Production and Characterization of Bio-Chars and Bio-Oils Formed by Pyrolysis of Persian Hogweed (*Heracleum persicum Desf.*) in A Fixed-Bed Reactor

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Abstract: Pyrolysis of Persian Hogweed (*Heracleum persicum Desf.*) stalks were performed in a fixed-bed tubular reactor with (K_2CO_3 , $ZnCl_2$) and without catalyst at three different temperatures (400, 500 and 600 °C) with a constant heating rate of 50 °C/min. and with a constant sweeping gas (N_2) flow rate of 100 cm³/min. The amounts of bio-char, bio-oil and gas produced were calculated and the compositions of the obtained bio-oils were characterized by GC-MS. The effects of pyrolysis parameters such as temperature and catalyst on the product yields were investigated. According to the results, both temperature and catalyst had significant effects on the conversion of *Heracleum persicum Desf.* into bio-chars, bio-oils and gaseous products. The highest bio-oil yield of 41.42% by weight including aqeous phase was achieved with 10% potassium carbonate catalyst at 500 °C. 71 different compounds were identified by GC-MS in the bio-oils obtained at 500 °C.

Keywords: Energy, Biomass, Pyrolysis, Bio-oil, Persian Hogweed, Heracleum persicum Desf.

1. INTRODUCTION

The demand for energy is increasing at an exponential rate due to the exponential growth of world population. This, combined with the widespread depletion of fossil fuels and gradually emerging consciousness about environmental degradation, suggests that the energy supply in the future has to come from renewable sources of energy. Statistics show that total renewable energy now accounts for nearly 18% of global primary energy supply, but out of this traditional biomass only about 30% account for over 55% by large hydro. Solar, wind, modern biomass, geothermal, small hydro (below 10 MW), and ocean energy all together account for only 12% of total renewable energy. The new and renewable account for only 2% of world primary energy supplies. Biomass contributes to about 12% of today's world primary energy supply, while in many developing countries its contribution ranges from 40% to 50% [1]. Renewable energy consumption was 8% of the total US energy consumption in 1997. Hydropower and biomass continued to dominate the renewable energy market, most of the year-to year drop was due to a decrease in biomass energy consumption due to a warmer than expected heating season [2].

The use of biomass as a substitute for fossil fuels, rather than solely for carbon sequestration, will enable biomass to play much wider roles in coping with greenhouse warming. With an increasing proportion of the world's population residing in developing countries, fossil fuels are decreasing and the countries have to import them. It is essential that greater effort should be put into producing and using biomass efficiently as a widely available and flexible fuel source [3]. Annually, photosynthesis stores 5-8 times more energy in biomass than man currently consumes from all sources [4]. Yearly 150 GT (4431 EJ) energy is produced by photosynthesis. This energy is approximately 10 times greater than the world primary energy consumption. Biomass provides a potential source of added value chemicals, such as reducing sugars, furfural, ethanol and other products, by using biochemical or chemical and thermochemical processes [5].

Production of energy from biomass by conversion could be achieved by using two main processes which are thermochemical and biochemical. Biochemical processes are used to produce mainly bio-ethanol, biogas and hydrogen [6]. Thermochemical processes include gasification, combustion, and pyrolysis [7]. In the thermochemical processes, pyrolysis has received much more attention than other processes in recent years. The yields of pyrolysis products depend on mainly the composition of raw material, pyrolysis process type and pyrolysis parameters such as temperature, heating rate, catalyst, residence time and sweeping gas flow rate [8].

One of the methods used in pyrolysis to produce hydrocarbon fuels is catalytic pyrolysis in carboncarbon bonds in bio-oil compounds are ruptured in the presence of some shape selective catalysts. Decarboxylation, dehydration, and decarbonylation of compounds are the cracking reactions which produce

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aromatic hydrocarbons, carbon dioxide and water. Using catalyst in pyrolysis processes produces a better quality of bio-oil at atmospheric pressure without using hydrogen gas that makes it cheaper than hydrodeoxygenation process [9]. It has been reported in a limited number of micro-scale studies [10, 11] that high aromatic carbon (30–40 wt. %) yields have been achieved by direct catalytic pyrolysis of lignocellulosic biomass or its constituent units of cellulose, hemicellulose and lignin in recent years [12].

