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Evaluation of the Role of the Pyrolysis Temperature in Straw Biomass Samples and Characterization of the Oils by GC/MS

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The aim of this study is to investigate the variation of thermal conversion of agricultural wastes in a fixed bed reactor with temperature and elucidating the chemical structure of oil products formed during the process. Pyrolysis of two similar biomass samples, namely wheat straw (WS) and oat straw (OS), was conducted in a fixed-bed reactor with a heating rate of 7 °C/min, mean particle size, and pyrolysis temperature ranging from 300 to 800 °C. Influence of pyrolysis temperature on product yields and compositions was investigated. The results indicated that the maximum oil yields were obtained at moderate temperatures (500−600 °C) for WS and OS as 19.1% and 20.3%, respectively. According to the column chromatography results, polar, aliphatic, and aromatic fractions were maximized in lower, moderate, and higher temperatures, respectively. The structure of oil was then explained in detail by analyzing with ^{1}H nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry (GC/MS) methods. The pyrolysis oils were found to be chemically highly heterogeneous and contained phenols, carbonyl groups, carboxylic acids, aromatic compounds, monoaromatic compounds, PAH's, esters, *n*-alkanes and alkenes, and nitrogenous compounds. According to these results, oils can be used as fuel and are a valuable source of chemical raw materals.

1. Introduction

Renewable energy is one of the most striking developments of our time. When compared to fossil and nuclear fuels, renewable energy resources are more environmentally friendly.[1] Apparently, effective use of renewable energy resources could prevent the extinction of the world's limited fossil fuel reserves. Among the renewable energy resources, biomass is of vital importance in keeping at minimum levels the greenhouse gases and particularly CO_2 which cause global warming and are among the most crucial environmental problems.[2,3] When biomass is compared with fossil fuels, it is seen that it may generate the same amount of CO_2 as fossil fuels per unit C, but every time a new plant grows, it removes the same amount of CO_2 from the atmosphere.[4]

Today, the use of agricultural waste as a biomass resource is critically important. Turkey has been one of the important agricultural countries in the world. 35% of the 78 million hectares total area is used as agricultural land and the climate is congenial for agricultural activities.[5]

Recently, the phenomenon of global warming and its impact on the environment has called a lot of attention to more environmentally friendly processes.[6] Among the thermochemical methods used to obtain energy from biomass, pyrolysis is increasingly gaining attention. Because this gives products of better quality compared to any other thermochemical process. Although it is still under the developmental stage, pyrolysis has received special attention as it can convert biomass directly into solid, liquid, and gaseous products by its thermal decomposition in the absence of oxygen.[7] In addition, as it is already known, one of the important problems of energy sector is storing. The liquid products obtained through pyrolysis and characterized as petroleum equivalent are considerably efficient in terms of use, transport, and storage.[3] Today, it is possible to convert the waste that constitutes the unused parts of globally important agricultural products into important energy and chemical raw material resources by pyrolysis.

There are many studies about biomass pyrolysis in the literature. Particularly, there are extensive studies regarding the effect of temperature on pyrolysis product yields. Data obtained in these studies demonstrates that the rise in temperature decreased solid product yield, while increasing gaseous product yield. As for the liquid product yield, it increased until a certain temperature and then showed a decrease due to the increase in the gaseous product yield, a result of secondary reactions. Generally, for all kinds of biomass samples, maximum liquid product yields were obtained at moderate temperatures (500−600 °C).[8−19]

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Nevertheless, except for a few studies in the literature, the possible effects of pyrolysis temperature on product analysis have not been sufficiently investigated.[20-23] Because of this reason, the influence of pyrolysis temperature on characteristics of oils obtained from agricultural wastes was investigated in this study.

In this study, wheat and oat straw was used as biomass resource. An annual plant, wheat is grown in almost all parts of the world since it can be cultivated under all soil and climatic conditions. It is the most common crop not only in Turkey but also worldwide. An important crop due to its starch-rich seeds, oat is also widely cultivated, particularly in Turkey. In Turkey, an agricultural country, wheat and oat production are approximately 22 million tons and 323 thousand tons, respectively. The waste amounts of these crops are 3.5 million tons and 48 thousand tons.[24]

This paper examines the pyrolysis of wheat straw (WS) and oat straw (OS) under slow pyrolysis conditions at temperatures ranging from 300 to 800 °C. First, the pyrolysis temperature for maximum oil product yield obtained from these experimental conditions was investigated; and later, the changes in the elemental composition of the oil product and subfractions under different temperature ranges were examined and product composition was analyzed in

Table 1. Proximate, Ultimate and Component Analysis (wt %) of Straw Biomass Samples

	WS	OS
proximate analysis (%)		
volatiles	74.2	75.9
fixed C	13.0	0.1
ash	6.9	17.3
moisture	5.9	6.7
ultimate analysis (%)		
C	52.9	48.5
H	6.3	6.0
N	0.4	0.4
O[a]	40.4	45.1
O/C	0.6	0.7
component analysis (%)		
extractives[b]	5.5	2.2
hemicellulose[c]	45.2	49.6
lignin[c]	18.1	16.6
cellulose[c]	31.2	31.6
calorific value (MJ/kg)	19.7	17.0
mean particle size (mm)	0.5	0.4

[a] By difference. [b] Benzene/alcohol (2/1) (v/v). [c] Extractive free basis.

detail through ^{1}H NMR and GC/MS at temperatures at which maximum oil product yields were obtained.

