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Humulus lupulus As a Raw Material for Bio-oil Production via Slow Pyrolysis

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Abstract

Humulus lupulus, a kind of hop plant agricultural waste was pyrolysed in a fixed bed reactor with a heating rate of 10^0C min^{-1} in the presence of N_2 atmosphere. The effect of pyrolysis temperature was investigated at 450, 500, 550 and 600^OC. The characterization of solid product (char) and liquid product (bio-oil) was performed by spectroscopic and chromatographic techniques. Column chromatography, GC-MS, and FT-IR analyses were used for the characterization of bio-oil; whereas FT-IR and SEM were the techniques for char characterization. Experimental results showed that liquid products are available to evaluate as valuable chemicals and environmentally friendly synthetic fuels whereas solid products can be used as a low-cost adsorbent for wastewater treatments.

1. INTRODUCTION

Environmental concerns and the possible future crisis in energy production and sustainability create the importance of renewable and sustainable energy sources. Among them, biomass which is accepted as a form of renewable energy is seen as a source of helping to reduce global warming, by replacing the use of fossil fuels [1]. Biomass resources include many natural and some derived materials, such as wood wastes, bagasse, waste paper, municipal wastes, food processing wastes, animal wastes and many agricultural and industrial residues and etc. Obtaining energy from these kinds of sources can be achieved by two pathways; biological (fermentation and anaerobic digestion) or thermochemical (gasification, liquefaction, and pyrolysis) processes [2]. Among these thermochemical processes, pyrolysis is considered as the most promising and important technology for obtaining liquid and gaseous fuels and also solid char as valuable by-products [3]. This thermochemical process is the thermal degradation of biomass in the absence of an oxidizing agent such as air, causing the vaporization of the volatile components of the solid carbonaceous raw material in primary reactions by heating. The vaporized gas can be collected as liquid [4]. This liquid which is referred as bio-oil can be replaced by fuel oil or diesel in many applications including boilers, furnaces, engines and turbines. Moreover, some chemicals can be extracted or derived including flavorings, resins, agrichemicals and fertilizers. Upgrading bio-oil to transportation fuels is not economic in nowadays although technically feasible [5]. Although produced gas is considered as a by-product, it contains a significant amount of carbon dioxide along with methane might be used as a fuel for combustion purposes. Gases released from biomass have generally energy content of 3.5-5.0 MJ m^{-3}. These gases can be used for firing up the furnaces and also for producing electricity [6]. Solid product namely char, can be used as a fuel either directly or as char-oil or char-water slurries because of having high calorific value or as a feedstock to prepare activated carbons [7].

Obtaining alternative liquid fuels by decomposing of biomass samples at different pyrolysis conditions is the objective of most of the studies, those can be found in literature extensively. Considering the product yields and the compositions, it has been found that the most important parameters for the pyrolysis are pyrolysis temperature, reactor design, biomass type, heating rate and if used catalyst [8]. Different types of biomass such as corncob [9], corn stalk [10], safflower [11], soybean cake [12], cotton stalk [13], sesame stalk [14], olive residue [15], rice husk [16], tobacco residue [17], sugarcane bagasse [18], and hazelnut shell [19] were studied and reported in literature by several authors.

Containing a high amount of organic constituents and having high energy content agricultural wastes are the most important ones among the biomass wastes. This means that its conversion to a kind of renewable energy would be very attractive because of solving pollution problems, reducing greenhouse gases emissions and providing a clean fuel with very low sulfur content [20].

Humulus lupulus, mainly known as a hop plant, is a perennial viniferous plant that grows in excess of 6-7 m per growing season. It is one of essential components for the production of beer in Turkey and in the World. The production of hop in the World along with its use and consumption is gradually raising. Turkey is among the top ten producing countries. The annual total hop production of Turkey is 1650 tons and the amount of hop waste is about 3600 tons [21]. The harvested portion of the plant namely cone is commonly used in the brewing (flavonoids) and pharmaceutical industries. After harvesting the cone, leaf and stem materials are burned or landfilled as a means of disposal. On the other hand, leaf and stem material make up the wide majority of the biomass generated by hop (approximately 75%). Thus, some means of the alternative use of leaf and stem materials would be highly desirable and hopeful for obtaining synthetic fuels [22].