Biomass feedstocks, such as wood, agricultural and forest residues, energy plants, urban and solid industrial wastes, lumber and municipal wastes have attracted great attention as renewable energy sources in the worldwide. Turkey has high potential of agricultural renewable source with diverse crops production in 25 million hectares of arable land [13, 14]. Numerous types of plants grow in the lands of Turkey and they could be used as a source of biomass for production of clean energy or chemicals [15]. One of them, commonly named as "Persian Hogweed", is Heracleum persicum Desf. is a flowering plant in the family of Apiaceae, native to Persia or modern day Iran. The genus Heracleum with more than 120 species in the world is one of the largest genera of the Umbelliferae (Apiaceae) family. This genus is widely distributed in Asia [16] and is represented by eight species in the flora of Iran, three of which (Heracleum rechingeri, Heracleum gorganicum and Heracleum anisactis) are endemic to Iran [17]. The Persian name for the Heracleum persicum Desf. Ex Fischer is Golpar and is used as flavouring agent and spice for food in many parts of Iran. In some areas of the country, Golpar is used as a flavouring agent for making pickles. The fruits and leaves of this genus are also used as antiseptic, carminative, digestive and analgesic in the Iranian folk medicine [18-21]. However, there is no reported study of utilization of its stalks which have no value in terms of industrial or medicinal respect in the literature. Therefore, pyrolysis experiments with its stalks were carried out with (K₂CO₃, ZnCl₂) and without catalyts at three different temperatures (400, 500 and 600 °C) for the purpose of production of bio-oil or value-added chemicals.

2. MATERIALS AND METHODS

2.1. Materials

Heracleum persicum Desf. plants were collected in an agricultural zones in Aydın province of Turkey. They were harvested in June and the stems cleaned from leaves and tops and dried naturally in open air and then were ground, milled, and screen-sieved. Samples of different particle size ranging between 0.425 and 0.850 mm were used to in this study.

Ultimate and proximate analysis of the *Heracleum persicum Desf.* were performed. Ultimate analysis of the sample was carried out using an Elemental analyzer (LECO CHNS 932). The results of ultimate and proximate analysis of *Heracleum persicum Desf.* are given in Table **1**. Chemical composition of *Heracleum persicum Desf.* was determined using Tappi Test methods [22]. Lignin and cellulose were determined according to Tappi T222 and Tappi T202 method respectively. Hollocellulose content was determined using the chloride method. Ash and moisture contents were determined by Tappi T211 and Tappi T264 respectively.

Table 1:	Main	Characteristics	of	the	Heracleum
	persic				

Components				
Moisture (%)	5.6			
Proximate analysis ^a (%)				
Ash	2.7			
Lignin	24.7			
Cellulose	36.3			
Holocellulose	67.8			
Soxhelet extractives (40-60 °C petroleum ether)	0.7			
Ultimate analysis ^b (%)				
Carbon	44.16			
Hydrogen	5.86			
Nitrogen	6.45			
Oxygen ^c	43.53			
H/C molar ratio	1.59			
O/C molar ratio	0.74			
Empirical formula	$CH_{1.59}N_{0.12}O_{0.74}$			
Higher Heating Value (MJ/kg)	15.54			

^aWeight percentage on dry basis. ^bWeight percentage on dry and ash free basis. ^cBy difference.

2.2. Experimental Procedure

The pyrolysis experiments were performed in a fixed-bed reactor made of stainless steel with dimensions of 70 mm inner diameter, 10 mm outer diameter and 200 mm height equipped with connection for inert gas input. Fixed-bed tubular reactor system is given in Figure 1. In each trial, 20 g of raw material was

temperature is controlled by a NiCr–Ni thermocouple placed inside the bed. The liquid collecting bottles were cooled to -10 $^{\circ}$ C using frozen salt-ethanol and water mixture and the temperature kept constant as -10 $^{\circ}$ C until no more gas is evolved from pyrolysis process. The gas product was discharged into a chimney through a hose and a fan. During the whole pyrolysis process, nitrogen gas is circulated in the reactor with 100 cm³/min constant flowing rate to provide the inert atmosphere inside the reactor. By inputing the desired variables to the control unit in heater, pyrolysis experiments at different conditions have been performed.

