Production of Bio-oil *via* Catalytic Pyrolysis of Medlar Seeds

Fatıma Topak, and Mehmet Kuddusi Akalin *

The pyrolysis of medlar seeds was performed at 350, 450, 550, and 650 °C with and without K_2CO_3, MgO, and expanded perlite (10 wt%). The maximum dichloromethane extract yield (6.70 wt%) was obtained at 450 °C in the pyrolysis experiments without catalyst, while the maximum bio-oil yield (50.3 wt%) was obtained at 650 °C in the presence of perlite. The dichloromethane extract and bio-oil yields decreased noticeably with the use of MgO and K_2CO_3. The bio-oils obtained from the non-catalytic runs mainly consisted of phenolic compounds. The use of catalysts had a noticeable effect on the composition and higher heating values of the bio-oils. The use of K_2CO_3 increased the relative content of 2-methoxyphenol at all tested temperatures and the relative content of 2,6-dimethoxyphenol and 2,6-dimethoxy-4-methylphenol increased with the use of expanded perlite at above 550 °C, while the use of MgO led to an increase in the relative content of 2,6-dimethoxy-4-methylphenol at above 550 °C. The bio-oil with the maximum higher heating value (30.4 MJ/kg) was obtained at 450 °C with the use of perlite. This study showed that medlar seeds are a good alternative source of waste biomass in the production of bio-oil that can be used as a biofuel.

*Contact information: Department of Environmental Engineering, Karabuk University, 78050, Karabuk, Turkey; *Corresponding author: mehmetakalin@karabuk.edu.tr*

INTRODUCTION

Biomass is one of the promising renewable resources to obtain products that can replace fossil fuels products. In addition to being renewable, biomass is an abundant and environmentally friendly resource because of its carbon neutrality when compared to fossil fuels. The use of fossil fuels causes a significant increase in emission of carbon dioxide and other pollutants such as NOx and SOx. Further, non-renewability and depletion of fossil resources cause fluctuations in fossil fuel prices, posing major economic problems in the world (Hu and Golizadeh 2019). Because of its abundancy, renewability, and the diversity of products that can be used in various applications, biomass has a great potential to be an alternative to fossil resources (Guedes *et al.* 2018).

Thermochemical conversion is one of the important and efficient ways to utilize biomass, in which pyrolysis occupies an important place among thermochemical conversion methods. Pyrolysis is a widely used thermal process to transform biomass under an inert atmosphere into value added solid, liquid, and gas products (Tan *et al.* 2022; Vuppaladadiyam *et al.* 2022). Yields of products (liquid, solid, and gas) vary depending on the process parameters such as pyrolysis temperature, residence time, heating rate, biomass type, *etc.*, in pyrolysis. Feedstock composition, which is related to the biomass

type, is an important factor that affects yields and characteristics of products as well as determining the experimental conditions for desired products and their subsequent applications (Chen *et al.* 2020; Al-Rumaihi *et al.* 2022). Therefore, a wide variety of biomass including agricultural residues (*e.g.*, peanut shell, hazelnut shell, or wheat straw) and forestry residues (*i.e.*, wood residues), which are considered as waste, have been used in the pyrolysis process (Al-Rumaihi *et al.* 2022). The most abundant form of biomass is lignocellulosic biomass, primarily consisting of hemicellulose, cellulose, and lignin, which can be converted into biofuels and value-added products *via* pyrolysis (Zhou *et al.* 2022). The hemicellulose and cellulose content of biomass mainly contributes to the formation of bio-oil, which is also known as pyrolysis oil, pyrolysis liquid, tar, and bio-crude. The pyrolysis oil is mixture of various types of compounds, and it has a high oxygen content which leads to a low heating value in comparison to coal. The pyrolysis oil can be used as a fuel in furnaces, boilers, diesel engines, and turbines with minor modifications to existing equipment, or it can be used in the production of chemicals and phenolic resins; furthermore, it can be upgraded to enhance its fuel properties by using various catalysts (Kim 2015; Krutof and Hawboldt 2016; Pawar *et al.* 2020). The char (also known as biochar, solid product, or charcoal) formation is mainly promoted by lignin decomposition. The char mainly consists of carbon, and it can be used as an adsorbent, fertilizer, or catalyst. The bio-oil is a dark brown liquid, and it contains a considerable amount of water depending on the moisture content of the biomass. Despite its undesirable properties, such as high oxygen content, low pH value, high corrosiveness, and high viscosity, bio-oil can be considered as a potential fuel for turbines, diesel engines, boilers, furnaces, and combustors in short term. It also has potential to be a chemical feedstock for resin manufacturing, fertilizer, pharmaceutical, and the food industry (Kan *et al.* 2016; Makepa *et al.* 2022; Liu *et al.* 2023).