In this study, the pyrolytic behavior of *Humulus lupulus* was studied in a fixed bed reactor with a heating rate of 10^0C min^{-1} in the presence of N_2 atmosphere and the effect of pyrolysis temperature was investigated at 450^0C, 500^0C, 550^0C, and 600^0C. The objectives of this study are: (i) determine the effect of pyrolysis temperature on product yields, (ii) characterize liquid product obtained under optimum pyrolysis conditions to detect if it can be used instead of conventional fossil fuels or chemical feedstock, and (iii) characterize solid products, chars, for their possible use of solid fuels.

2. EXPERIMENTAL

2.1. Material

Biomass samples have been taken from Pazaryeri-Bilecik, located in the mid-west part of Turkey. Harvested *Humulus lupulus* was dried at room temperature, ground in a high-speed rotary cutting mill and stored in a cool and dark room. Average particle size of 1.25-0.60 mm was selected for the pyrolysis experiments. Proximate and ultimate analyses were performed to investigate the characteristics and elemental composition of raw material.

The ASTM Standard Test Method for Proximate Analysis of Wood Fuels (E 870-82) was used to determine the weight fractions of moisture, volatile, and ash contents. The fixed carbon was obtained by subtracting the percentages of volatile matter, moisture, and ash from 100%. The carbon, hydrogen and nitrogen contents of the samples were determined using LECO-CHN-628 elemental analyzer according to the ASTM Standard Test Methods for Determination of Carbon, Hydrogen, and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke (D 5373). The oxygen content was determined from the difference. The calorific value of biomass was calculated by using Dulong’s formula with the obtained elemental analysis results [23]. The component analysis was performed to determine the percentage distribution of cellulose, hemicellulose, and lignin structures in biomass.

2.2. Pyrolysis in thermogravimetric analyzer

The pyrolysis experiments were first carried out with a Thermogravimetric Analyzer (TGA) (SETARAM-Labsys evo) under an inert atmosphere to investigate thermal degradation profile of raw material during pyrolysis. The sample is suspended by a microbalance located above an electrically heated reactor. The temperature of the sample is measured by a thermocouple that is located near the sample. Al_2O_3 crucibles without lids were used in order to achieve the best possible heat transfer between the thermocouples and crucibles. 10.0±1.0 mg of sample was pyrolyzed under 100 cm^3min^{-1} N_2 flow at a heating rate of 10 °C min^{-1} from room temperature to 800 °C. This nitrogen flow rate ensures an inert atmosphere on the sample during the run, while the small amount of sample and the slow heating rate ensure the heat transfer limitations.

2.3. Pyrolysis in fixed-bed reactor

Pyrolysis experiments of *Humulus lupulus* were carried out at different temperatures in a fixed-bed Heinze retort at 450, 500, 550 and 600 °C under nitrogen (N_2) flow of 100 cm^3min^{-1} at a heating rate of 10 ºC/min. A schematic diagram of the unit is represented in Fig 1. The 316-stainless steel Heinze retort has a volume of 400 cm^3 (70 mm ID) and is externally heated by an electrical furnace in which the temperature is measured by a thermocouple inside the bed. The connecting pipe between the reactor and the trapping system was heated to 400 °C to avoid condensation of the bio-oil vapor. After reaching the final pyrolysis temperature the reactor was set to cool to room temperature. Pyrolysis product yields were determined gravimetrically by weighing the three products. The liquid phase was collected in cold traps maintained at about 0ºC using salty-ice. The traps and reactor were washed with dichloromethane solvent to obtain the liquid products. The liquid phase consisted of aqueous and oil phases which were separated and weighed. Char yields were determined from the overall losses of the reactor tube. The gas yield was calculated by the difference.

All the yields are calculated on a dry-ash-free (daf) basis and the average yields from at least three experiments are presented within the experimental measurement error less than ±0.5%.

