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Fast pyrolysis of fig leaves: Influence of pyrolysis parameters and characterization of bio-oil

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Abstract

Liquid yields achieved by fast pyrolysis of ligno-cellulosic biomass can be used in the production of chemical raw materials or as an energy source. Pyrolysis product yields generally depend on the type of biomass, temperature, retention time, heating rate, sweeping gas flow rate and particle size. In this study, fast pyrolysis of fig leaves selected as biomass was carried out in a fixed bed pyrolysis reactor. Fig leaves used in fast pyrolysis experiments in this study as an agricultural by-product can be obtained in large quantities from Türkiye. In the experiments, the effect of temperature, entraining gas flow rate, and particle size on pyrolysis product yields were investigated. The experiments were carried out at 400, 500, 600, 700 °C, four different particle sizes. The highest liquid product yield was obtained at 600 °C, while the heating rate was 200 cm^3/min and the particle size was < 0.150 mm. According to the test results, the most effective parameter on liquid product yield is temperature. Based on the results of this analysis the H/C molar ratio (1.71) and the high calorific value (14.25 MJ/kg) indicate that FL can be used the source of raw materials in obtaining liquid fuel. Instrumental techniques such as FT-IR, SEM-EDS, TG/DTG and GC-MS were used for the characterization of bio-oil. The bio-oil contains alkenes, aldehydes, carboxylic acids, and aromatic structures such as indole derivative as well as alkanes. The heating value of the bio-oil is 32.16 MJ/kg which is close to those of petroleum fractions.

Keywords: Renewable energy, biomass, fast pyrolysis, fig leaves, bio-oil

1. Introduction

There are two major problems that have occupied the world agenda in recent years**.** One is environmental problems and the other is increasing energy demand. Meeting the rising energy demand from fossil fuels in large quantities brings with it the environmental pollution and the energy crisis. As fossil fuels burn, gasses such as carbon dioxide, methane, sulfur oxides, nitrogen oxides are released to the environment, which causes global warming. Unless that gases emissions are limited, humans will face more threats from global warming and climate change. Moreover, the fact that existing fossil fuel resources will not meet future demand will lead to an increase in energy prices, bringing about the energy crisis and wars. With the awareness of the environment becoming more apparent after the second half of the 20th century, mankind has begun to recognize and diminish the damage it inflicts on the environment. Recently, the increase in energy demand has led to the search for alternative energy sources for fossil energy sources with an increase in environmental awareness [1]. Renewable and clean energy is a type of energy derived from continuous and sustainable sources of energy, such as solar, geothermal, biomass, wind, hydropower, which are not exhaustible, such as fossil fuels [2]. Clean energy investments have some of advantages that reducing dependence on foreign energy sources, reducing greenhouse gases and conventional pollutants, and creating new business areas [3]. The three main components of biomass are cellulose, hemicellulose, and lignin. Moreover, there are a few amounts of minor components, minerals, and organic extracts in the structure of the biomass. Before the use biomass should be converted into more valuable products (i.e., liquid fuels). Among the biomass conversion technologies, the most preferred thermal conversion technologies. One of the most important of the thermal conversion technologies is pyrolysis.

Biomass secondary fuels and chemical by-products are obtained as a result of pyrolysis processes with heating and partial combustion. The raw materials used in pyrolysis process are composed of wood, coal, biomass residues and local wastes while gasses, liquids,