The pyrolysis experiments were done in two series. In the first one, experiments without catalyst at three different temperatures (400, 500 and 600 °C) with a constant heating rate 50 °C/min. were carried out to investigate the effect of temperature. The condensed liquid products which contain an aqeous and oil phase were collected in bottles. They were washed with dichloromethane, put in a separating funnel and separated from each other by decantation. Bio-oil is dried with anhydrous sodium sulphate and recovered by evaporating the solvent in a rotary evaporator at temperature of 313 K and reduced pressure of 11 kPa and its yield was calculated. After cooling the pyrolysis reactor, the amount of bio-char left behind was

removed and weighed. The amount of gas evolved was calculated by subtraction of amount of bio-char and liquid product from 20, the amount initial raw material. In the second group of experiments, two different catalysts (K_2CO_3 , $ZnCl_2$) with 10% by weight were added to reactor and pyrolysis experiments at the same temperatures used in non-catalytic runs with a constant heating rate of 50 °C/min. were carried out to investigate the effect of catalyst on product yields. Upon completion of all experiments, the product yields were calculated and expressed on dry and ash free basis.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature and Catalyst on Product Yields

The conversion^a and distribution of products obtained by pyrolysis of at different temperatures with and without catalyst in Table **2**. The effects of temperature and catalysts on conversion and product yields are given in Figures **2-5**. The data given in the Figures **2-5**. were obtained from the experimental runs (Table **2**) at different temperatures ranging from 400 °C to 600 °C with heating rate of 50 °C/min. Figures **2** and **5** indicate that temperature has a positive effect on both conversion and gas yields at all temperatures. As for the bio-oil yields, temperature has increased the yields when temperature was increased from 400 °C until 500 °C, but then decreased slightly at 600 °C. As it is seen from Table **2**, when temperature is increased from 400 to 500 °C, liquid product yield was increased



Figure 1: Fixed-bed tubular reactor system.

Table 2:	The Conversion [®]	and Distribution	of Products	Obtained by	Pyrolysis of	Heracleum	persicum D	esf. at D	ifferent
	Temperatures								

Temperature (°C)	Conversion (%)	Bio-char (%)	Bio-oil (%)	Gas (%)
No catalyst				
400 °C	64.17	35.83	33.41	30.76
500 °C	70.62	29.38	37.26	33.36
600 °C	73.46	26.54	35.72	37.74
Potassium carbonate (10%)				
400 °C	69.53	30.47	36.91	32.62
500 °C	77.13	22.87	41.42	35.71
600 °C	79.21	20.79	39.28	39.93
Zinc chloride (10%)				
400 °C	67.96	32.04	24.86	43.10
500 °C	75.64	24.36	26.14	49.50
600 °C	77.37	22.63	25.63	51.74

^aMass fraction percentage of the dry and ash free feedstock.



Figure 2: Effect of temperature and catalyst on conversion.

from 33.41 % to 37.26 %, but decreased to 35.72 % at 600 $^{\circ}$ C in the non-catalytic runs.

According to literature, temperature is considered as the most important parameter on product yields in pyrolysis of biomass [23-25]. The amount of gasesous products were increased constantly with increasing pyrolysis temperature. When temperature was increased from 400 to 600 °C, the gaseous product yields were increased from 30.76 % to 37.74 % in the non-catalytic runs. The reason for decreasing of liquid product yields and increasing of gaseous product yields at higher temperatures is due to be the formation of secondary cracking reactions of the pyrolysis vapors. Besides, secondary decomposition of the biochars may produce non-condensable gaseous substances at higher temperatures which condributes an increase in gaseous products [26, 27]. Bio-char yields have decreased constantly with increasing the pyrolysis temperature. This is because of greater primary



Figure 3: Effect of temperature and catalyst on bio-char yields.



Figure 4: Effect of temperature and catalyst on bio-oil yields.

decomposition of the biomass or secondary decomposition of the char residue, leading the higher conversions with increasing temperature. As pyrolysis temperature increases from 400 to 600 °C, bio-char yields were decreased from 35.83 % to 26.54 % in the non-catalytic runs.

