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Investigation of Pyrolysis of Walnut Shells and Pyrolysis Oil Quality

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Abstract
The energy demand is increasing in parallel with the technological developments and population in the world. Fossil fuels are the main source for this demand. As a result of energy production from fossil fuels, natural environment is adversely affected. Furthermore, many countries depend on the fossil fuels for their energy need. Researchers have been interested in alternative energy sources such as solar, biomass, and wind. There are many studies for investigating pyrolysis of lignocellulosic biomass. Studies mainly focused on the chemical structure of pyrolysis oil from different feedstocks. In this study, pyrolysis oil was produced from walnut shells in a pyrolysis reactor. Pyrolysis oil properties were investigated and compared with fossil fuels. The effect of pyrolysis reaction temperature on pyrolysis oil yield is studied. The results indicate that pyrolysis oil can be produced from walnut shells, the reaction temperature is an important factor on pyrolysis oil yield and pyrolysis oil has complex nature compared to fossil fuels.

1. Introduction

The amount of fossil fuels has been consumed dramatically over the decades. This consumption has had a detrimental impact on our environment because of releasing harmful exhaust gases. The demand on the fossil fuels is very high while the sources for these fuels are limited. Having environmental considerations and limited sources for fossil fuels has caused a need for researchers to find alternative energy sources [1].

There have been many studies about producing fuels from different alternative energy sources. In one of the studies, researchers focused on producing biodiesel from fish fat and vegetable oils with the transesterification method. After emission tests, it was concluded that there was reduction in HC and CO emissions while using the new biodiesel compared the diesel fuel [2]. Similar results were obtained by [3]. In their study, an alternative biodiesel was produced from micro algae, yeast and bacteria, and this type of biodiesel was tested in an internal combustion engine.

According to the Environmental Protection Agency, lignocellulosic biomass is considered one of the alternative energy sources. Because plants convert the energy taken from the sun into chemical energy by photosynthesis and store it in their body. When vegetable wastes are burned, the chemical energy in their body is thrown out in the form of heat [4]. It is very crucial to utilize lignocellulosic biomass as an alternative energy production.

Understanding the chemistry of lignocellulosic biomass and oil produced from this source has a great importance to be able to use it as an alternative fuel. Some researchers have used different methods to produce valuable oils from different feedstocks. For instance, pyrolysis oil was obtained from rice husk with using fast pyrolysis method. The relationship between reaction temperature and oil yield was studied and some properties oil was presented [5].

Akubo et al studied the pyrolysis of coconut shell, cotton stalk, palm kernel shell, rice husk, sugarcane, and wheat straw. Elemental analysis and the effect of temperature on product yield were

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studied. According to elemental analysis of raw material, the raw materials mainly consisted of carbon and oxygen elements. Main weight loss was observed at temperature range between 200 ºC and 400 ºC [6].

In another study, the pyrolysis of demineralized softwood sawdust was investigated. Ultimate and proximate analysis of raw material were conducted. GC-MS analysis of pyrolysis oil shows that the oil has complex nature [7].

Moreover, R. Maggi and B. Delmon indicated that pyrolysis oils were produced from the wastes of acacia tree, eucalyptus tree, red pine bark in pyrolysis reaction and the oil quality was studied using GC-MS and FTIR analysis [8]. According to results, pyrolysis oil had good amount of oxygen content and contained different groups and functions. In another study, pistachio soft shells used as a feed stock in a fixed bed reactor. The pyrolysis oil was investigated with elemental analyzer, FT-IR, and H NMR. It was determined that the pyrolysis liquid is a mixture of aliphatic, aromatic and polar hydrocarbons [9].

Yücedağ and Durak presented their study on pyrolysis of lactuca scariola. According to GC-MS analysis results, 98 different compounds identified within pyrolysis oil [10].