2. Experimental Section

2.1. Materials and Methods. The samples of WS and OS investigated in this study were taken from the city of Edirne located in northwest Anatolia. Before the experiments, the samples were dried, ground in a high-speed rotary cutting mill, and then prepared to give the mean particle size. Table 1 shows the main characteristics of the feedstock pyrolyzed: their proximate, ultimate (Carlo Erba, EA 1108), and component analysis.

The pyrolysis experiments were carried out using a fixed-bed reactor. The 316 stainless steel retort had a volume of 250 cm^3 (54 mm i.d.) and was externally heated by an electrical furnace in which the temperature is measured by a thermocouple inside the bed. The connecting pipe between reactor and the trapping system was heated to 400 °C to avoid condensation of tar vapor. A schematic diagram of the unit is presented in Figure 1.

In order to investigate the effect of the final pyrolysis temperature on the product yields, during experiments 10 g of sample, having an average particle size, was placed in the reactor and the temperature was raised at 7 °C/min to the final pyrolysis temperatures ranging from 300 to 800 °C. Experimental apparatus was held at adjusted temperature either a minimum of 30 min or until no further significant release of gas was observed. The flow of gas released was measured using a soap film for the duration of experiments. The liquid products consisting of aqueous and oil phases were collected in a glass liner located in ice-cooled traps. At the end of the experiments, the oil fraction was separated from the water by use of dichloromethane and weighed. The solid char was removed and weighed. Gas yield was determined by overall material balance.

All the yields were calculated on a dry and ash-free (daf) basis and each experiment was performed three times at each experimental condition and reproducibility of the experimental data was calculated to be within ±2%.

2.2. Characterization. The examination of pyrolysis oils requires the use of various spectroscopic and chromatographic methods owing to their complex structures. The main methods of analysis used to determine the composition of oil product in this study are elemental analysis, ^{1}H NMR, column chromatography, and GC/MS.

C, H, N, and O contents in the bio-oils were measured using a CHNS-O Carlo Erba EA 1108 instrumental analyzer. Because the biomass samples have different ash and water contents, the elemental analysis was additionally calculated on a dry ash-free basis, like pyrolysis product yield calculations.

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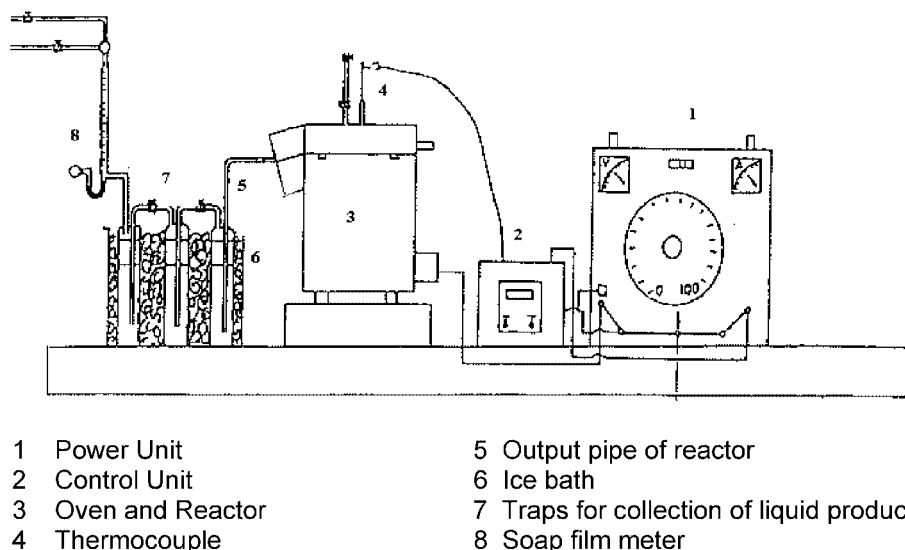
1	Power Unit	5	Output pipe of reactor
2	Control Unit	6	Ice bath
3	Oven and Reactor	7	Traps for collection of liquid product
4	Thermocouple	8	Soap film meter

Figure 1. Schematic diagram of the fixed-bed reactor.

The ^{1}H NMR spectra of the bio-oils were obtained at a H frequency of 500 MHz using a Bruker Avancell 500 MHz instrument. The samples were dissolved in chloroform-*d*.