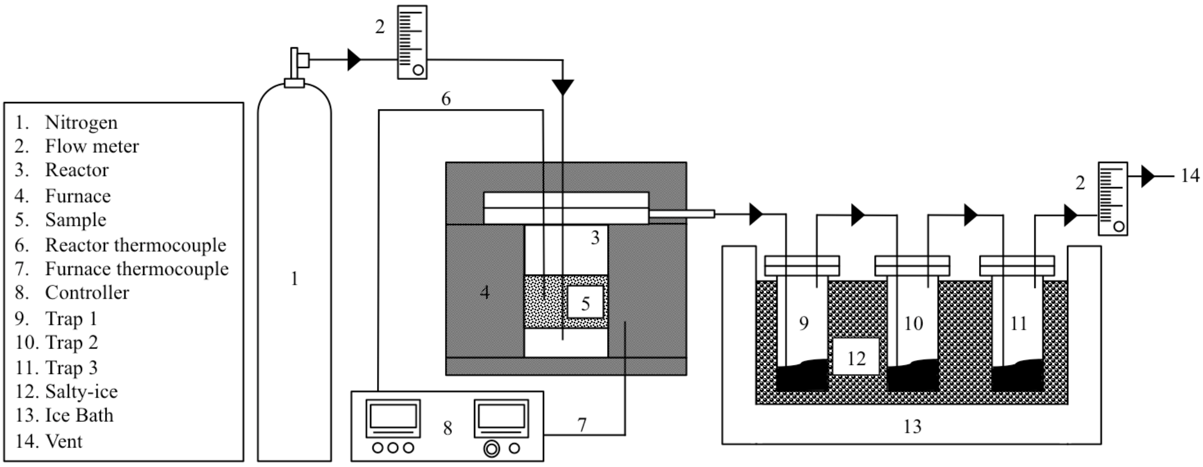

***Figure 1**. Schematic diagram of the fixed-bed reactor*

2.4 Characterization of products

Characterization studies for bio-oil and char were conducted according to the experimental conditions which gave the maximum bio-oil yield.

The chemical class compositions of the bio-oils were determined by liquid column chromatography technique. The oils were first separated into n-pentane soluble and insoluble compounds (asphaltenes), of which the n-pentane soluble compounds were further separated by adsorption chromatography. Glass column used was packed with silica gel 70-230 mesh, pre-treated at 600 ºC for 2 h prior to use. The column (1.4 cm i.d. × 100 cm long) was eluted successively with 150 mL n-pentane, 200 mL toluene and 200 mL methanol to produce aliphatic, aromatic, and polar sub-fractions, respectively. Each fraction was dried and weighed and then subjected to FT-IR and GC-MS analyses.

The FT-IR spectra of the products were recorded in the transmission mode between 4000 and 400 cm^{-1} using a Bruker Tensor 27 Fourier Transform Infrared Spectrometer. Dried KBr was used to prepare pellets from chars. Typically 10 mg of a sample at a concentration of 99% in KBr was used. Pure KBr disc was used as the background and for each sample, multiple spectra were recorded to obtain highest signal-to-noise ratio.

GC-MS analysis of liquid samples was performed using a Hewlett-Packard 6890 Model gas chromatograph coupled to an HP 5973 mass selective detector using a 30 m * 0.25 mm capillary column coated with a 0.25 mm thick film of 5% phenyl-methylpolysiloxane (HP-5). Helium with a purity of 99.999% was employed as a carrier gas at a constant flow rate of 1.2 ml min^{-1}. The initial oven temperature was 50 °C held for 5 min and then programmed from 50 to 280 °C at 5 °C min^{-1} with an isothermal held for 30 min. Splitless injection was applied at 280 °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 were used. Chromatographic peaks were then identified by means of WILEY 275 mass spectral data library.

The surface area of the chars was calculated from N_2 adsorption isotherms by BET (Brunauer-Emmett-Teller) method using Quantachrome Autosorb 1 analyzer. Before adsorption measurement, the samples were outgassed at 150 °C for 15 h. SEM images of raw materials and chars were recorded by using Zeiss EVO 50 Scanning Electron Microscope. Samples were mounted on an aluminum stub using carbon bands and coated with a thin layer of gold-palladium in an argon atmosphere using Agar Sputter Coater.

3. RESULTS AND DISCUSSION

3.1. Properties of biomass

The properties of *Humulus lupulus* are given in Table 1. As seen from the table raw material contains 9.00% moisture, 12.80% ash, 63.96% volatiles and 14.24% fixed carbon. Using elemental analysis results, the calorific value of biomass was calculated from Dulong's formula as 35.00 MJ kg^{-1} [23].