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tars, chars, oils and ashes are formed as a result of this process. Fuel products from pyrolysis are much more suitable for cleaning, handling and transporting fuel products obtained from the original biomass. The fast pyrolysis has become increasingly popular in recent years [4]. By means of fast pyrolysis, more liquid products (bio-oil) can be obtained compared to traditional pyrolysis methods [5]. While low vapor residence time, high heating rate and medium temperatures are required to increase liquid product efficiency, slower heating rate is required to increase solid product efficiency [6,7]. After cooling and condensing the pyrolysis vapors a dark brown liquid is formed which has a heating value about half that of conventional fuel oil [8]. Liquid yield is dependent on biomass type, temperature, retention time, char separation and raw material ash content. Char and ash content shows a catalytic effect for cracking of the formed steam [9,10]. Due to decreased fossil fuel reserves, increased fuel demand and CO_2 emission problems, interest in bio-oil as a sustainable liquid hydrocarbon fuel source is constantly increasing [11,12]. Bio-oil contains hundreds of kinds of compounds such as carboxylic acids, aldehydes, ketones, furans [13,14]. In this case, bio-oil causes some negative properties such as high viscosity, thermal instability and corrosivity [15]. Both methods are not useful because they negatively affect cellulose. Stainless steel and polyolefin materials are suitable for storage. High acidity can be reduced by esterification reactions or by using magnesium alloy and powder [16]. Aging is one of the major problems that negatively affect the structure of bio-oil. This problem is usually caused by the ongoing degradation reactions in the bio-oil [17,18]. Polar solvent addition is generally used as a simple method to reduce the viscosity of liquid fuels obtained by pyrolysis of biomass. Addition of 10% by weight of methanol to the bio-oil significantly decreased the viscosity increase [19,20]. All types of biomasses usually contain ash which is dominated by alkali metals such as sodium and potassium [21]. Potassium and some other alkali metals catalyze secondary degradation reactions [22]. These negative factors result in reduced liquid product yield, phase separation because of higher water content and loss of surfactant. Bio-oil's viscosity is one of the most important parameters for direct combustion applications and combustion efficiencies in engines and turbines requiring atomization [23]. Tests of bio-oil in engines and combustors are available in the literature. [24]. The preferred viscosity in engine applications with high pressure is 17 cSt. In conventional fuels, preheating is carried out to reduce the viscosity. However, because of the non-recyclable changes in the properties of bio-oil at temperatures above 55 °C, one-time heating is performed in very short retention [25]. As discussed in Diobold's review, the viscosity is most swayed by the temperature and water content. Bio-oil contains only a small amount of sulfur, so there is not much work to regulate or reduce the sulfur content [26]. A number of studies have shown that bio-oil does not pose a significant risk to living health and the environment [27,28].

In this study, the samples of fig leaves (FL) separated into different particle sizes were burned in a fixed bed pyrolysis reactor. Türkiye is the world's leading country in terms of production figs. In this respect, figs, which are an agricultural by-product, constitute an important raw material potential for clean energy production. Using a fixed bed reactor, the effects of pyrolysis temperature, particle size and sweeping gas flow rate on pyrolysis product yields were studied. In addition, the properties of bio-oil obtained from FL were investigated. This study is a unique study to examine the pyrolysis behavior of fig leaf and to investigate the characterization of bio-oil.

2. Materials and methods

2.1. Materials

The FL used in the present study was obtained from Trabzon located in the Black Sea region, in the northern part of Türkiye.

2.2. Methods

2.2.1. Biomass preparation

Prior to use, sample was dried in an electrical oven for 24 h at 105 °C to ensure the reduction of free moisture. Before pyrolysis, the biomass was passed through in high-speed rotary cutting mill and then screened to give fractions of $0.425 < Dp < 1.000$ mm, $0.250 < Dp < 0.425$ mm, $0.150 < Dp < 0.250$ mm and $Dp < 0.150$ mm particle sizes.

2.2.2. Pyrolysis experiments

The fixed bed reactor used in this study has also been used in previous research [1,29]. The experimental set up consists of reactor, liquid collecting system, and power supply. During the experiments, pyrolysis temperature was controlled by a PT100 temperature controller. A liquid nitrogen trap was used to condensed pyrolysis vapors. Three groups of experiments were realized to determine the effect of pyrolysis conditions on solid, liquid and gas product yields. The first is to determine the effect of pyrolysis temperature on pyrolysis yield. In this part experiments, 3 grams of air-dried sample was placed in the reactor. After placing the sample, it was heated to the desired final temperature (400, 500, 600 and 700 °C) at 200 °C/min heating speeds. In the second group of experiments, the effect of particle size on pyrolysis yields was investigated by selecting four different particle sizes. In the last group of experiments, the effect of sweeping gas flow rate (100, 200, 300 and 400 cm^3/min) on product yield was examined.

The pyrolysis vapors are sent to the liquid collection unit where they are liquefied. The non-liquefied part was sent to outside with the aid of a discharge hose. The pyrolysis liquid accumulated in the liquid collection unit. The amount of solid part is calculated by weighing the solid product while the amount of gas is determined by the difference.