The oil products were analyzed by GC/MS using a Hewlett-Packard HP 6890 gas chromatograph coupled to a HP 5973 quadrupole detector. The gas chromatograph was equipped with a 30 m × 0.25 mm capillary column coated with a 0.25 μm thick film of 5% phenylmethylpolysiloxane (HP-5). Helium was employed as a carrier gas at a constant flow rate of 1.2 mL/min. The initial oven temperature was 45 °C held for 2 min and then programmed from 45 to 290 at 5 °C/min with an isothermal held for 10 min. Splitless injection was applied at 290 °C. The ion source and transfer line temperatures were 230 and 300 °C, respectively. Data were acquired in the full-scan mode between m/z 33−533, and a solvent delay of 3 min was used. Chromatographic peaks were identified by means of NIST mass spectral data library and from their retention times using standard compound when available. The percentages of the peaks were calculated from the TIC (total ion chromatogram) peak area.

The chemical class compositions of the bio-oils were determined by liquid column chromatographic technique. All of the oils were separated into two fractions as *n*-pentane soluble (deasphalted oil) and insoluble compounds (asphaltanes) by using *n*-pentane. Deasphalted oils were then separated on activated silica gel (70−230 mesh) pretreated at 170 °C for 6 h before packing a 0.2 × 0.025 m^2 i.d. column. The column was then sequentially eluted with *n*-pentane, toluene, and methanol to obtain fractions enriched in aliphatic, aromatic, and polar fractions. Aliphatic base subfraction contains predominantly paraffins, olefins. Aromatic base subfraction contains monocyclic, bicyclic, and polycyclic aromatics, and considering polar base subfraction it contains oxygenated compounds. Each fraction was dried by rotary evaporation and weighed.

3. Results and Discussion

3.1. Influence of Pyrolysis Temperature on Product Yields Obtained from Straw Biomass Samples. Pyrolysis temperature is a significant parameter that affects the amount and composition of volatile component. Through decomposition of raw material in the absence of oxygen during pyrolysis, the volatile component which produces the liquid product starts to form at a temperature between 350 and 400 °C for coal and oil shale, while biomass requires a lower temperature range (250− 300 °C), which demonstrates the compositional differences
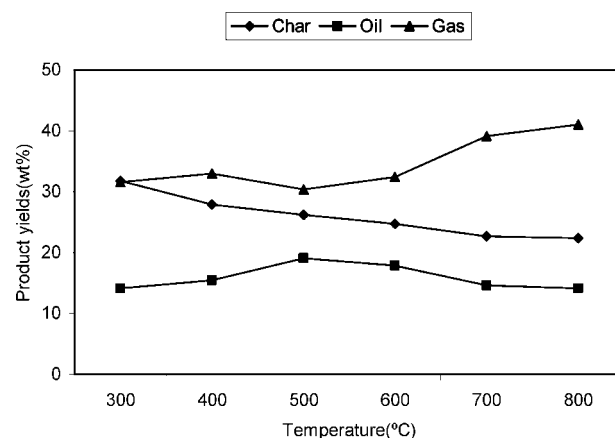

Figure 2. Product yields from WS pyrolysis at different temperatures.

between coal and biomass.[25] Biomass is held together by weaker bonds than those of coal (R−O−R), and coal is made of C=C bonds which are more resistant to heat.[26] Generally, products produced under lower temperatures are water and low amounts of carbon oxides.

Figures 2 and 3 reveal that the temperature at which volatiles start to form for straw biomass samples is lower compared coal. At 300 °C, oil yield was 14.1 and 15.0% for WS and OS, respectively. At this step of the study, approximately 74% of the required maximum oil yield for both biomass samples was obtained at this temperature.

As expected, char product yields at this temperature are at maximum levels when compared to other temperature ranges owing to uncompleted decomposition mechanisms. Thus, high char product yield and low oil product yield were obtained due to the low level of pyrolysis conversion at low temperatures.

Oil product maximized at moderate reaction temperature of 500 and 600 °C for WS and OS biomass samples, respectively. The optimum oil yields for WS and OS are 19.1% and 20.3%, respectively. The similarity of pyrolysis conversion of straw biomass samples shows that pyrolysis reactions were more

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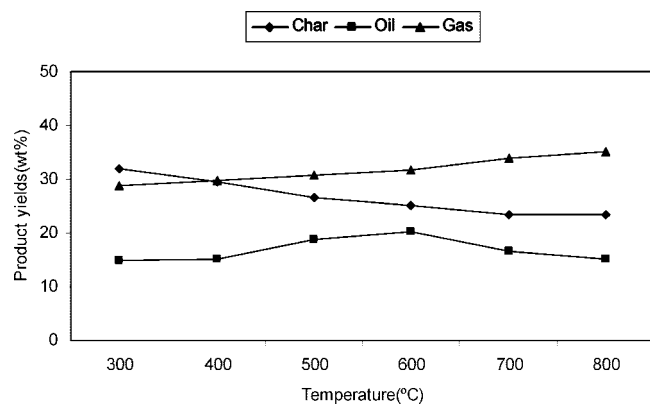
Figure 3. Product yields from OS pyrolysis at different temperatures.

affected by temperature rather than physical composition. Although the trends on oil and gas yields as a function of temperature are the same for both straw biomass samples, the oil yield was lower for WS due to its higher reactivity producing more gas. Nevertheless, it is believed that this difference was affected by considerably different amounts of ash and fixed carbon content that exists in each biomass material. The decomposition interval for OS which has a lower amount of fixed carbon was wider.

