33.721	phenol, 2-methoxy-4-(1-propenyl)-, (E)-		4.23	4.94	8.14
33	34.036	butanoic acid, butyl ester			5.06	
34	35.162	ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.24	0.68	0.33	0.67
35	36.337	phenol, 2,4-bis(1,1-dimethylethyl)	1.51	0.51	0.64	3.82
36	36.883	benzene, 1,2,3-trimethoxy-5-methyl		2.81	1.08	
37	37.002	phenol, 2-methoxy-4(methoxymethyl)-	2.5	1.2		
38	37.016	benzeneacetic acid, 4-hydroxy-3-methoxy-			1.04	1.06
39	37.191	pentanoic acid			5.11	
40	38.786	methyl-, β -arabinopyranoside			4.54	
41	39.604	butanoic acid, 3-methyl-			1.29	
42	39.863	phenol, 2,6-dimethoxy-4(2-propenyl)-	1.72	1.83	3.57	1.5
43	40.123	4-propyl-1,1'-diphenyl	0.46	1.05		0.41
44	41.435	benzeneacetic acid, 4-hydroxy-3-methoxy-	1.72	1.04	0.6	0.6
45	41.926	benzaldehyde, 4-hydroxy-3,5-dimethoxy-	5.04	1.87	0.66	1.45
46	43.479	phenol, 2,6-dimethoxy-4(2-propenyl)-	0.57	3.94	9.76	14.96
47	43.607	heptane, 1,1-diphenyl-			0.54	1.17
48	44.485	4-hydroxy-2-methoxycinnamaldehyde		0.18	0.39	1.05
49	44.591	ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.89	0.61	1.08	0.91
50	44.662	4-((1E)-3-hydroxy-1-propenyl)-2-methoxyphenol				1.51
51	45.991	2-pentanone, 1-(2,4,6-trihydroxyphenyl)	3.97	3.34	1.90	2.46
52	47.579	5-tert-butylpyrogallo		0.23	0.36	1.31
53	52.878	3,5-dimethoxy-4-hydroxycinnamaldehyde		0.4	0.97	4.03
54	53.182	9-methyl-1-phenazinol			1.92	
55	53.202	phenol, 2-(2-imidazo[1,2-a]pyridyl)-				6.26
		Total	79.43	67.35	58.97	73.9

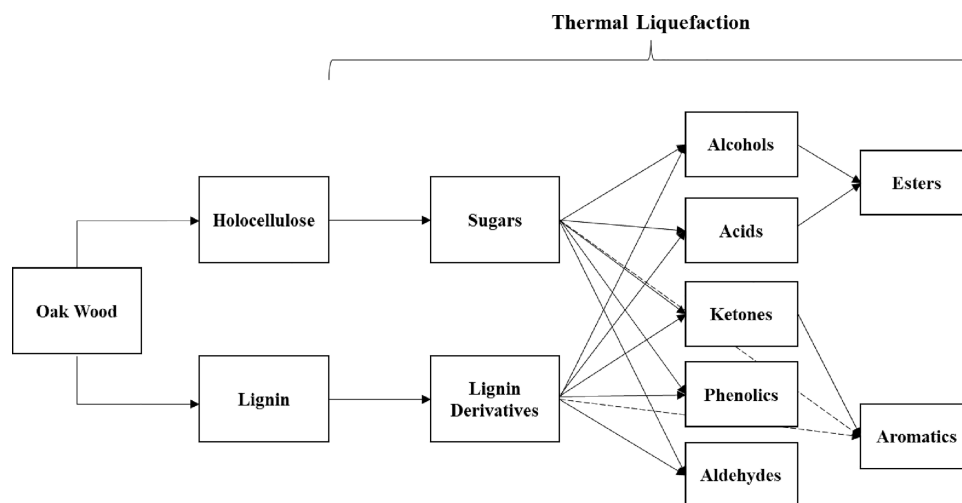


Figure 9. Representative basic possible reaction pathway.