2.2.3. Characterization of biomass and pyrolysis products

The pyrolysis liquid was kept in dichloromethane to separate the aqueous and oil phase. Both separated phases are weighed. Then, dichloromethane was blown on a rotary evaporator to determine the bio-oil yield. The resulting bio-oil was kept in *n*-pentane overnight and divided into two phases, soluble and insoluble (asphaltenes) in *n*-pentane. *n*-pentane soluble fraction was used in the characterization of bio-oil. Several instrumental techniques have been used to illuminate the structure of the biomass and its bio-oil, obtained under appropriate conditions (600 °C, 200 cm^3/min, $Dp \leq 0.250$ mm particle size). Proximate (moisture content, ash content, fixed carbon and volatile matter) and ultimate (elemental composition) analyzes of FL and its bio-oil were carried out. The ultimate analysis was performed using an elemental analyzer (Leco/TrueSpec Micro). The gross calorific values of the raw material and bio-oil are calculated by Dulong-Berthelot's formula given below:

$$QGCV\ (kJ/g)\ 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211ASH \qquad (1)$$

To determine the water content of bio-oil, Karl-Fischer titration was applied with METTLER TOLEDO COULOMETER DL 39. An FT-IR spectrometer (Spectrum 400, Perkin–Elmer, USA) examined the functional groups and fingerprints of the bio-oil from the fast pyrolysis. The HHV of the bio-oil was analyzed on a bomb calorimeter (Model: IKA C 200) according to ASTM D2015. The inorganic elemental compositions of the biomass were determined using SEM-EDS analysis. TG and DTG experiments of the biomass and its bio-oil were carried out using a TG analyzer (TagongsiSDTQ600, USA), under nitrogen atmosphere, heated from room temperature to 800 °C. The GC-FID analysis was carried out on an Agilent 7890A-(5975C inert MSD).

3. Results and discussion

3.1. Physicochemical characteristics of FL

Table 1 shows the physicochemical characteristics of the FL, prepared for fast pyrolysis experiments. The FL contained 11.07 wt% cellulose, 33.73 wt% hemicellulose, and 13.12 wt% lignin. During the pyrolysis of biomass, organic vapors are formed by breaking down this lignocellulosic content at high temperatures. These vapors are liquefied to produce bio-oil. The remaining solid residual is left as bio-char. Considering the characteristics of FL used as biomass samples, it is seen that H/C ratio (1.68) which is an important parameter is very close to that of traditional crude oil (1.82). The H/C molar ratio of biomass is between 1.0 and 2.0, indicating the potential for producing liquid fuel from the biomass [30,31]. In this study, the high heating value of the fig leaf samples was found to be 14.73 kJ/g and this value is among the thermal values that should be the typical biomass samples that can be used for liquid fuel production [32].

In Fig. 1 the SEM images of raw material are compared with different magnifications (×200, ×1000, ×2000 and ×5000). The morphological structure of FL showed long uniform fibrous lignocellulosic structures. The morphological structure help to predict their agglomeration properties. Images revealed that FL show a fibrous pattern on their surface. Fig leaves exhibited a compact morphology, complex and very ordered in macrofibrils. Lignocellulosic blends interact via intermolecular hydrogen bonding, preventing the material to self-assemble [33].

Table 1. Main characteristics of FL samples

Characteristics	**Values**
Moisture content[a] (%)	9.11
Holocellulose content[a] (%)	44.80
Cellulose content[a] (%)	11.07
Hemicellulose content[a] (%)	33.73
Lignin content[a] (%)	13.12
Organic extractive[a] (%)	20.72
Proximate analysis (%)	
Volatiles	62.44
Fixed carbon	16.89
Ash	11.56
Ultimate analysis [b](%)	
Carbon	39.68
Hydrogen	5.57
Nitrogen	2.37
Oxygen[c]	52.38
H/C molar ratio	1.68
O/C molar ratio	0.99
Empirical formula	$C_{20}H_{34}O_{20}N$
Higher calorific value (MJ/kg)	14.73