Moreover, in the view of the oil yield, considerably differences were observed at the pyrolysis temperatures of 500 and 600 °C than at 400 and 700 °C. After experiencing a peak at approximately 500 and 600 °C, the oil yields showed a sharp decline. Afterward, as the temperature rises, long-chained primary pyrolysis products forming the oil product disintegrated and converted into gaseous product. However, at high temperatures, it is important to distinguish between secondary cracking reactions and gasifying reactions that occurred in char. Therefore, gaseous product yield reached a maximum level at 800 °C, which is the highest operating temperature (41.0% for WS, 35.1% for OS).

3.2. Influence of Pyrolysis Temperature on Elemental Compositions of Oil Obtained from Straw Biomass Samples. Tables 2 and 3 show the results of an elemental analysis of the oils obtained from straw biomass samples. Especially in the recent years, there have been extensive studies about biomass pyrolysis in the literature. However, in many of these studies, when the influence of pyrolysis temperature on product yields is researched, particularly elemental analysis data of oil product on a single temperature is used.[11–13,16,27–29] Elemental composition of oil product at different pyrolysis temperatures was given by only a few studies.[20,22]

However, elemental analysis of products enables us to make preanalysis of products. The contents of C and H are important indicators for the quality of the liquid product. For example, for high-quality liquid product, the content of C and H should be sufficiently high and oxygen content should be as low as possible.[30] Because of the pyrolysis mechanism and biomass

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Table 2. Variation of the Elemental Composition of the WS Bio-Oil with Temperature

component	pyrolysis temperature					
	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
C (wt %)	69.4	70.4	71.7	71.1	72.0	73.0
H (wt %)	7.3	7.6	8.3	8.5	8.5	9.1
N (wt %)	0.4	0.4	0.4	0.5	0.5	0.4
O[a] (wt %)	22.9	21.6	19.6	19.8	19.0	17.5
O/C	0.3	0.2	0.2	0.2	0.2	0.2
calorific value (MJ/kg)	29.89	30.88	32.69	32.74	33.19	34.67

[a] By difference.

Table 3. Variation of the Elemental Composition of the OS Bio-Oil with Temperature

component	pyrolysis temperature					
	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
C (wt %)	63.3	63.9	64.8	65.0	64.6	68.1
H (wt %)	6.4	6.7	6.9	6.9	6.9	7.3
N (wt %)	1.3	0.8	0.9	1.3	1.2	1.6
O[a] (wt %)	29.0	28.6	27.4	26.9	27.3	23.0
O/C	0.3	0.3	0.3	0.3	0.3	0.2
calorific value (MJ/kg)	25.42	26.13	26.94	27.09	26.89	29.42

[a] By difference.

sample used, the oxygen content of the pyrolysis oils was very high. Its content was calculated by a difference equation.

As demonstrated in Tables 2 and 3, as the temperature increases, oxygen percentage showed a downtrend whereas percentages of C and H increase. It was observed that when the temperature is increased from 300 to 800 °C, carbon content for WS and OS increased from 69.4 to 73.0%, and 63.3 to 68.1%, respectively; furthermore, H content for WS and OS increased from 7.3 to 9.1% and 6.4 to 7.3%, respectively. Since H_2, which is produced in high temperatures, stays in the reactor more than a fast pyrolysis product in a sweeping gas atmosphere, it is presumed that H_2 has enough time to saturate the unsaturated aliphatics or it can be replaced by the oxygen in the existing oxygen-containing compounds in slow pyrolysis.

The molar ratio of O/C was decreased from 0.3 to 0.2 with an increase of pyrolysis temperature from 300 to 800 °C for both biomass samples. It is considered that there was a significant decrease in the O/C rates obtained at all temperatures when compared to the original raw material. High oxygen content formed in pyrolysis oils in accordance with the pyrolysis mechanism also leads to the formation of low-energy content oil products. Some of the oxygen in the original feedstock is thought to have turned into products such as H_2O, CO, and CO_2.

The high oxygen content of pyrolysis oil results in a very low energy density in comparison to customary fuel oils. Generally, the HHV (higher heating value) is reported. The heating values are increased with decreasing of oxygen content in pyrolysis oils at high temperatures. The HHV can be calculated from elemental analysis data by equation.

$$HHV\ (MJ/kg) = (338.2 \times \%C + 1442.8 \times (\%H - \%O/8)) \times 0.001$$

3.3. Dependence of Hydrogen Distribution on Biomass Type. The most reliable method used for elucidating an aromatic structure is probably NMR spectroscopy. Through this method, it is possible to find out the presence of a monosubstitute benzene ring, the way the methyl or methylene groups are attached to the ring, detection of the phenolics consisting of the OH group, and the percentage between them.

The ^{1}H NMR spectra of the oils are compared and the hydrogen distribution and estimated carbon aromaticity are given in Table 4.