***Table 1**. Characteristics (wt. %) of Humulus lupulus (as received)*

Proximate analysis (%)		*Component analysis (%)*	
Moisture	9.00	Cellulose*	25.36
Ash	12.80	Hemicellulose	29.45
Volatiles	63.96	Lignin	23.74
Fixed C*	14.24	Extractive	8.65
Elemental analysis (%)			
C	55.42		
H	5.91		
N	0.66		
O*	38.01		
H/C	1.28		
O/C	0.51		
HHV (MJ/kg)	35.00		
Empirical formula	$CH_{1.28}N_{0.01}O_{0.51}$		

*by difference

3.2. Thermogravimetric analysis: Pyrolytic characteristics

Biomass pyrolysis can be divided into four individual stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition. It was also suggested that the pyrolysis of any biomass can be considered as the superposition of these three main components [24]. It is known from previous studies that thermal decomposition of hemicellulose and cellulose are considered to be the first and second stages occurring between the temperatures of 150-350 °C and 275-350 °C respectively, following the initial weight loss (30–150 °C) associated with the moisture evolution. However, lignin undergoes a gradual decomposition over a wide temperature interval (275–500 °C) [7, 25]. Figure 1 represents the weight loss curve of *Humulus lupulus*. This curve is a typical for the pyrolysis of lignocellulosic materials. It is seen from the figure that all moisture is lost until 150 °C, and then the thermal decomposition starts approximately at 220 °C, followed by the main devolatilisation depending on the degradation of biomass components occur up to 600 °C [26]. After this point, a slow further loss of weight loss occurs until 720 °C where the decomposition of *Humulus lupulus* is completed. It is obvious from dTG curve that maximum weight loss rate is 0.7 mg/min at around 325 °C. The undecomposed part of the raw material is about 27% which is higher than ash content (Table 1). This indicates that an incomplete decomposition occurs due to the presence of highly aromatic structure resulting from lignin [27]. According to the weight loss curve, the maximum temperature used in fixed-bed experiments is selected as 600 °C where nearly all pyrolysis reactions are completed.