Walnut shells are one of the lignocellulosic biomass sources. There are a few studies on using walnut shell as an alternative energy. In one study, proximate and ultimate analysis of walnut shell were studied according to American standard testing methods. High heating value was found as 21.6 MJ / kg [11]. This study shows that walnut shells have calorific value. Onay et al studied pyrolysis of walnut shell to determine the effect of pyrolysis conditions on oil yield such as reaction temperature, heating rate, and particle size and conducted elemental analysis on pyrolysis oil. They concluded that oil yield increased with temperature up to 500 ºC and it decreased beyond this temperature. Pyrolysis oil contains high amount carbon and oxygen [12]. It is crucial to investigate the chemistry of pyrolysis oil obtained from walnut shells. In this study, walnut shells from Bitlis region are chosen as a feed stock to produce pyrolysis oil in a fixed bed reactor. The chemistry of walnut shells is investigated. The effect of different reaction temperatures on pyrolysis oil yield was studied while determining the optimum temperature for maximum oil yield. The chemical analysis of this oil was conducted by using different methods to understand chemical structure and quality of pyrolysis oil to be able utilize as an alternative energy source.

2. Material and Method

2.1. Material

Walnut trees are planted commonly in higher elevations in Turkey. According to the data obtained from TUİK [13], there were 26,618 pieces walnut trees in Turkey and 325,000 tones walnut fruits produced in 2021. Walnut is considered as a hard-shelled fruit. Due to its different fatty acid composition, it is a type of fruit that has an important health benefit, and the consumption of this fruit has been increasing [14]. The shells are wastes of walnut fruit and burned directly in ovens for baking or thrown away. Walnuts are grown in Bitlis region, Turkey. Bitlis is located in Eastern Turkey and at the elevation of 1,545 meters. They were procured from local producers in the city of Bitlis. Walnut shells were separated from walnuts and let air dried for experimental studies.

2.2. Method

Air dried walnut shells were grounded as maximum 0,5 cm sample size in a grinder. Then raw material was dried in the oven at 105 ºC. Ash, volatile, moisture, and fixed carbon content of the material were determined according to ASTM E1755, ASTM E871 & E872 specifications. Fixed carbon content was calculated by difference between 100 and sum of ash, volatile and moisture content. Moreover, the samples were tested for Ultimate analysis in an elemental analyzer named LECO-CHNS-932.

The pyrolysis experiments were conducted in mechanical engineering department laboratory, Bitlis Eren University. The experimental set up is shown in Figure 1. It is fixed bed reactor. Reactor was made of stainless steel and has the diameter of 10 cm and the height of 20 cm. Further information can be found in this study [15].

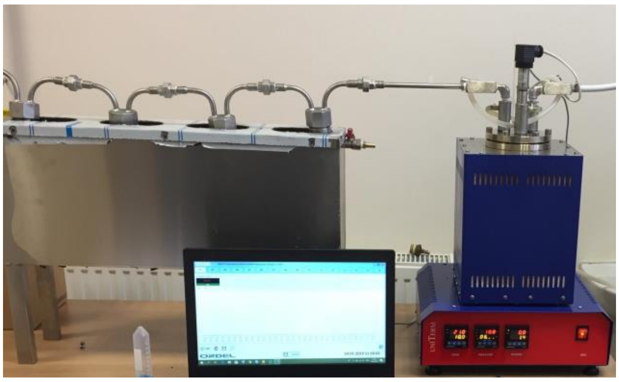

Figure 1. Pyrolysis experimental set up.

Table 1. Technical Properties of Fixed Bed Pyrolysis Reactor.

Capacity	Material	Temperature Range	Temperature Display	Heater	Temperature Control	Data Saver	Gas Nozzle	Power
1 lt	316 Stainless Steel	50℃ /800℃	Digital	Heating Mantle	PID Control , 10 steps 80 programs	Transferring data to computer	¼ npt threaded gas inlet, needle valve (2)	220 V, 50 Hz

Technical properties of the reactor are given in Table 1. Nitrogen gas was used as a sweep gas to provide vacuum environment in the reactor. Traps were placed to condense the gasses leaving the reactor. Salt-alcohol-ice mixture was used to keep the temperature of the traps below 0 ℃. The reactor temperature change with time was recorded in the computer. Experiments were performed at 5 different reaction temperatures (400, 450, 500, 550, 600 ℃), 40 ℃/min constant heating rate, in vacuum environment by providing nitrogen gas at 100 ml/min gas flow rate. 100-gram raw material was used in experiments.