Table 4. Percentage of Hydrogen Distribution from ^{1}H NMR Spectra of the Bio-Oils Obtained from WS and OS

| type of hydrogen	chemical shift (ppm)	A[a]	B[b]
aromatic	6.5–9.0	11.2	14.3
phenolic (OH) or olefinic proton	5.0–6.5	20.2	43.7
ring-join methylene (Ar–CH$_2$–Ar)	3.3–4.5	18.5	12.4
CH$_3$, CH$_2$, and CH α to an aromatic ring	2.0–3.3	26.3	18.2
CH$_2$ and CH β to an aromatic ring (naphthenic)	1.6–2.0	7.1	2.9
CH$_3$, CH$_2$, and CH γ or further from an aromatic ring	1.0–1.6	13.4	6.9
CH$_3$ γ or further from an aromatic ring	0.5–1.0	3.3	1.6

[a] Bio-oil of WS obtained at 500°C (% of total hydrogen). [b] Bio-oil of OS obtained at 500°C (% of total hydrogen).
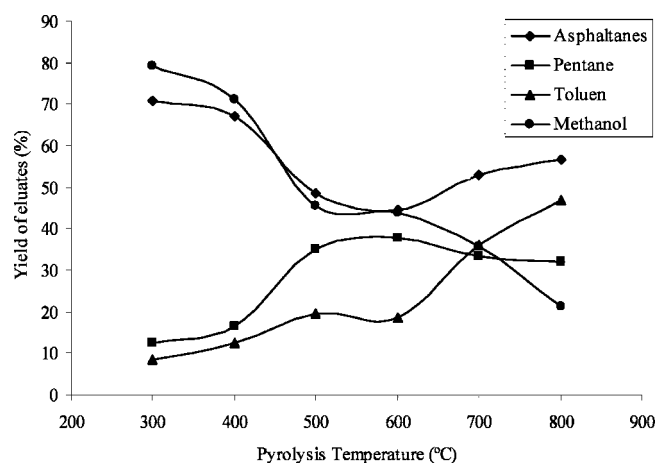
Figure 4. Dependence of the oil eluates of WS on the pyrolysis temperature.

While OS pyrolytic oil has the greatest portion of protons in the phenolic (OH) or olefinic, having a value of 43.7%, α positions to aromatic ring protons have the greatest portions in the other oils. Furthermore, significant amounts of phenolic or olefinic protons (20.2%) were also detected in WS oil. Considering these results, it could be argued that pyrolysis liquids are important phenolic components under these circumstances. While a considerable amount of ring-joining methylene protons was also detected in the WS oil among other protons, one-ring aromatic compounds were found in both biomass pyrolysis oils.

3.4. Influence of Pyrolysis Temperature on Chemical Class Composition of Oil Obtained from Straw Biomass Samples. Figures 4 and 5 show the dependence of the oil eluates on the pyrolysis temperature. Asphaltanes were obtained at a minimum amount under a pyrolysis temperature of 600 °C, which may be described as a moderate pyrolysis temperature. This fraction is 44.7% for WS and a higher rate for OS (59.1%). After reaching a minimum peak at about 600 °C, the asphaltane fraction started to show an inconsiderable increase under higher temperatures. For both biomass samples, *n*-pentane fraction reached its maximum level at moderate temperatures. After 600 °C, the decreasing trend was observed to be less than the increasing trend.

Toluene fractions reached their maximum level at high temperatures. Studies in the literature also demonstrate that aromatics have derived under high temperatures.[20,23] During the transition from low to high temperatures, aromatics experienced a significant increase from 8.4% to 46.7% and from 9.6% to 40.2%, for WS and OS, respectively. This increase occurring in the aromatic fraction due to rising temperature could be explained by the increase in the rate of PAHs. Pyrolysis vapors
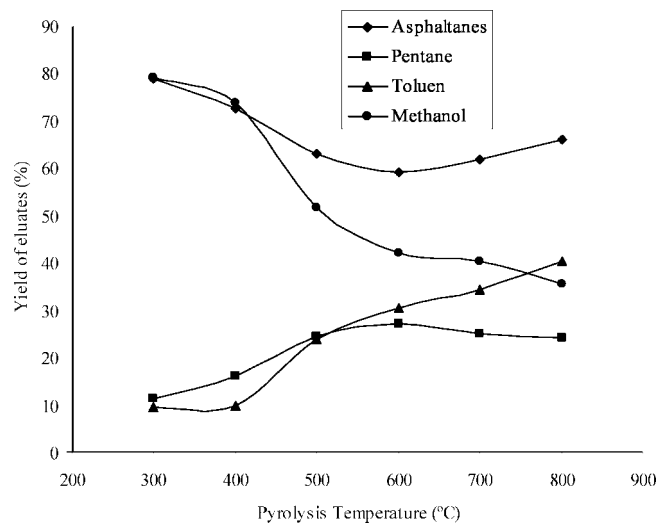
Figure 5. Dependence of the oil eluates of OS on the pyrolysis temperature.

forming due to increasing temperature stay longer in the atmosphere and, thus, the newly forming one-ring aromatic components can find enough time to form bonds among themselves and with other functional groups.