Pyrolysis experiments with catalysts were also carried out at a constant heating rate of 50 °C/min. at the same temperatures used in non-catalytic runs to determine the effect of catalysts ($ZnCl_2$ and K_2CO_3) on

the product yields. As seen from Figures **2-5**, catalysts effected the product yields differently. Both catalysts have increased the conversion with increasing temperature with non-catalytic runs. Potassium carbonate, on the other hand, was more effective than zinc chloride in terms of conversion. The highest conversion of 79.21% was achived with potassium carbonate in the catalytic runs at 600 °C. On the other hand, effects of catalysts on liquid product yields were very different from each other. In the experiments performed with zinc chloride, the liquid product yields



Figure 5: Effect of temperature and catalyst on gas yields.

were lower than in the non-catalytic runs at all temperatures. The liquid products yields were 24.86%, 26.14% and 25.63% at 400, 500 and 600 °C respectively. On the other hand, potassium carbonate, which had more positive effect on conversion than zinc chloride, the liquid product yields were higher than the ones obtained in the non-catalytic runs at all temperatures. The liquid product yield, which was 37.26% without catalyst, reached the maximum value of 41.42% with potassium carbonate at 500 °C. Both catalysts have increased thegaseous product yields in comparison with non-catalytic runs. For example, the gas product yield of 37.74% at 600 °C without catalvst has increased to 39.93% and 51.74% with 10% potassium carbonate and zinc chloride at the same temperature respectively.

In recent years, many studies have been conducted investigating the effect of catalysts on product yields of biomass samples. The using of a catalyst could make significant changes on the properties and yields of pyrolysis products. Using a catalyst had different effects on the liquid yields, which has increased the yields in some studies while in others, it had negative effect and decreased the liquid yields Similar results were obtained for bio-char and gaseous product yields which were either increased or decreased with catalysts. Nishimura *et al.* [28] has performed the cellulose pyrolysis with potassium carbonate (K_2CO_3) under relatively high heating rate to elucidate the role of alkali metals on wood pyrolysis. With the addition of potassium carbonate, an increase in gaseous yield and a decrease in tar yield and a significant decrease in the initiation temperature of pyrolysis were observed.

The liquid product obtained in pyrolysis contains an aqueous phase and bio-oil or oil phase which is generally named as pyrolytic liquid. It is a black liquid containing highly oxygenated compounds used as boiler fuel in power stations for heat production. If it is intended to be used as transportation fuels, they should be upgraded first by hydrodeoxygenation to produce aromatics or hydrocarbons, or catalytic cracking by using zeolite to produce aromatic light alkanes.

3.3. Characterization of Bio-Chars by Elemental and FT-IR Analysis

Some of the bio-chars obtained at optimum conditions (500 °C) were analyzed and characterized by elemental and FT-IR analysis. Elemental analyses were performed with LECO CHNS 932 Elemental Analyser and infrared analysis with a Perkin Elmer Spectrophotometer. The results of elemental analyses of four bio-chars are given in Table **3**. Tables **3** shows that bio-chars have higher carbon and lower oxygen contents than the original raw material and accordingly have higher heating values than the raw material. As seen Table **3**, the higher heating values of bio-chars are higher than 20 MJ/kg, in comparison with the low higher heating value (15.54 MJ/kg) of the raw material.

The FT-IR spectrums of the bio-chars obtained at 500 $^{\circ}$ C are given in Figure **6**. When they are compared

Table 3: Elemental Analyses of Bio-Chars Obtained at 500	٣(
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Components	Without catalyst	With ZnCl₂(10%)	With K ₂ CO ₃ (10%)
Carbon	62.781	63.827	66.821
Hydrogen	3.024	3.192	3.531
Nitrogen	0.754	0.824	0.984
Oxygen ^ª	33.441	32.157	28.664
H/C molar ratio	0.578	0.600	0.634
O/C molar ratio	0.399	0.377	0.321
Higher Heating Value (MJ/kg)	19.57	20.39	22.53

^aBy difference.



Figure 6: FT-IR spectrums of bio-chars obtained at 500 °C.

with raw material, there have been significant changes in the FT-IR spectrum as a result of pyrolysis. The O-H stretching vibration band at 3335 cm⁻¹ has been dissappeared for all bio-chars which shows that the oxygen was removed from raw material during pyrolysis which causes the phenolic and aromatic structures to crack producing carbonaceous solid products. The FT-IR spectrums of bio-chars are very similar to each others. The observed two weak intense bands at 2987 cm⁻¹ are assigned to aliphatic C-H stretching. The C-C stretching vibrations between 1350 and 1650 cm⁻¹ indicate the presence of aromatics and alkanes. The C-O stretching absorbance peaks observed between 1050 and 1350 cm⁻¹ indicate the



Figure 7: GC-MS spectrums of bio-oils obtained at 500 °C.

presence of primary, secondary and tertiary alcohols, phenols, ethers and esters. Besides, C-H out-of-plane bending vibrations observed between 700 and 900 cm⁻¹ shows the presence aromatic compounds. From FT-IR analyses, it can be conclude that bio-chars obtained by pyrolysis are mainly composed of aromatic and aliphatic compounds.