Oil yield was calculated by equation (1), ash content was calculated by equation (2), and non-condensable gas content was calculated by equation (3). At the end of the experiment, the liquid product was taken from the traps and stored in glass bottles. The liquid product is called pyrolysis oil. The amount of solid product called ash is the amount remaining in the reactor at the end of the experiment. The weight difference between total amount in the beginning of experiments and the sum of liquid product and ash is non-condensable gases.

$$n_{oil\ yield}(\%) = \frac{Oil\ product\ (\ gram\ )}{initial\ weight} x\ 100 \qquad (1)$$

$$n_{ash\ yield}(\%) = \frac{Solid\ \ product\ (\ gram\ )}{initial\ weight} x\ 100 \qquad (2)$$

$$n_{\substack{non-condensable \\ gas\ yield}}(\%) = $$
$$= 100 - n_{\substack{oil \\ yield}}\ (\%) - n_{\substack{ash \\ yield}}\ (\%) \qquad (3)$$

Further, pyrolysis oil obtained at 500 ℃ was analyzed to determine its chemical structure. Ultimate analysis was performed with same method used for walnut shells. In addition, different devices were used for further chemical analysis. Table 2 shows the additional devices were used in experimental studies.

2.3 Cost Analysis

In cost analysis calculations, the cost of a liter pyrolysis oil is calculated with below equations. Main inputs for production of pyrolysis oil are electricity and nitrogen gas. Equation (4) is the correlation between raw material and pyrolysis oil. ‘m’ is the required raw material (kg) to produce required ‘v’ amount (liter) pyrolysis oil. ’d’ is the density of pyrolysis oil (kg/liter), $n_{oil\ \ yield}$ is the pyrolysis oil yield.

$$m = v\ x\ d\ /\ n_{oil\ yield} \qquad (4)$$

Capacity of reactor (f) is 500 gr. Required experiments (t) can be found below equation:

$$t = m\ /\ f \qquad (5)$$

Table 2. Experimental devices for oil analysis.

The Type Analysis	Density	Calorific Value	FTIR Analysis	GC-MS	pH
Name of The device	Density meter DS7000	IKA C 2000 Basic Version 1 Calorimeter	Perkin Elmer	Agilent 7890A and 5975C	Merck - pH indicator strips

Table 3. The main properties of walnut shell (Weight %).

Moisture Content	Volatile Content	Fixed Carbon	Ash	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
4,33	74,21	20,95	0,51	46,91	5,82	5,82	46,56	0,06

The heater is on total 0,72 hours (43 minutes) in each experiment. E (Turkish Lira), the total cost of electricity for t amount experiments can be found in equation (6). The constant, 2,23 is found by multiplying 0,72 hours with power of furnace,4 KW and unit electricity cost, 3,1 Turkish Lira / kwh

$$E = 8{,}93 \; x \; t \qquad (6)$$

Nitrogen gas is on total 0,72 hour (43 minutes) in each experiment at 100 ml/min (0,006 m^3 / hour) gas flow rate. N, the total nitrogen gas cost can be found in equation (7). The constant 0,384 is found by multiplying 0,72 hour with 0,006 m^3/hour and unit gas cost 89 Turkish Lira / m^3.

$$N = 0{,}384 \; x \; t \qquad (7)$$

Total unit cost for producing a liter pyrolysis oil (T) is the sum of E - the total cost of electricity and N - the total nitrogen gas cost.

3. Results and Discussion

3.1. The Analysis of Feedstock

The chemical properties of walnut shells were studied before pyrolysis experiments. Proximate and ultimate analysis results were given in Table 3. According to proximate analysis results, volatile content is the highest component. It means that we could obtain up to %74,21 gas or liquid products with pyrolysis regarding to pyrolysis reaction conditions.