[a] weight percentage on dry basis

[b] weight percentage on dry and ash-free basis

[c] by difference

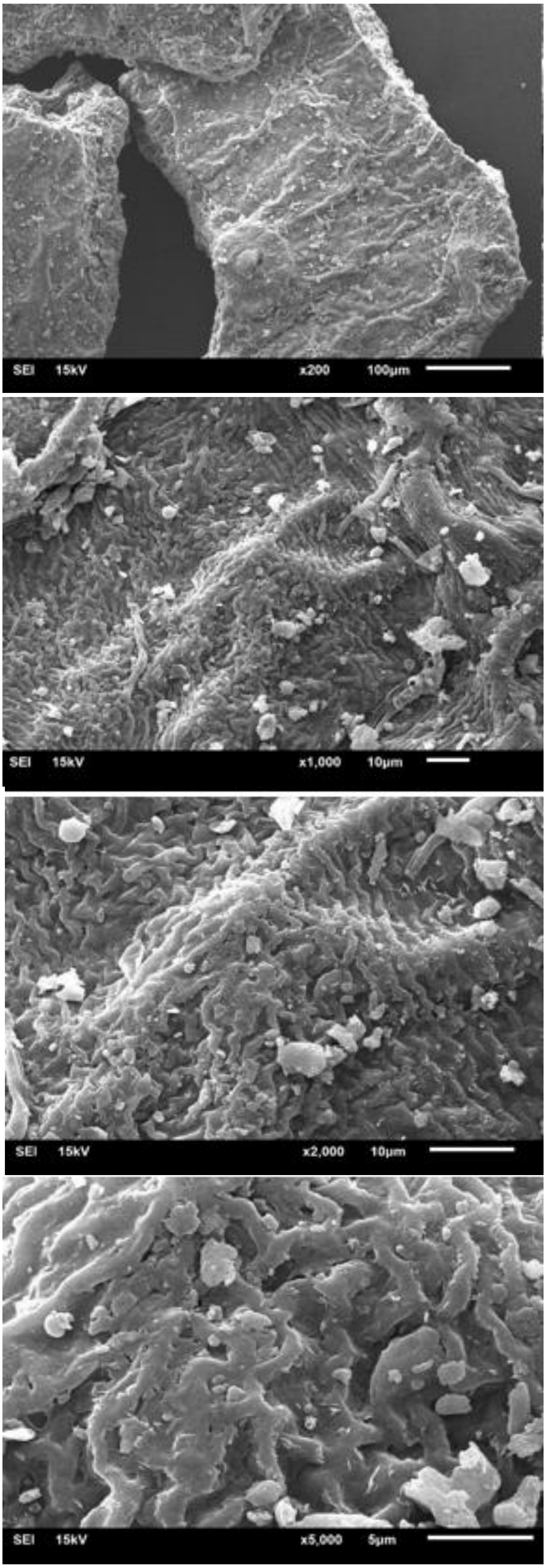

Figure 1. Scanning electron microscopy (SEM) images of raw FL, where A, B, C and D shows different

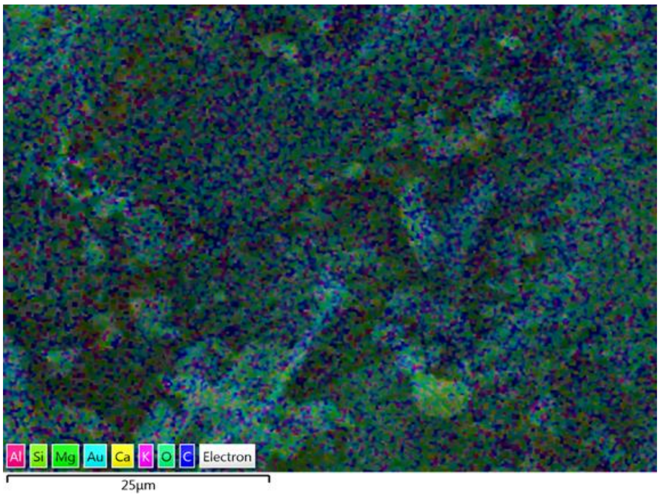

Figure 2. SEM-EDS photograph of the FL

Fig. 2 shows SEM-EDS photograph of the FL. Fig. 3 shows the inorganic elements (C and O are removed) present of the FL. When the inorganic element contents of FL are examined, Ca and K are the major elements. Si, Mg and Al were also found in large quantities.