Bio-oil contains a large number of oxygenated organic compounds with a wide range of molecular weights. Polar fractions that are oxygenated compounds show just the opposite trend to that of aromatic fraction and due to the increase in temperature, oxygenated compounds were reduced. While at a pyrolysis temperature of 300 °C, the oxygenated compounds were 79.3% and 79.2%, the increase in temperature reduced them to 21.1% and 35.6% for WS and OS, respectively. This is a significant influence of heat on the pyrolysis mechanism; oxygenated compounds are a sign for fuel quality and the lower the amount of oxygenated compounds in the fuel, the higher the energy content of the fuel.

According to the column chromatographic results, it can be concluded that polar, aliphatic, and aromatic fractions were maximized in lower, moderate, and higher temperatures, respectively. In harmony with these results, Milne suggested that oxygenated components as carboxylic acids, aldehydes, ketones, furans, and phenol compounds are obtained with high yield under low temperatures, but aromatics, especially PAHs, are maximized under higher temperatures.[31] Under these conditions, reactions occurring in pyrolysis under high temperature speed up deoxygenation reactions, and oxygen breaks away from its attached oil compounds, converting to gaseous phase. These results obtained with column chromatography are consistent with the results of elemental analysis. Although, the subfraction yields obtained were different for each biomass, the trend was shown to be the same for both, and thus pyrolysis temperature was observed to be a more effective parameter than the type of biomass. Evans and Milne[21,32] showed the change in pyrolysis product distribution of biomass depends on only the temperature and time. Elliot[33] and Baker et al.[34] determined a relationship between the tar product composition and reaction temperature for biomass. Mixed oxygenates and phenolics were produced at lower and moderate temperatures, while PAHs were produced at higher temperatures. The previous studies mentioned above are supporting our results.

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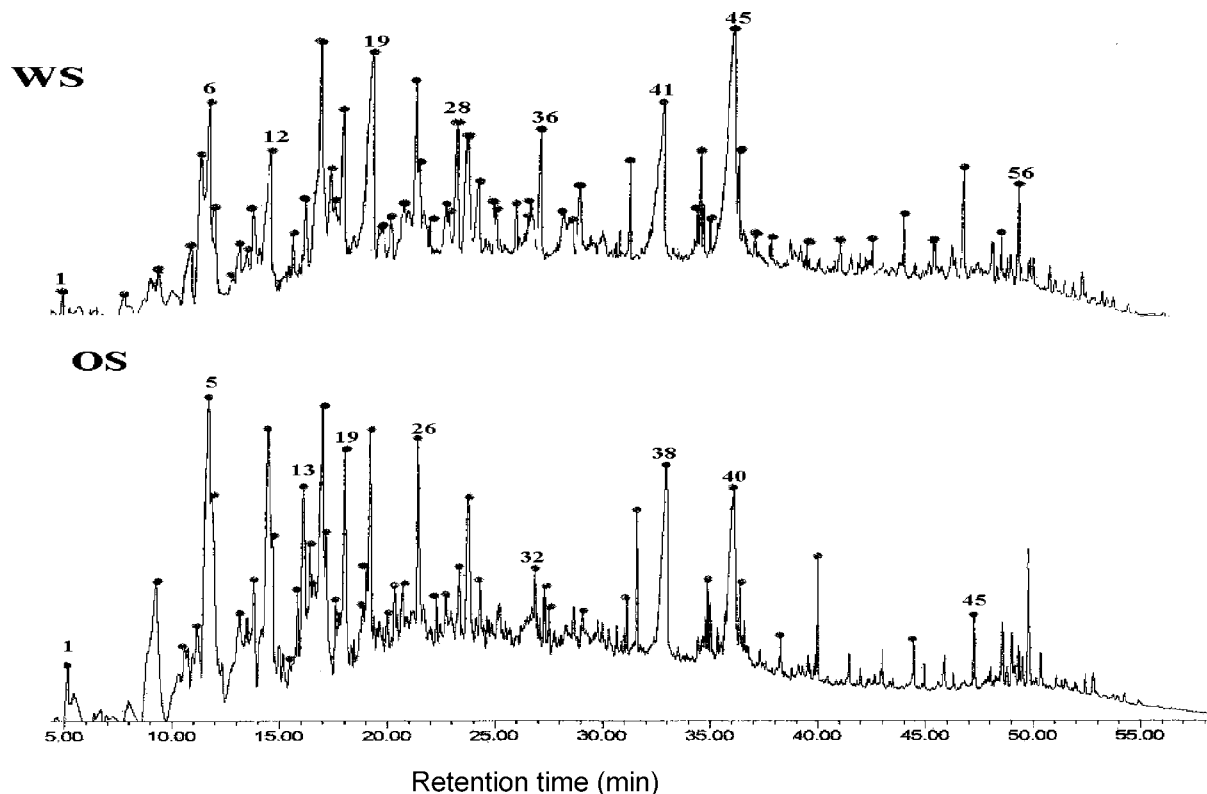
Figure 6. GC/MS chromatogram of the pyrolysis oils obtained at 500 °C.