Moreover, elemental analysis results indicate that Carbon and Oxygen elements constitute a great proportion the walnut shell while small amounts of Hydrogen, Nitrogen and Sulfur. Walnut shell shows similar properties compare to other lignocellulosic biomass feedstocks, such as pistachio soft shell [9] and corn and cotton stalks [16]. Higher Oxygen content is one of the disadvantages of lignocellulosic biomass feedstocks.

3.2. Pyrolysis Experiments

The main products of pyrolysis reaction are pyrolysis oil, non-condensable gases, and solid products. Figure 2 shows pyrolysis oil and solid product that are produced from walnut shells at 500 ℃. The oil has a strong smell that is similar to vinegar. Solid product is black and alike a char coal. Same products are obtained at different temperatures ranging from 400 ℃ to 600 ℃.

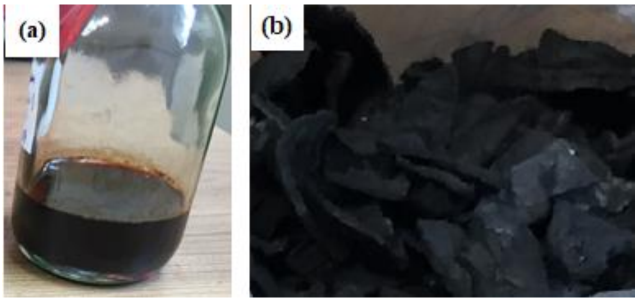

Figure 2. The products of pyrolysis reaction: pyrolysis oil (a), solid product (b).

Temperature is a main variable on pyrolysis oil yield. Figure 3. shows the relationship between reactor temperature and yield of pyrolysis oil, non-condensable gas and solid products. There is slight change on yield when temperature changed from 400 ℃ to 450 ℃. When reaction temperature was increased from 450 ℃ to 500 ℃, pyrolysis oil yield increased to maximum level of 31,6 % and solid production yield was decreased with slight increase on non-condensable gases. When temperature was increased from 500 ℃ to 550 ℃, pyrolysis oil and solid production yield were decreased whereas non-condensable gas yield was increased. Same pattern was seen when temperature changed from 550 ℃ to 600 ℃. This shows that higher temperature caused formation of strongly bonded molecules and it made harder to condense those molecules [17]. 500 ℃ is the optimum temperature for production of pyrolysis oil for walnut shells. The correlation between temperature and yield is similar with pyrolysis studies of furniture saw dust [18], palm kernel shells [19], and [20].