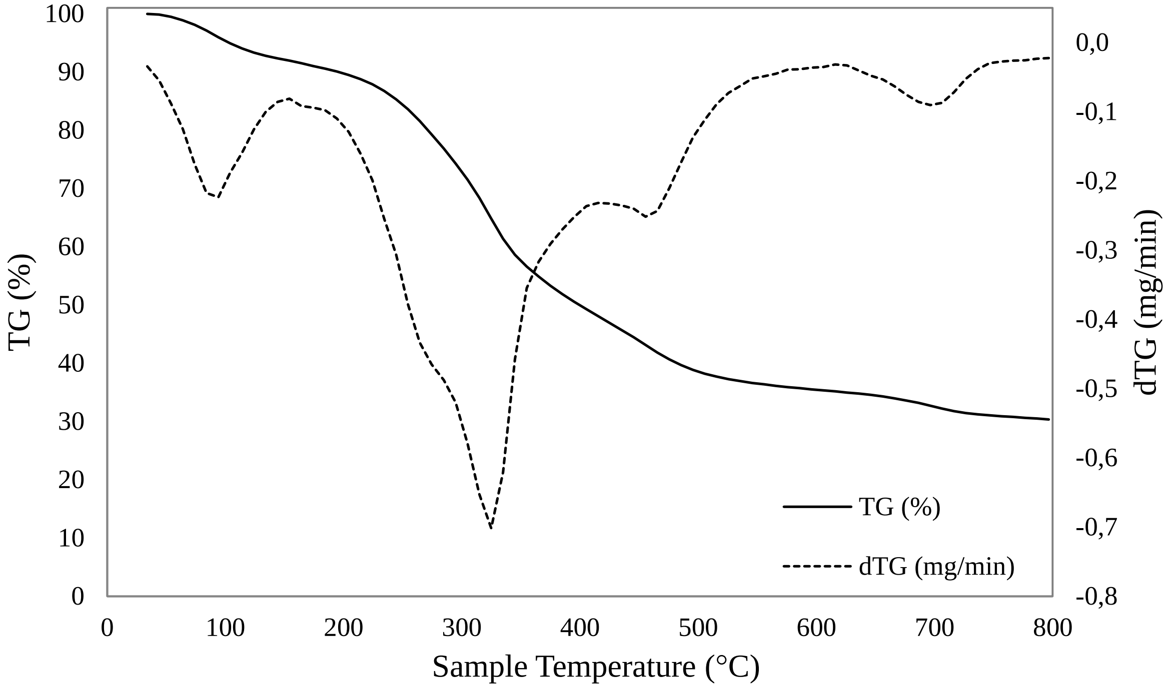

Figure 1. *Weight loss curves (TG and dTG) of Humulus lupulus*

3.3. Pyrolysis Yields

To investigate the effect of pyrolysis temperature on pyrolysis product yields, the experiments were conducted with a heating rate of 10°C min^{-1} in the presence of N_2 atmosphere at final temperatures of 450, 500, 550 and 600°C. Product yields are calculated on the dry-ash-free basis and they are given in Figure 2. Depending on the type of the feedstock; 20-40 wt. % liquid oil, 20-35 wt. % solid char, 30-40 wt. % of gaseous, and a small portion of water products are achieved typically as a result of slow pyrolysis [28]. Figure 2 showed a balanced distribution between the product yields. Approximately equal amounts of these products are obtained as well as water that is removed to improve the quality of bio-oil.

According to the literature, lower temperatures (<450°C) favor char production, while higher temperatures (>600°C) favor gas production [9]. As seen from the figure, increasing the pyrolysis temperature increased the gas yields while it decreased the solid yields (char). Char yield decreased with the increasing temperature from 26.5% to 17.8%. However, bio-oil yield shows a different trend. It is found to be 21.6, 23.3 and 26.0% at final temperatures of 450, 500, 550°C, respectively and decreased to a value of 22.9% when pyrolysis temperature is increased to 600°C. In most cases, an increase in temperature favored gasification of the tar that had been formed; hence at higher temperatures (>600 °C), a smaller quantity of liquid was obtained. It may be concluded that secondary reactions of the liquid fraction of volatiles and further decomposition of the char particles proceeded in the reactor with increasing temperature [6, 7]. Therefore, the maximum char yield obtained at 450 °C was 26.5%, while the minimum gas yield was obtained at the same temperature. The water content of bio-oil decreased as the temperature was increased from 450 to 600 °C. At a pyrolysis temperature of 550 °C, the liquid yield reached a maximum value of 26.0%. Further increases of the temperature up to 600 °C enhanced gas products only while minimizing char formation. For the slow pyrolysis of lignocellulosic materials, similar behavior for bio-oil yield is observed [11, 15].