3.4. Characterization of Bio-Oils by GC-MS Analysis

The bio-oils obtained at optimum conditions (500 °C) were analyzed and characterized by GC-MS. The GC-MS analyses were performed at scientific and technological research center in Malatya Inonu

University on Agilent GC-MS 7890A/5975C series. The column (HP –INNOWAX, length: 60m., I.D.: 0,250 mm, film: 0,25 μ m and temperature limits: from 40°C to 260°C) and injector temperatures were the same as those for GC. Chemical constituents were identified by comparison of their retention indices with literature values [29] and their mass spectral data with those from the Wiley7n.1, ADAMS.1 and NIST05a.L mass spectral databases.

The GC-MS spectrums of the bio-oils obtained at 500 °C are given in Figure 7. The list of the compounds identified by GC-MS is given in Table 4. There are different types of compounds with different molecular

Numbor	Compounds	Relative abundance (% area)			
Number	Compounds	Without catalyst	ZnCl ₂	K ₂ CO ₃	
1	Hexane	1.86	1.00	-	
2	Pentane, 3-methyl	-	-	0.66	
3	Acetamidine Hydrochloride	-	-	45.52	
4	Methanamine, N-methyl-N-nitroso-	-	-	1.02	
5	Methylamine, N,N-dimethyl-	-	35.36	-	
6	2-Cyclopenten-1-one	-	-	0.80	
7	1-Hydroxy-2-butanone	-	-	0.75	
8	2-Cyclopenten-1-one, 2,3-dimethyl	-	1.48	0.70	
9	2-Cyclopenten-1-one, 3-methyl	-	-	1.06	
10	2-Methoxy-3-methyl pyrazine	-	0.27	-	
11	Trans-1-Nitro-1-propene	1.00	-	-	
12	Propanoic acid	-	-	1.12	
13	2-Methyl-2-cyclopenten-1-ol	2.06	-	-	
14	Propanenitrile, 3-(ethylamino)-	1.78	-	-	
15	Acetic acid	2.79	-	5.51	
16	Furfural	-	-	1.58	
17	Furan, 2-acetyl-	-	-	1.58	
18	1-Penten-3-ol, 2-methyl-	-	-	0.72	
19	2 (3H)-Furanone	1.64	-	0.68	
20	2 (3H)-Furanone, dihydro-	0.98	-	0.91	
21	2-Furancarboxaldehyde, 5-methyl-	-	-	0.61	
22	2-Furanmethanol -		-	2.79	
23	2 (5H)-Furanone 0.79		-	-	
24	Pyrazine, 1,4-dioxide 1.08		-	-	
25	Diethylketene -		-	0.52	
26	Guaicol <ortho></ortho>	2.17	-	3.99	
27	Cresol <2-methoxy para>	-	-	0.53	
28	Cresol <meta/>	3.48	3.84	1.70	
29	Phenol 5.19 1.26		1.26	2.22	
30	Phenol, 5-methyl-2-(1-methylethyl)-	-	1.67	-	
31	1,2-Cyclopentanedione, 3-methyl-	-	-	1.27	
32	1H-Inden-1-one, 2,3-dihydro-	1.12	-	0.67	
33	Phenol, 2-ethyl-4-methyl-	-	2.76	-	
34	Benzeneethanol, 2-methoxy-	-	-	0.34	
35	Phenol, 2-ethyl-5-methyl-	-	0.75	-	
36	Phenol, 2-ethyl-6-methyl-	-	1.77	-	
37	Phenol, 2-ethyl-	0.69	1.46	-	
38	Anisole <para-methyl-></para-methyl->	1.00	-	-	
39	Phenol, 2,4-dimethyl-	1.12	1.93	-	
40	Phenol, 3,4-dimethyl-	-	4.86	0.48	