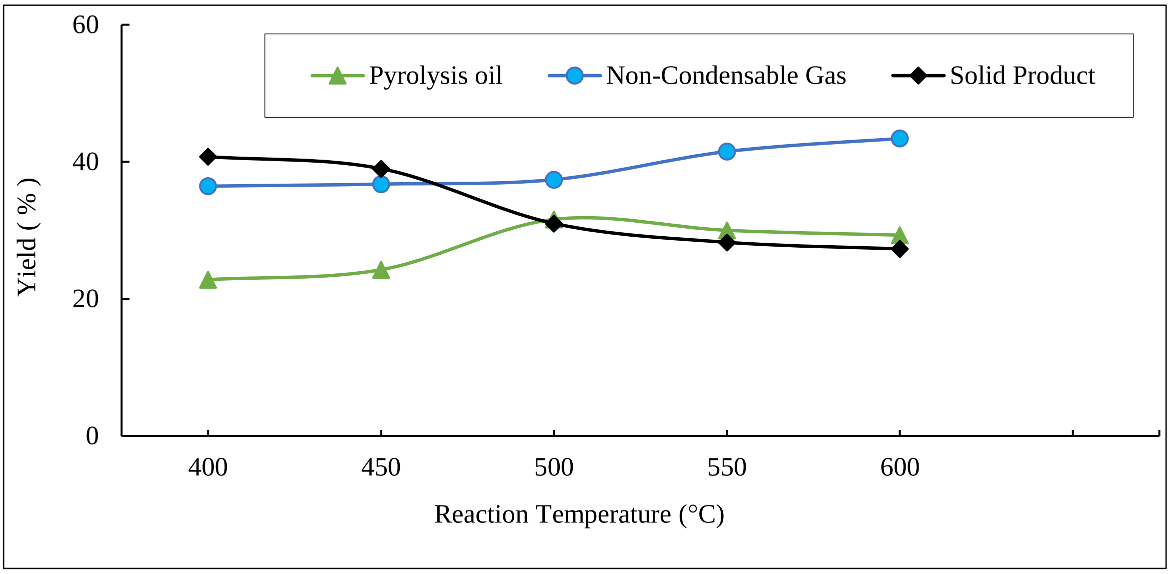

Figure 3. The effect of temperature on product yield.

3.3. Characterization of Pyrolysis Oil

The chemical properties of the pyrolysis oil obtained at 500 °C were investigated. The analysis results are shown in Table 4. Elemental analysis results are given by weight.

These results show that pyrolysis oil has high oxygen content and is denser than fossil fuels and a highly acidic product. Diesel fuel has %86,13 carbon, % 13,87 hydrogen by weight. The pyrolysis oil containing %43,04 oxygen is one of the drawbacks. Similar results were obtained from rice straw [21], wheat shell [22], and switch grass [23].

Higher oxygen content, density and being acidic for the oils is a big disadvantage to be utilized in combustion engines, or boiler as an alternative energy. Acidic oil would cause corrosion on metals. Moreover, the density of the oil is 1,0493 g/cm^3. It is quite higher than diesel fuel of 0,85 g/cm^3. Since there is difference in density, the oil and diesel do not mix homogenously. Figure 4. shows the mixture of %95 diesel + %5 pyrolysis oil. It can be seen that the oil stayed in the bottom since it is denser than diesel fuel. The ethanol addition to mixture didn't change the result. It can be concluded that pyrolysis oil has different chemical structure than fossil fuels. In one study, waste engine oil that has 870 kg/m^3 density was able to mix with diesel fuel since waste oil has a close density with diesel and has similar chemical properties. The waste oil was successfully utilized in a diesel generator [24].

Figure 4. The mixture of diesel and pyrolysis oil.

Table 4. The chemical properties of pyrolysis oil.

Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Calorific Value (cal/g)	Density (g/cm^3)	pH Value
48,10	8,64	0,18	43,04	0,04	7059	1,0493	2,5