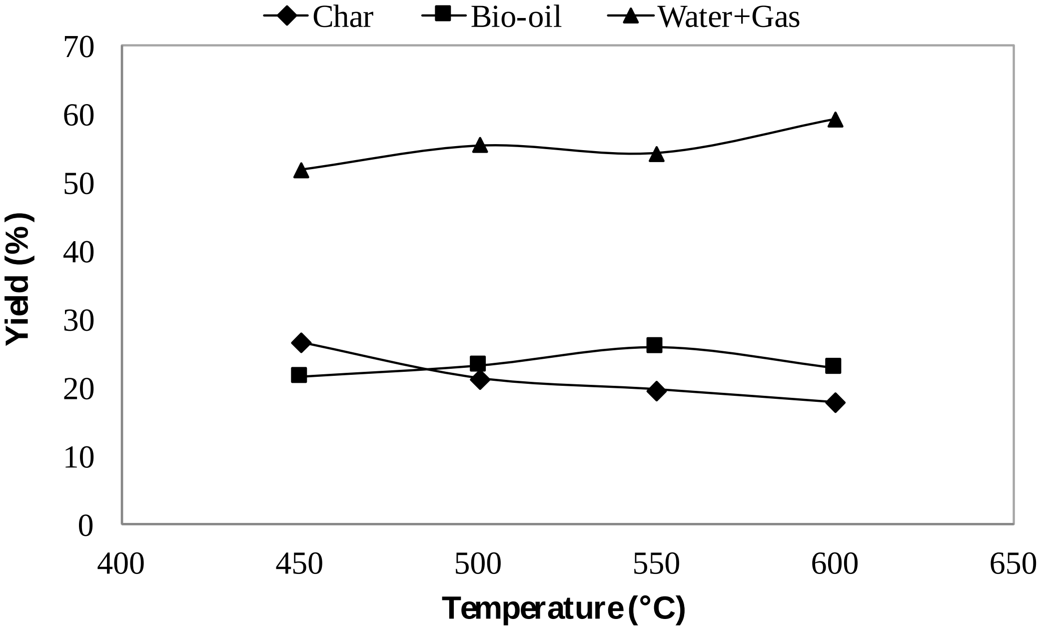

Figure 2. *Pyrolysis product yields at different temperatures*

Table 2 shows the comparison of bio-oil yield with the reported studies from literature. Bio-oil yields strongly depend on the type of the raw material and on the applied pyrolysis conditions. Moisture content, cellulose-lignin ratio, particle size, the presence of inorganics can be listed as the feedstock related effects, whereas pyrolysis temperature, heating rate, pyrolysis atmosphere and type, reactor geometry are the processes related effects [28]. It can be said that the bio-oil yield of *Humulus lupulus* is comparable with other raw materials and was found to be higher than some of the reported studies. For different biomass samples, the pyrolysis temperatures that have given the highest liquid product yield were determined to be the temperatures between 500 and 550 °C.

Table 2. *Comparison of bio-oil yield with various biomass materials*

Biomass	Pyrolysis temperature (ºC)	Reactor type	Heating rate (ºC/min)	Pyrolysis atmosphere	Bio-oil yield (wt.%)	Ref.
Pinewood	500	Conical spouted bed reactor	Fast pyrolysis	Nitrogen	75.0	[29]
Hardwood or softwood feedstocks	450	Tubular vacuum pyrolysis reactor	Slow pyrolysis	Nitrogen	50.0-55.0	[30]
Rice straw	550	Fixed-bed reactor	5	Steam	35.86	[31]
Apricot pulp	550	Fixed-bed reactor	5	Steam	27.7	[32]
Olive residue	500	Well-swept and high-speed heated fixed-bed reactor	500	Nitrogen	46.72	[33]

Euphorbia rigida	550	Fixed-bed reactor	7	Static	30.98	[34]
Saw dust	475	Fixed-bed reactor	10	Nitrogen	26.0	[35]
Safflower oil cake	500	Continuous fluidized bed reactor	10	Nitrogen	22.0	[36]
Corn stover	400	Pressurized batch reactor	Slow pyrolysis	Nitrogen	31.4	[37]
Humulus lupulus	550	Fixed-bed reactor	10	Nitrogen	26.0	This study

3.4. Characterization

Column chromatography of bio-oil

Pyrolytic oils are complex mixtures consisting of organic compounds from a wide variety of chemical groups. To characterize the pyrolytic oil, the oils were separated into four fractions; asphaltenes, aliphatics, aromatics and polars [6]. The results of the adsorption chromatography of the oil show that the pyrolysis oil consists of 59 % n-pentane soluble and the rest is asphaltenes. Bio-oil also contains 28.8 % aliphatic, 27.1 % aromatic, and 44.1 % polar subfractions. Moreover, the aliphatic and aromatic subfractions make up nearly 56.0 % indicating that the bio-oil is more appropriate for the production of hydrocarbons and chemicals.

FT-IR Spectroscopy

Functional groups of raw material, bio-oil and char are detected by FT-IR (Fig.3) and Table 2 lists the functional groups and their related compound classes of the oils. It is seen from Figure 3 that lignocellulosic raw material and bio-oil have similar spectra, meaning that both contain similar functional groups; whereas, char has a more plain and superficial spectrum. The main reason for this is the evolution of volatile components during pyrolysis that leads to form a carbon rich, porous, a large-surface-area solid product having only some basic functional groups.

Typically, broad band related with O–H stretching vibrations between 3200 and 3600 cm^{-1} indicate the presence of phenols, alcohols, and moisture in the raw material. The presence of alkanes is indicated by the absorbance peak of C–H stretching vibrations between 3000 and 2800 cm^{-1} and by the bending C–H vibrations between 1490 and 1325 cm^{-1}. The absorbance peak between 1775 and 1650 cm^{-1} shows the C=O stretching vibration indicating the presence of aldehydes, ketones, and carboxylic acids. C–O stretching and O–H bending vibrations between 1300 and 950 cm^{-1} are due to the presence of primary, secondary and tertiary alcohols and phenols.