Another preferable method for eliminating oxygenated compounds is catalytic pyrolysis. In most studies, catalyst was demonstrated to reduce oxygenated compounds at moderate temperatures. Furthermore, in a previous study using *Euphorbia rigida* and sesame stalk as biomass samples, it was observed that at moderate temperatures, the use of catalyst reduced oxygenated compounds in the sesame stalk oil as expected, whereas it increased these compounds in the oil product of *Euphorbia rigida*, which is known to be a terpenic compound.[29,35] In the studies, this phenomenon was attributed to the difference in biomass materials.

3.5. Determination of Detailed Component Analysis of Oil Obtained from Straw Biomass Samples by GC/MS. Although many analytical techniques are required to obtain a complete analysis of bio-oil, the most extendedly used analyzing method for pyrolysis oils is GC/MS. Owing to the complex structure of biomass, a related complexity is shown in the oil products derived through pyrolysis. However, it has been reported that bio-oils produced from different types of biomass samples under similar conditions have similar compositions.[36]

The GC/MS analysis of oils is given in Figure 6. Table 5 shows the detailed component analysis of the oils by GC/MS, including peak number, compound name, and peak area for both oils obtained from straw biomass samples. The distribution of

compounds in bio-oils was determining using a semiquantitative study by means of the percentage area of the chromatographic peaks.

The most important point at investigating the similarity of bio-oil as a fuel is the aliphatic compounds, i.e., alkanes and alkenes. A high resemblance was determined as a result of the comparison of the aliphatic subfractions of biomass samples with standard diesel in GC. It follows that the carbon range is $C_{14}-C_{31}$ for WS oil product, while it is $C_{14}-C_{32}$ for OS. The areas with intensive peaks were determined as to be $C_{24}H_{50}-C_{30}H_{62}$ and $C_{21}H_{44}-C_{27}H_{56}$ for WS and OS oil products, respectively.

As shown in Table 5, the most important compounds forming pyrolysis liquids are phenols. The same result was also confirmed with ^{1}H NMR results. Besides paraffins, phenols are valuable products, because they have high commercial value. They are present as monomeric units and oligomers derived from lignin. These compounds were determined as 44.5% for WS, and 58.1% for OS. The main phenolic compounds obtained from the oils are phenols, alkylphenols, methoxyphenols, and eugenols.

Biomass liquids are known to have an acidic structure. Also, carboxylic acids were determined in the oils obtained straw biomass samples and the total percentages of these acids were calculated as 18.9% and 12.7% for WS and OS, respectively. The main acidic compounds were ($C_{16}H_{32}O_2$) hexadecanoic acid (palmitic acid) with 16 carbon atoms, ($C_{18}H_{34}O_2$) 9-octadecenoic acid (oleic acid) with 18 carbon atoms, ($C_{18}H_{32}O_2$) 9,12-octadecadienoic acid (linoleic acid) with 18 carbon atoms, and ($C_{18}H_{36}O_2$) octadecanoic acid (stearic acid) with 18 carbon atoms. The presence of acids in pyrolysis oils is undesirable due to their corrosive effects; however, they could be used as chemical feedstock detaching from oil products. Methyl esters of these acids were also found in bio-oils.

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Table 5. Relative Proportions (area %) of the Main Pyrolysis Compounds in the Oils