3.2. Product Yields

3.2.1. *Effect of temperature on pyrolysis product yields*

Four different pyrolysis temperatures were used in the experiments. According to the obtained results, the highest liquid product yield was achieved in particle size ≤ 0,150 mm and nitrogen flow rate of 200 cm^3/min. Fig. 4 shows the effect of pyrolysis temperature on the product yields and pyrolysis conversion for four different temperatures (400, 500, 600 and 700 °C). The optimum temperature was 600 °C, producing the maximum bio-oil yield of 41.82%. The result shows that as the temperature begins to increase from 400 to 600 °C, the liquid yield increases to the maximum from 30.37 wt% to 41.82 wt%. An increase in temperature up to a certain temperature increases the yield of liquid products. The pyrolysis conversion efficiency increases with rising temperature; this is owing to increase in gas and liquid product yield. The highest pyrolysis conversion was obtained at a temperature of 600 ° C, and this result was 79.21% by weight. When the temperature rises from 400 °C to 600 °C, a steady decrease in char product yield is observed. Contrary to expectations, the yield of the solid product increased with the increase of the temperature to 700 °C. This unexpected increase in char product yield is due to the fact that small particle size biomass prevents heat transfer by agglomeration at high temperature. Gas product yields increased with increasing temperature and reached the highest with 50.75 wt% at 700 °C.

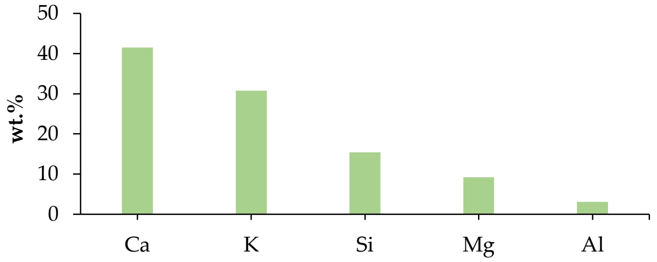

Figure 3. Inorganic elements (wt.%) present of the FL determined using SEM-EDS

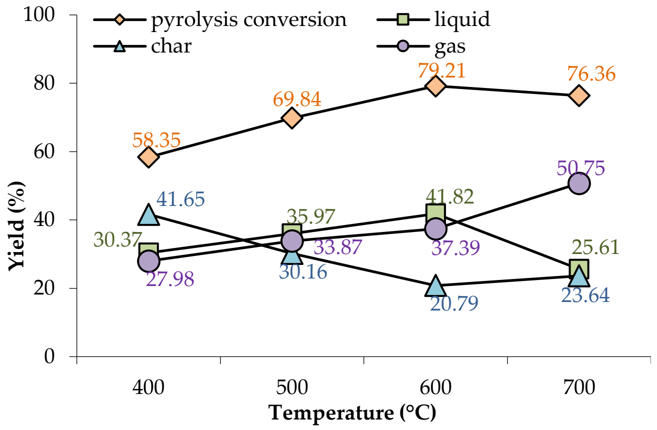

Figure 4. Effect of pyrolysis temperature on product yields (Particle size of Dp < 0.150 mm and nitrogen flow rate of 200 cm³/min)

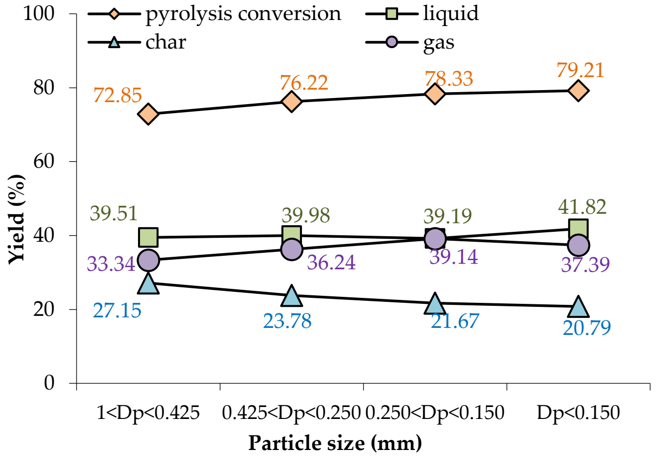

Figure 5. Effect of particle size on product yields (Pyrolysis temperature of 600 °C and nitrogen flow rate of 200 cm³/min)