Figure 10, results of TOC analysis that was performed on the water-soluble phases with respect to different liquefaction

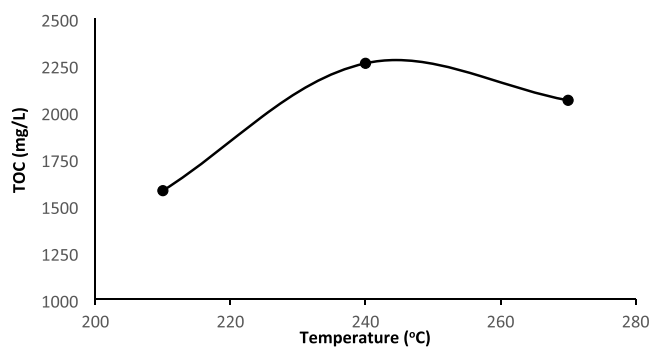


Figure 10. TOC analysis of water-soluble phases obtained from liquefaction of OWP using water as the solvent at optimum conditions (270 °C, 1 h).

temperatures at a 1 h retention time are shown. The results were consistent with product yields since when the liquid product yield increased, the TOC value increased, and while the liquid product decreased, it decreased as expected. According to de Caprariis et al., the decreases in TOC of water-soluble phases resulting from the thermal liquefaction process on lignocellulosic biomasses with a high holocellulose composition can be clarified as the degradation mechanism difference of cellulose and hemicellulose with respect to lignin. During hydrothermal liquefaction, holocelluloses are initially converted to water-soluble compounds like sugars (such as glucose and fructose) around 250 °C, although the sugars react to participate in the structure of bio-oils at higher temperatures.²⁵ In the present study, high-area furfural, one of the main components of bio-oil formed from sugars as determined by GC–MS in the bio-oil produced with water at 270 °C, supported this idea.

5. CONCLUSIONS

The bio-oil production by the decomposition of OWP to valorize forestry residues in Turkey via subjecting to subcritical water, 1-butanol, 1,4-dioxane, and sub-/supercritical ethanol liquefaction for 1 and 2 h residence times at investigated temperatures ranging from 210 to 270 °C was successfully

carried out. Ethanol, 1-butanol, and 1,4-dioxane were used as a solvent on the conversion of oak wood into bio-oil for the first time in the literature. Because changing the residence time from 1 to 2 h has negligible effects on conversions of OWP and bio-oil yields, 1 h was chosen as the optimum liquefaction time for this study. On the other hand, increasing the temperature increased conversion and product yields; thus, all solvents showed the best performance at the end of the 1 h residence time at the highest temperature for this study, 270 °C. The bio-oil production was achieved in yielding between 25 and 51.8% at the optimum conditions (270 °C and 1 h) using selected solvents. It was proven that the bio-oil yield highly depends on the dielectric constant at the same process conditions, while the liquid product yield is related to the density of the used solvent in the subcritical region. The lower dielectric constant induced lower polarity, thus increasing the dissolving power of solvents on OWP composed of nonpolar organic molecules, resulting in higher bio-oil. 1,4-Dioxane, with the highest density, showed the best performance in producing liquid products at 52.2%. In addition, the maximum bio-oil yield was provided again by 1,4-dioxane as 51.8% (almost all of the liquid products formed) due to it having the lowest dielectric constant. Also, higher heating values of the oils ranged from 22.1 to 35 MJ/kg. According to GC–MS results consistent with FTIR, the major components of bio-oils varied depending on solvents except for predominance of phenolic groups. The highest yielded bio-oil obtained with 1,4-dioxane had the maximum phenolic compound area of 40.17%. Ketones and furans were also dominant in the bio-oil produced with water such as furfural. Acid groups, mainly derivatives of butanoic acid, were primarily observed in bio-oils when using alcohols (1-butanol and ethanol) as solvents. Finally, based on energy recovery calculations, the enhancement of pristine OWP's energy efficiency depends on bio-oil yield, and quality was confirmed for all solvent types (1,4-dioxane > 1-butanol > water > ethanol).

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Notes

The authors declare no competing financial interest.

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