peak number			area (%)	
WS	OS	compound	WS	OS
1	1	2-furanmethanol	0.24	0.50
2		furfuryl alcohol	0.27	
3	2	phenol	2.64	7.87
4	3	corylone	2.21	3.76
	4	phenol, 2-methyl-		3.48
5		phenol, 4-methoxy-	4.60	
6	5	phenol, 2-methoxy-	4.27	10.13
7	6	phenol, 4-methyl-	2.51	4.71
8	7	4*H*-pyran-4-one, 3-hydroxy-2-methyl	0.28	1.46
9		2-cyclopenten-1-one, 3-ethyl-2-hyd-	0.74	
10		phenol, 3,5-dimethyl-	0.25	
11	8	phenol, 2,4-dimethyl-	1.02	1.81
	9	phenol, 3-ethyl-		8.06
12	10	2-methoxy-4-methylphenol	3.69	1.00
	11	phenol, 2,3,5-trimethyl-		0.33
13	12	1,1,3,3-tetramethylindane	0.32	0.85
14	13	4-vinylphenol	1.61	4.09
	14	7-methoxy-3,6,9-trimethylnaphthone		1.75
	15	1,2-benzenediol		1.68
15	16	phenol, 4-ethyl-2-methoxy-	7.49	6.56
16		1,2- benzenediol, 3- methoxy-	1.91	
	17	naphthalene, 2-methyl-		2.18
	18	naphthalene, 1-methyl-		0.81
17		2,5- diethylphenol	1.08	
18	19	phenol, 4-vinyl-2- methoxy-	3.73	3.32
	20	5-chlorobenzofuran		0.81
	21	eugenol		1.05
19	22	phenol, 2,6,dimethoxy-	7.39	3.18
20		benzene, [(2-methylpropyl)thio]-	0.43	
21	23	naphthalene, 1,3-dimethyl-	0.58	0.49
	24	phenol, 2-methoxy-4-(2-propenyl)-		0.61
22	25	benzaldehyde, 4-hydroxy-3-methoxy-	2.84	0.56
23	26	*cis*-isoeugenol	2.44	1.92
24		2*H*-pyran-2,4(3*H*)-dione, 3-acetyl-6-	1.46	
25	27	pentadecane	0.34	0.28
	28	ethanone, 1-(4-hydroxy-3-methoxyph)-		0.52
26		stibine, trimethyl-	0.90	
27		naphthalene-1,6,7-trimethyl-	0.81	
28	29	2,3,5- trimethoxytoluene	2.25	0.85
29		benzenamine, 4- methoxy-*n*-methyl-	3.27	
30		4-methyl-2,5-dimethoxybenzaldehyde	1.38	
	30	2-propanone, 1-(4-hydroxy-3-methoxy)-		2.76
31		2-propenoic acid, 3,2-(methoxyphenyl)-	0.55	
32	31	3-crotyl-5-methyl-4-thiouracil	0.33	0.68
33	32	2-propenoic acid, 3-(4-hydroxy-3-m)-	0.42	0.56
34		heptadecane	0.36	
35	33	benzaldehyde, 4- hydroxy-3,5-dimethyl-	1.30	0.42
	34	*cis*-2-methyl-7-octadecene		0.32
36		phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.81	
37		benzaldehyde, 3,4,5- trimethoxy-	1.07	
38		2,4-dimethoxyallylbenzene	0.47	
39	35	1-butanone,1-(2,4,6-trihydroxy-3-)-	1.18	0.21
	36	hexadecanenitrile		0.35
40	37	hexadecanoic acid, methyl ester	0.69	0.91
41	38	hexadecanoic acid	6.12	5.71
42		9,12- octadecadienoic acid, methyl ester	0.40	
43	39	9-octadecenoic acid, methyl ester	1.26	0.77
44		9,12-octadecadienoic acid	0.29	
45	40	9-octadecenoic acid	11.21	5.46
46	41	octadecanoic acid	0.83	0.41
47		docosane	0.20	
48		tricosane	0.13	
49	42	tetracosane	0.15	0.18
50		pentacosane	0.32	
	43	hexanedioic acid, dioctyl ester		0.74
51		hexacosane	0.21	
52	44	heptacosane	0.41	0.43
53		octacosane	0.11	
	45	nonacosane		0.51
54		tetracosane, 9-octyl-	1.27	
55		corymine	0.63	
56		aplysteryl acetate	0.83	

Carbonyl groups are also oxygenated compounds. Since they affect the stability of the bio-oils, these compounds are supposed to be separated from bio-oil structure via appropriate separation techniques.

The components of the pyrolysis oil obtained were observed in other studies as well. Phenols, carboxylic acids, and carbonyls were determined as the main compounds forming liquid product, especially.[23,28,30,37–40]

The aromatic compounds forming the oil product could be examined under the categories of monoaromatics and PAHs. Among these compounds, PAHs are rather important compounds because the presence of PAHs in liquid products is described as hazardous for the environment, and it is known to have a mutagenic and carcinogenic effect on human health. Moreover, studies reveal that PAHs in oil product is at minimum levels at moderate temperatures, while at high temperatures, it reaches maximum levels.[21,37–39,41]

As shown in Table 5, oxygenated compounds are attached to benzene and toluene monoaromatic rings in the oil product. The PAHs which consist of methylindanes and methylnaphthalenes have a rather low percentage in the total oil product.

Furthermore, nitrogenous compounds are found in structure of liquid product. Some detected nitrogenous compounds are benzenamine, 4- methoxy-*N*-methyl-, corymine, and 3-crotyl-5-methyl-4-thiouracil.

4. Conclusion

In this work, pyrolysis of WS and OS biomass samples was performed in a fixed bed reactor at different final temperatures. Pyrolysis oils were thoroughly identified using different analysis procedures including elemental analysis, column chromatography, and gas chromatography/mass spectrometry. According to this procedure, the following was concluded:

1. Pyrolysis temperature was observed to be a more effective parameter than the type of biomass.

2. Pyrolysis temperature showed important effects on product yields. While maximum oil yields were obtained at moderate temperatures (500−600 °C), on increasing the pyrolysis temperature to 800 °C the oil yield was decreased and the gas yield was increased.

3. Pyrolysis temperature showed considerable effects on the characterization of oils. It was determined that the polar, aliphatic, and aromatic fractions were maximized at lower, moderate, and higher temperatures, respectively, using column chromatographic techniques. Also, it was fixed that the oxygenated compounds in oils were decreased at high temperatures, by using elemental analysis techniques.

4. The pyrolysis oils were found to be chemically highly heterogeneous and mainly contained phenols, carbonyl groups, and carboxylic acids and with a small percentages of aromatic compounds, esters, *n*-alkanes and alkenes, and nitrogenous

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compounds. It is obvious that if one wishes to obtain pure chemicals by biomass pyrolysis, some further processing for separating the mixture is necessary.

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