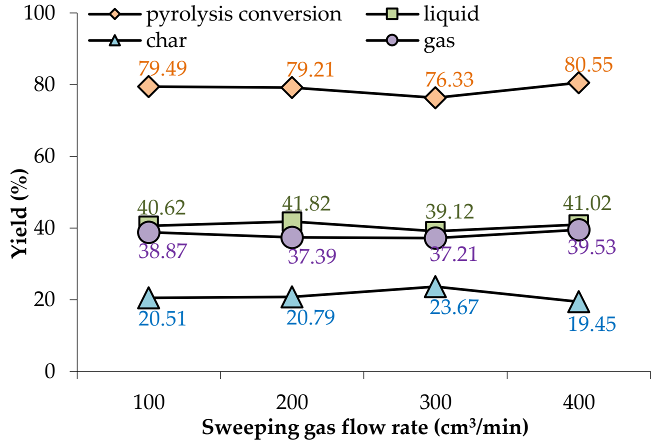

Figure 6. Effect of sweeping gas flow rate on product yields (Particle size of Dp < 0.150 mm and pyrolysis temperature of 600 °C)

3.2.2. Effect of particle size on pyrolysis product yields

Fig. 5 shows the effect of particle size on pyrolysis product yields at four different particle sizes. In this group of experiments, the temperature of the pyrolysis was 600 °C degrees and the flow rate of the sweeping gas was 200 cm³/min. These selected values of the temperature and the sweeping gas flow rate are the values at which the liquid product yield is optimum. The highest liquid product yield was achieved with a minimum particle size of Dp < 0.150 mm, even though there was no significant change in the liquid product yields with the change in particle size. Generally, in cases where particle size is less than 2 mm, there is no significant change in liquid product yields if heat transfer is not adversely affected by agglomeration in biomass. If the pyrolysis conversion yields of Fig. 5 are considered, the pyrolysis conversion efficiencies are increased with the reduction of the particle size. This increase in pyrolysis conversion was due to the increase in gas product yield up to 0.150 < Dp < 0.250 mm. The increase in pyrolysis conversion after this particle size is due to the increase in liquid product yield. Finally, the graph in Fig. 5 also shows that the char product yield decreases continuously as the particle size decreases. As mentioned above, if the agglomeration reactions were realized, there would be a significant increase in the yield of char products as the particle size decreased.

3.2.3. Effect of sweeping gas flow rate on pyrolysis product yields

In this section, the effect of sweeping gas (nitrogen) flow rate on product yield was investigated. In the experiments, FL with a particle size of < 0.150 mm were selected. The values obtained from the experimental results are shown in the graph in Fig. 6. It is seen that there is no significant change in the liquid and gas productions by increasing the entraining gas flow rate from 100 cm³/min to 400 cm³/min. The gas flow rates, which are optimal for liquid and gas product yields, are determined as 200 cm³/min and 400 cm³/min respectively. When the nitrogen flow rate increases to 400 cm³/min, the solid product yield is the lowest. High heating rates and temperatures often lead to a decrease in solid product yields, while the situation in gas product yields is quite the opposite. The highest gas product yield seen in the graph in Fig. 6 was obtained at a gas flow rate of 400 cm³/min, while the lowest solid product yield was also obtained at this flow rate.

3.3. The properties of the bio-oil

The properties of bio-oil are presented in Table 2. From Table 2, it can be seen that the energy content of bio-oil is more than twice that of the FL and It is also seen that bio-oil contains 6.68% nitrogen.