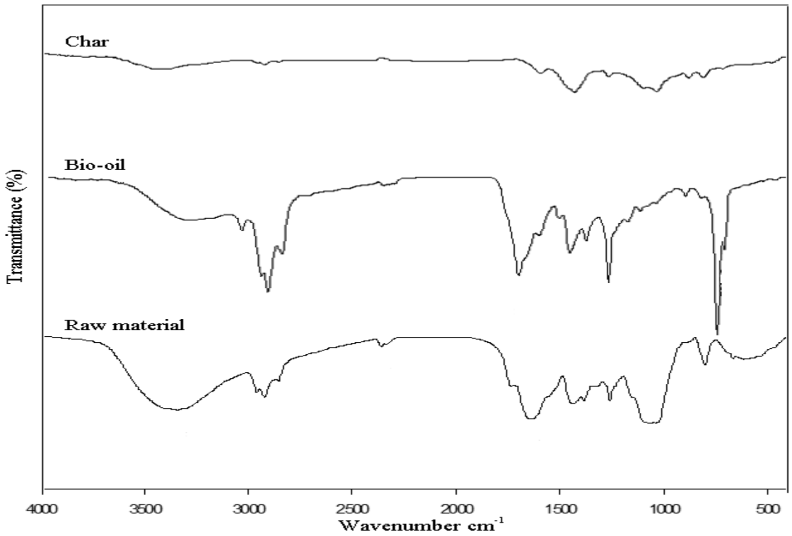

Figure 3. *FT-IR spectra of raw material, bio-oil, and char*

Table 2. *Functional group composition of raw material (Humulus lupulus), bio-oil and char*

Wave number (cm^{-1})	**Functional groups**	**Compound class**	**Raw material**	**Bio-oil**	**Char**
3600-3200	-OH stretching	Polymeric –OH, water content	3344	3316	3418
3100-3010	C-H stretching	Aromatic ring	-	3054	-
3000-2800	C-H stretching	Aliphatic	2972 28924 2852	2927 2857	2923 2855
1775-1650	C=O stretching	Ketones, aldehydes, carboxylic acids	1748	1706	-
1680-1575	C=C stretching	Alkenes	1643	1625	1590
1490-1325	C-H bending	Alkanes	1439	1458 1403	1424
1300-950	C-O stretching	Alcohols, phenols, esters	1261 1078	1267	1260 1028

GC-MS analysis of bio-oil

GC-MS results of the bio-oil obtained by the pyrolysis of *Humulus lupulus* is given in Table 3. As it can be seen, various chemical compounds can be obtained from the biomass sample. The main constituents of the bio-oil are phenolic compounds, straight chain and/or cyclic alkanes and alkenes, ketones and –oic acids. It is found that 25.81 % of all peaks are due to aromatics, 21.55 % for alkanes, 18.03 % for alkenes and the rest is for ketones anodic acids.

Table 3. *Tentative identification of Humulus lupulus bio-oil via GC-MS*

Compound	**Retention time (min)**	**Peak area (%)**
Phenol	9.14	3.50
Phenol, 2-methyl-	11.22	1.42
Phenol, 4-methyl-	11.86	3.99
Phenol, 2-methoxy-	12.16	2.38
Phenol, 2,4-dimethyl-	13.96	2.42
Phenol, 4-ethyl-	14.51	2.61
Naphthalene	14.83	1.14
Benzenepropanenitrile	16.52	1.62
7,7-dimethyl bicyclo[3.3.0]octan-2- one	17.57	1.57
Naphthalene, 1-methyl-	17.93	1.16
Tridecane	18.07	1.15
2-Decene, 7-methyl-	18.24	0.93
2-Methoxy-4-vinylphenol	18.52	1.08
1H-Indole, 3-methyl-	20.44	1.18
2-Tetradecene	20.49	1.66
Naphthalene, 1,3-dimethyl-	21.27	1.05
Octadecane	22.26	0.81
11-Methylsqualene	22.34	1.22
1-Pentadecene	22.98	1.35
Dodecane	23.18	1.16
Tetradecane	27.76	0.84
Cyclobutane, 1-butyl-2-ethyl-	28.43	3.20
Tetradecanoic acid	29.17	1.33
2-Hexadecene-1-ol, 3,7,11,15-tetramethyl-	30.60	11.44
2-Heptadecanone	31.97	4.39
Methyl palmitate	32.44	2.71
Oxacyclohexadecan-2-one	32.64	1.51
Hexadecanoic acid	33.27	8.28
9,12,15-Octadecatrienal	36.46	1.19
Dodecanamide	37.17	0.79
Tricosane	45.31	1.77
Nonadecane	46.72	0.83
2,6,10,14,18,22-Tetracosahexaene	47.16	1.49
Tetracosane	48.09	5.20
Eicosane	50.68	6.59

Surface properties of char

The solid product of pyrolysis, char, is a complex material consisting of mainly carbon, inorganics and volatile hydrocarbons. The most important differences between biomass and its related char are mainly porosity, surface area, pore structure (micropores, mesopores, and macropores). In any case, as a product or by-product, char is a valuable carbonaceous material due to its surface area, porous structure and adsorption capacity [38]. Among them, the surface area of char is important because, like other characteristics, it may strongly affect the reactivity and combustion behavior of the char [39]. The chars from static pyrolysis around 400°C has an omitted surface area. A high surface area of 190 m^2 g^{-1} was obtained with the char produced at 550°C. This value is typical for a char. It might be increased by applying activation steps before or after pyrolysis.