Table 4: Main Chemical Compounds Present in the Bio-Oils Obtained at 500 °C

Number		Relative abundance (% area)			
Numper	Compounds	Without catalyst	ZnCl ₂	K ₂ CO ₃	
41	Phenol, 2,5-dimethyl-	-	2.81	0.44	
42	Cresol <para></para>	2.57	4.00	2.54	
43	Phenol, 3-ethyl-	1.98	1.36	0.95	
44	Phenol, 3-ethyl-5-methyl-	-	2.82	-	
45	Phenol, 2-ethyl-	3.82	-	1.55	
46	Phenol, 3,4-diethyl-	-	1.01	-	
47	Phenol, 2,6-dimethoxy-	11.85	-	6.97	
48	1,2,3-Trimethoxybenzene	-	0.72	-	
49	1,4-Benzodioxin, 2,3-dihydro-	4.07	-	-	
50	Benzene, 1-ethyl-4-methoxy-	-	3.31	-	
51	Phenol, 2,6-dimethyl-	0.97	1.80	-	
52	Phenol, 2,3-dimethyl-	1.17	6.80	-	
53	Phenol, 2,4,6-trimethyl-	-	1.03	-	
54	2-Methoxy-4-vinylphenol	-	-	1.27	
55	Phenol, 2-methoxy-4-(2-propenyl)-	-	-	1.35	
56	1,4:3,6-Dianhydroalphaglucopyranose	-	-	0.68	
57	Phenol, 2,4,5-trimethyl-	-	5.53	-	
58	Phenol, 2,3,5-trimethyl-	-	5.86	-	
59	Phenol, 3,4,5-trimethyl-	-	1.15	-	
60	3-Pentanone, 2,2-dimethyl-	4.46	-	3.41	
61	Phenol, 2-(1,1-dimethylethyl)-	-	1.43	-	
62	2-Hepten-4-ol	1.51	-	-	
63	Benzeneamine, 2-methoxy-5-nitro-	1.39	-	-	
64	2-acetyl-3-methy-imidazo [2,1-b] thiazol	-	-	0.77	
65	2-Pentenoic acid, 2-methyl-	1.37	-	-	
66	1,2-Benzenedicarboxylic acid, diisooctyl ester	22.01	-	-	
67	trans-Benzene dioxide	-	-	2.25	
68	Phthalic anhydride	12.61	-	-	
69	Cinnamic acid, 3-hydroxy-4-methoxy-	-	-	1.13	
70	Methanamine, N,N-dimethyl-	1.48	-	-	
71	5-isopropyl-2-methyl phenol	-	1.15	-	

(Tahle	4)	Continued

structures and molecular weights in the bio-oils produced by the thermal degradation of hemicellulose, cellulose and lignin found in the raw material.

The compounds identified by GC-MS are consist of complex mixtures of organic compounds including furans, ketones, alcohols, carboxylic acids, benzene derivatives, alkenes, amines and amides. Furans and its derivatives are obviously formed from decompositon of cellulose while acetic acid is formed from the decomposition of hemicelluloses. Many of the compounds identified in bio-oils are phenolics and its derivatives which are formed by degredation of lignin in the raw material. They consist of phenols, methoxy phenols and alkyl phenols. The most abundant compounds produced from decomposition of lignin in the bio-oils are 2,6-dimethoxy-phenol, cresol and guaicol. As bio-oils obtained by pyrolysis can be used not only as a fuel in engines or boilers, but also as a valuable organic chemicals, phenols could be considered as one of them for its commercial value.

4. CONCLUSION

In this study, pyrolysis of *Heracleum persicum Desf.* was carried out to obtain solid (bio-char) and liquid (bio-oil) products at three different temperatures ranging from 400 to 600 °C with and without catalyst. It was found that the optimum condition for bio-oil formation is at 500 °C both in catalytic and non-catalytic runs. The effects of different catalysts on degradation of *Heracleum persicum Desf.* were also investigated and potassium carbonate was found to be more effective than zinc chloride in terms of bio-oil formation. The compositions of the bio-chars and bio-oils were characterized by elemental, FT-IR and GC-MS analysis. From the results, it is concluded that *Heracleum persicum Desf.* could be used to produce bio-chars and bio-oils with higher heating values or valuable chemicals by pyrolysis process.

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