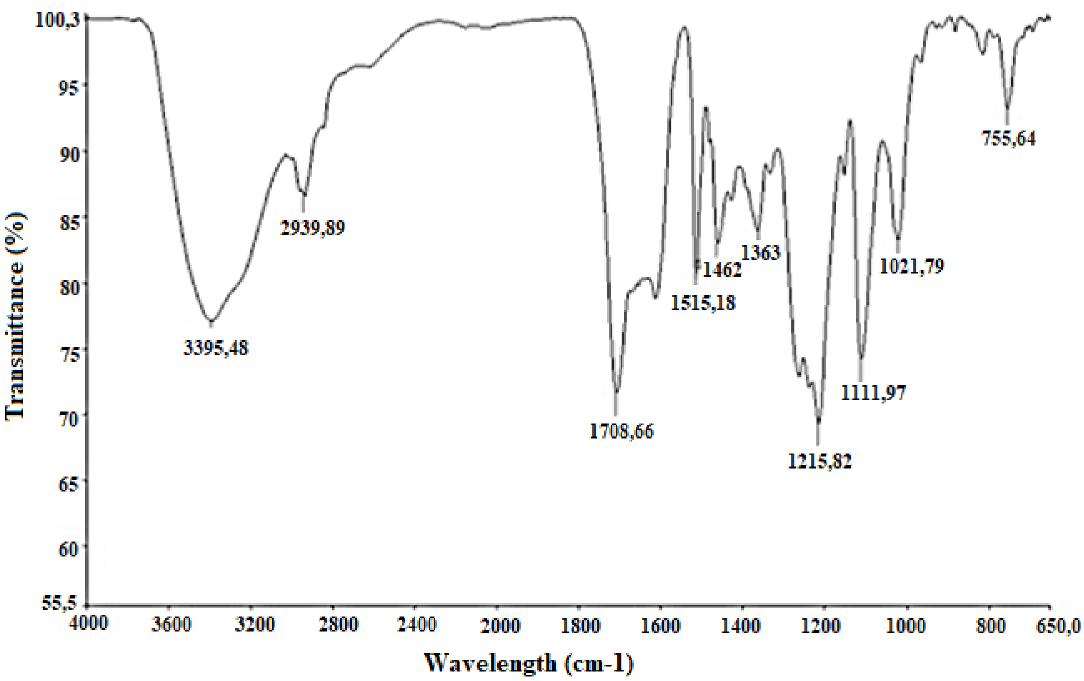

Figure 5. FTIR spectra of pyrolysis oil.

FTIR spectra of pyrolysis oil obtained at 500 ℃ reaction temperature is given on figure 5. According to figure 5 and the IR frequency table obtained from [25], the peak at 3395 cm-1 is indicative of O-H stretching, the presence alcohols. The peak at 2939 cm-1 indicates C-H stretching, the presence of alkenes [26]. The peak at 1708 cm-1indicates the C=O stretching, the presence of ketones or aldehydes. The peak at 1515 cm-1 indicates skeletal stretching. The peaks at 1363 and 1462 cm-1 indicate C-H bending and O-H bending, the presence of alkane groups and phenols. The peaks between at 1021 and 1215 cm-1 indicate C-O stretching, the presence of ethers, esters, and alcohols. The peak at 755 cm-1 indicates the presence of aromatics.

In addition to FTIR spectra analysis, GC-MS analysis was also performed. Table 5. shows GC-MS analysis results. Pyrolysis oil obtained from walnut shells is consisted of many different chemical groups. These groups are furans, esters, ketones, aldehydes, phenols, alkenes, alcohols, sugars, guaiacols, amides, and carboxylic acids. These groups were confirmed in FTIR spectra analysis. Total 17 compounds were identified. The highest amount of component in oil is $C_7H_8O_2$ (Guaiacol – monomethoxybenzene) at %15,1. Guaiacol consists of phenol with a methoxy substituent at the ortho position. The lowest amount component is $C_{16}H_{34}$ (Hexadecane) at %0,5. Hexadecane is a straight-chain alkane with 16 carbon atoms [27]. Carbon distribution oil is in the range of C_4 – C_{16}. Molecular weights of these compounds are between 88 and 270. The similar results were obtained from [28]. They studied pyrolysis of mongolian type pine tree. Further, they applied distillation of the oil by molecular distillation method. However, the fractions of the oil have more complex nature than the bio oil because the oil doesn't have a stable nature. The chemical composition of the oil changes with temperature. In another study, the pyrolysis oils obtained from the wastes of the beech tree and the flax plant have the similar characteristics [29]. In the same study, pyrolysis of cellulose, hemicellulose and lignin was also investigated by GC-MS method. It was determined that many components were found in the pyrolysis oils obtained from the wastes of the beech tree and the flax plant, also found in pyrolysis of cellulose, hemicellulose and lignin.

Table 5. GC-MS analysis results.