Table 2. Main properties of bio-oil from FL

Characteristics	Values
Water (%)	15.46
Carbon (%)	67.86
Hydrogen (%)	7.60
Nitrogen (%)	6.68
Oxygen[a] (%)	17.86
H/C molar ratio	1.34
O/C molar ratio	0.55
Empirical formula	$C_{75}H_{98}O_{15}N_6$
Higher calorific value (MJ/kg)	32.16

[a] by difference

The water content of bio-oil is 15.46%. This ratio shows that bio-oil does not contain a lot of water. The average chemical composition of the bio-oil is $C_{75}H_{98}O_{15}N_6$. The bio-oil contains a small amount of oxygen content than FL. Due to the increase in the percentage of carbon and hydrogen and the decrease in the oxygen content, the higher calorific value of the bio-oil increased to 32.16 MJ/kg. The TG and DTG curves of the thermal decomposition of FL at heating rate of 5 °C /min under inert atmosphere are shown in Fig. 7. When bio-oil's thermal analysis curves are examined, it can be seen that it can be divided into three stages. The first stage reached from room temperature to 300 °C. The onset thermal temperature of thermal decomposition is therefore 21 °C corresponding to about 16.547 mg and the final decomposition temperature is 290 °C with the amount of residue being 7.488 mg. This means that almost half of the content of bio-oil goes away at this step. This shows that the bio-oil losses weight very fast, a characteristic of water and lighter organic products. The second stage went from 300 °C to the temperature of 450 °C. Bio-oil starts with 7.488 mg at 300 °C and decreases to 4.144 mg when the temperature rises to 450 °C. At this stage, only 20% of the initial bio-oil is broken down. The third stage reached from 450 °C to 600 °C. Bio-oil starts with 4.144 mg at 450 °C and decreases to 0.080 mg when the temperature rises to 600 °C. In this last stage, the carbonaceous and other residues continuously were decomposed at a very fast rate and a severely continued loss of weight was shown in the weight loss curve. The Ar-H stretching vibration at 3013 cm^{-1} indicate the presence of aromatic structures. The C–H stretching vibrations at 2958, 2918 and 2850 cm^{-1} indicate the presence of alkanes. The C=O stretching vibrations with absorbance at 1707 cm^{-1} and indicate the presence of aldehydes, ketones, and carboxylic acids. The C–O stretching vibrations at 1377 and 1260 cm^{-1} indicate the presence of alcohols and carboxylic acids. The stretching vibration at 1514 represent C–C stretching vibrations indicative of alkenes and aromatics.

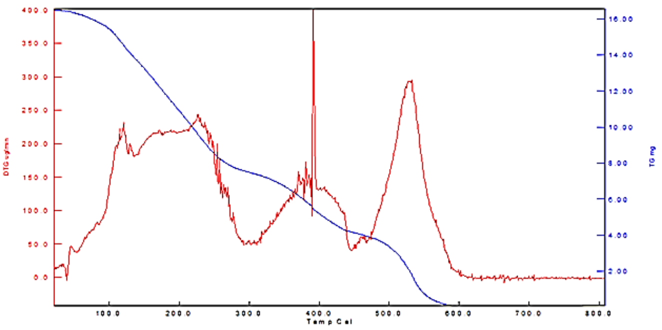

Figure 7. TG and DTG curves of the bio-oil at a heating rate of 5 °C /min. Left hand side y axis: DTG curve; right hand side y axis: TG curve