The SEM images of raw material and char obtained at 550°C are given in Figure 4. The difference of the surface morphology of the raw materials and char can be observed from the figure. It is seen that a thick wall structure of *Humulus lupulus* exists along with a little porosity at the raw material. The escape of evolved volatile compounds from inside the particle gradually increases, when the final temperature increases during the pyrolysis process. Therefore, the porosity of char and size of voids increase with increasing temperature. It is obvious that thick wall gets opened and a wider porosity is created, thus the external surface area of the char is full of cavities. Another way to increase microporosity is to apply chemical activation using impregnating chemical compounds such as H_3PO_4, KOH, $ZnCl_2$, K_2CO_3, H_2SO_4, etc. [40, 41]. Thus, the obtained char can be used as alternative activated carbon precursor for adsorption studies.

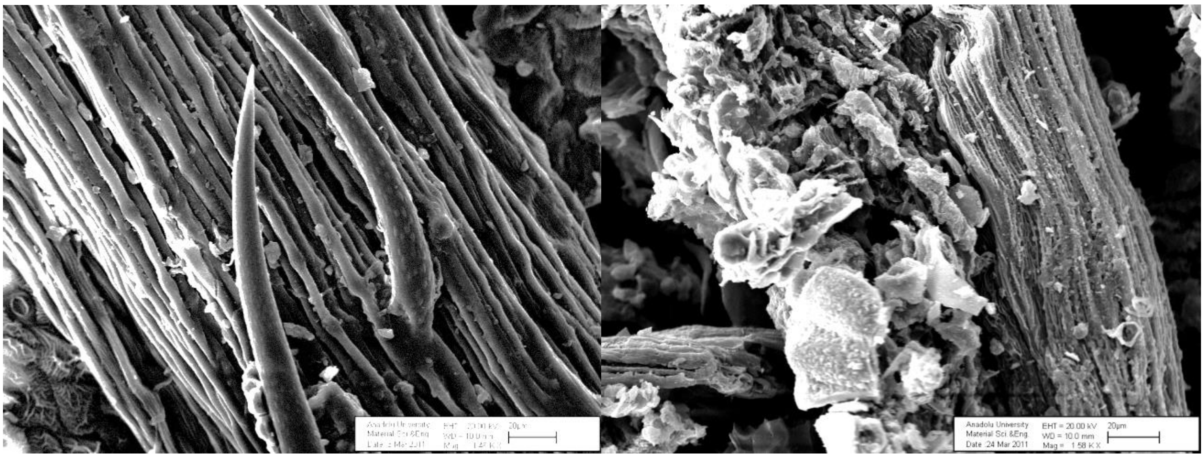

Figure 4. *SEM images of (a) Humulus lupulus, (b) char*

4. CONCLUSION

In the present study, the pyrolytic behavior of *Humulus lupulus* is studied in a fixed bed reactor with a heating rate of 10^0C min^{-1} in the presence of N_2 atmosphere. The effect of pyrolysis temperature is investigated at 450, 500, 550 and 600^0C. Product yields are calculated as approximately 26 % for bio-oil and 20 % for char at 550ºC which is the temperature where highest bio-oil yield is obtained. The characterization of solid product (char) and liquid product (bio-oil) was performed by spectroscopic and chromatographic techniques. GC-MS and FT-IR results for bio-oil seem to be consistent indicating that bio-oil mainly contains aromatics, aliphatics, and olefins. Char is characterized by surface area and it is found to be 190 m^2 g^{-1} which is relatively a low value when compared with the commercial activated carbons. Experimental results showed that liquid products are available to utilize as valuable chemicals and have the potential to be a substitute for synthetic fuels in an environmentally friendly manner whereas solid products can be further processed to produce activated carbons.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors

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