Pick No	RT	Tentative Assignment	Empirical Formula	CAS#	Molecular Weight	Amount
1	6,284	Methyl propionate	$C_4H_8O_2$	000554-12-1	88	0,8
4	8,007	2-Hexanone	$C_6H_{12}O$	000591-78-6	100	0,7
11	11,748	2-Cyclopenten-1-one	C_5H_6O	000930-30-3	82	1,8
13	12,708	Hexadecane	$C_{16}H_{34}$	000544-76-3	226	0,5
15	12,972	Furfural	$C_5H_4O_2$	000098-01-1	96	5,3
19	13,896	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	002758-18-1	96	1,2
28	17,346	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	000080-71-7	112	4,3
29	17,668	Phenol, 2-methoxy-	$C_7H_8O_2$	000090-05-1	124	15,1
31	18,120	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$C_7H_{10}O_2$	021835-01-8	126	1,6
33	18,804	Creosol	$C_8H_{10}O_2$	000093-51-6 93	138	7,3
36	19,313	Phenol	C_6H_6O	000108-95-2	94	3,4
37	19,707	Benzeneethanol, 2-methoxy-	$C_9H_{12}O_2$	007417-18-7	152	4,5
40	20,278	p-Cresol	C_7H_8O	000106-44-5	108	1,9
45	22,924	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	91-10-1	154	27
48	24,242	3,5-Dimethoxy-4-hydroxytoluene	$C_9H_{12}O_3$	6638-05-07	168	13,6
51	25,171	Benzocyclooctene-7,8-dicarboxylic acid dimethyl ester	$C_{16}H_{14}O_4$	099027-76-6	270	10,3
68	32,113	2-(Propynylthio)-5-methylthiophene-3-carbaldehyde - oxime	$C_9H_9NOS_2$	2000236-59-0	211,3	0,7
	Total					100,0

On the other hand, crude oil consists of paraffin, cycloparaffinic (naphthenic) aromatic hydrocarbons, and a trace amount sulfur, nitrogen, and oxygen compounds [30]. GC-MS analysis of pyrolysis oil obtained from walnut shells shows that the pyrolysis oil has a different chemical structure than crude oil.

3.4. Cost Analysis

Unit cost of pyrolysis oil was found after solving required equations in section 2.3. Table 6. shows the results of cost analysis.

Required raw material was found as 3,32 kg. 6,64 times required experiments to produce 1-liter pyrolysis oil. Total electricity cost was 59,30 Lira and nitrogen gas cost was 2,54 Lira. The cost of 1-liter pyrolysis oil was found as 62 Lira. The electricity cost is the main variable for oil production. The result indicates that the small size reactor is not cost effective to produce pyrolysis oil since it was designed solely for research purposes. It is advised to have larger scale reactors for pyrolysis oil production.

Table 6. Cost analysis results

Variables	Results
v (liter)	1
d (kg/m^3)	1.05
$n_{oil\ yield}$ (%)	31.6
m (kg)	3,32
t (times)	6,64
E (Lira)	59,30
N (Lira)	2,54
T (Lira)	62

4. Conclusion and Suggestions

The aim of this study is to produce bio oil from walnut shells in a pyrolysis reactor. Walnuts were procured from Bitlis, Turkey region. Pyrolysis oil, non-condensable gases, and solid products were obtained from the pyrolysis of walnut shells. The temperature effects the product yields greatly. Optimum temperature for pyrolysis oil yield is found at 500 ^oC reaction temperature.

To be able to understand if pyrolysis oil is similar to fossil fuels, a variety of chemical tests such as elemental analysis, calorific value, density, pH value, FTIR spectra and GC-MS analysis conducted. According to results, pyrolysis oil is highly acidic, denser than diesel fuel, and has high oxygen content and low calorific value. The pyrolysis oil also has a complex chemical groups in its nature. They are furans, esters, ketones, aldehydes, phenols, alkenes, alcohols, sugars, guaiacols, amides, and carboxylic acids. Since the oil has a complex nature, and high density, it doesn't mix with diesel fuel. The chemical nature changes with temperature and it makes the pyrolysis oil unstable.

It can be concluded that pyrolysis oil obtained from walnut shells is different than fossil fuels. The oil has similar characteristics with the oils obtained from different lignocellulosic biomass sources. The pyrolysis oil may be utilized in producing different chemical raw materials using appropriate chemical methods.

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Contributions of the Authors

Authors did the work together and co-authored the publication

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The study is complied with research and publication ethics

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