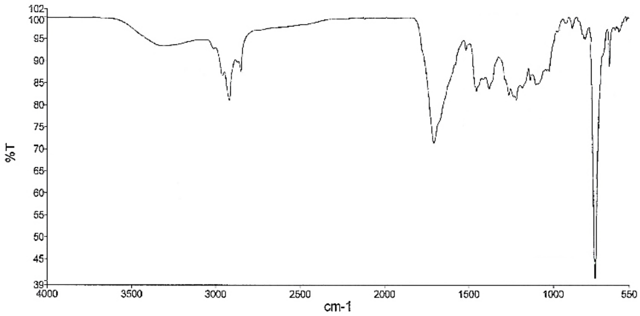

Figure 8. IR spectra of the bio-oil from fast pyrolysis of FL

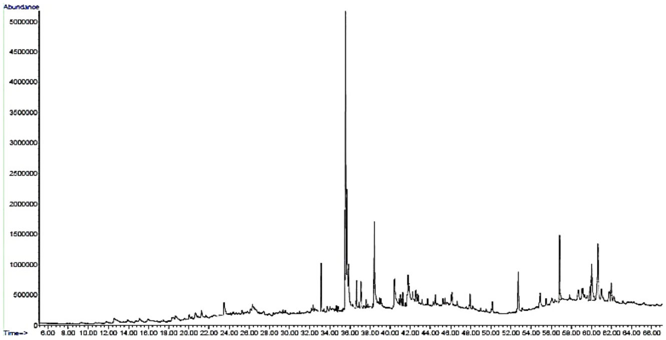

Figure 9. Gas chromatogram of the bio-oil

Table 3. Compositions of bio-oil from FL

No	Compound	Retention Time (s)	Area (%)
1	1H-Indole, 5-methyl	23.49	2.10
2	1-Heptene, 2-isohexyl-6-methyl	33.14	2.68
3	Psoralene	35.56	25.11
4	Ficusin	35.71	8.91
5	Isopsoralen	35.86	4.02
6	(E)-2,4-Phytadiene	36.67	2.14
7	2-Heptadecanone	37.08	2.66
8	n-Hexadecanoic acid	38.43	7.60
9	7H-Furo[3,2-g][1]benzopyran-7-one	40.41	5.50
10	9-Octadecenoic acid, methyl ester	41.01	1.59
11	2-Hexadecen-1-ol	41.27	0.93
12	9-Octadecenoic acid	41.79	5.84
13	Cyclopropaneoctanal, 2-octyl-	42.23	1.72
14	Hexadecanamide	42.53	0.92
15	Eicosane	46.14	2.67
16	Docosane	47.94	1.32
17	Tetracosane	52.72	3.55
18	Octacosane	54.91	1.79
19	Nonadecane	56.82	4.97
20	1H-Indole, 5-methyl-2-phenyl-	59.85	1.17
21	3-O-Acetyl-6-methoxy-cycloartenol	60.02	4.50
22	Stigmastan-3,5-diene	60.63	6.43
23	14.alpha.-Cheilanth-12-enic Methyl	61.97	1.87

Fig. 9 shows the gas chromatogram of bio-oil obtained from FL. When this chromatogram was examined, it was observed that bio-oil contains a large number of components. The most important of these components are given in Table 3. Both non-aromatic and aromatic hydrocarbon compounds were determined in organic phase of liquid product. When Table 3 is examined, it can be seen that the bio-oil obtained from FL contains different alkanes from 20 carbons to 29 carbons. We can see that bio-oil contains alkenes, aldehydes, carboxylic acids, and aromatic structures such as indole derivative as well as alkanes. It can be seen from the table that bio-oil contains a very high percentage of psoralene. This compound results from the breakdown of lignin and hemicellulose in the FL. FL can be an important source of raw materials for the production of this compound.

4. Conclusions

In this study, fast pyrolysis of FL was performed in a fixed bed pyrolysis reactor. The effects of pyrolysis temperature, sweeping gas flow rate and particle size on the product yield were researched.

In the research findings, it was found that the most important parameter in the change of pyrolysis product yields was temperature and the optimum temperature for liquid product yield was determined to be 600 °C. The liquid yield was decrease after 600 °C because of secondary reactions that produced more gases. When the main component analysis results of FL were examined, it was determined that the holocellulose ratio was high. This means that it will form a liquid product with a high aliphatic content. The 13.6 wt% lignin found in FL shows the presence of phenolic and aromatic compounds in the structure. Especially the H/C ratio of 1.71 is an important parameter in the use of the liquid product obtained from FL as an alternative and clean energy source. Instrumental techniques such as FT-IR, SEM-EDS, TG / DTG and GC-MS were used for the characterization of bio-oil obtained by fast pyrolysis of FL. The heating values of raw material and bio-oil were determined as 14.73 and 32.16 MJ/kg, respectively. Considering these rates, it is seen that the energy content of bio-oil is more than two times higher than the raw material. The energy content of bio-oil is thought to be close to the energy content of petroleum-derived fuels. Bio-oil contains alkenes, aldehydes, carboxylic acids, and aromatic structures such as indole derivative as well as alkanes. Türkiye ranks first in the world fig production. For this reason, FL poured on the ground constitute a significant potential both as a chemical raw material and as a waste. The liquid of FL from fast pyrolysis has good properties for a potential biofuel candidate or as a source of chemicals.

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