The medlar fruit (*Mespilus germanica* L.) is a member of the Rosaceae family. It is shaped like a pear and apple with brown (sometimes reddish tinged) color in various sizes ranging from 1.5 to 3 cm. The weight of the fruit is around 10 to 80 g, and it generally contains five large seeds with diameters around 1 to 1.25 cm. The plant can grow wild in different regions of the Middle East, and it is also cultivated for jam, marmalade, and jellies production in the food industry (Solgi *et al.* 2017). It is a widely consumed fruit in Turkey, and it is also used in many local recipes such as in jams and jellies. In addition, it can be used for medicinal purposes. It was reported that medlar has the ability to act as a diuretic, and blatted pulp or syrup of the medlar fruit can be used for treatment of kidney and bladder stones (Ayaz *et al.* 2008; Gruz *et al.* 2011). Therefore, high amounts of seeds are produced as waste every year, serving various usage areas. Activated carbon was produced from medlar seeds *via* chemical activation with KOH (mass of seed/mass of KOH, 1:3) at 450 to 750 °C for chromium removal (Solgi *et al.* 2017). Experimental analysis and modeling of chromium removal were investigated using artificial neural network and support vector regression. It was reported that maximum adsorption capacity was achieved with the use of activated carbon produced at 750 °C, and it could be considered as a good alternative for removal of Cr(VI) from wastewaters. Pyrolysis of different biomass (including plum seed, pine seed, and date seed) waste was performed at 400 to 600 °C for liquid oil production (Islam *et al.* 2013). The effect of temperature, particle size, and time on the yields and composition of products from biomass wastes was investigated.

The optimum operating temperatures were 500, 500, and 520 °C with a running time of 120 min for pine seed (liquid product yield 40%), date seed (liquid product yield 50%), and plum seed (liquid product yield 39%), respectively. The higher heating values of all liquid products were higher than the corresponding raw biomass waste. The higher heating values of bio-oils obtained from the pyrolysis of pine seed, date seed, and plum seed were reported as 20.00, 28.64, and 22.39 MJ/kg, respectively.

Perlite is a naturally occurring alumino-silicate amorphous volcanic rock. Raw perlite contains combined water (2 to 6 wt%), whereas expanded perlite is produced from raw perlite by rapid heating at high temperatures (900 to 1200 °C). In this process, water that is held in the structure of perlite vaporizes rapidly. As a consequence, perlite expands up to 5 to 20 times of its original volume, resulting in hollow and porous particles with a low bulk density. Expanded perlite is a lightweight and porous material that has insulating properties. Thus, expanded perlite is a commonly used material in construction, petrochemical, and chemical industries (Rashad 2016; Różycka and Pichór 2016; Papa *et al.* 2018). Turkey, Greece, USA, China, Japan, Hungary, and Italy are the countries that have a large share in world's total perlite production (Rashad 2016; Różycka and Pichór 2016). Perlite was also used in the pyrolysis process in the literature. Balat and Balat (2010) used perlite (2.5 to 10 wt%) in the pyrolysis of black locust wood. It was reported that liquid product yield increased with increasing the perlite ratio from 2.5 to 10 wt% between 5 to 15 min reaction times (Balat and Balat 2010). Pyrolysis of car tire waste was carried out using different ratios (0.05 to 0.25) of expanded perlite as a catalyst at 425 °C with 10 °C/min heating rate (Kar 2011). It was reported that maximum pyrolytic oil yield (65.11 wt%) was obtained with the use of perlite at a ratio of 0.10. The yield increase achieved by using expanded perlite was 8.48 wt% when compared to the non-catalytic pyrolysis experiments. A further increase in perlite ratio up to 0.25 resulted in a decrease in pyrolytic oil yield. In another study, using perlite (9 wt%) in the catalytic pyrolysis of hazelnut shell at 500 °C increased the liquid yield from 41% to 46% while using higher amount of perlite (18 wt%) resulted in a slight decrease in the liquid yield (40%) (Aydinli and Caglar 2012). It was reported that this may be due to the high adsorption capacity of perlite. Catalytic pyrolysis of *Styrax officinalis* L. seeds were carried out at 450 °C with a heating rate of 25 °C/min in the presence of natural zeolite and expanded perlite (Kar and Sen 2012). The authors reported that the bio-oil yields were lower in the catalytic pyrolysis experiments than the bio-oil yields that were obtained from the non-catalytic experiments in their previous study. They also reported that increasing the amount of perlite from 10 wt% to 30 wt% led to an increase in bio-oil yield from 35.23% to 37.49%.

To the best of the authors' knowledge, there has been no study regarding the bio-oil production from the medlar seeds *via* pyrolysis in the literature so far. The main objective of the study is to produce bio-oil from medlar seeds and investigate the effect of pyrolysis temperature on the yields of bio-oil and biochar. The effect of the temperature on composition of the bio-oils was also investigated. In the second part of the study, the effect of the temperature on the yields and composition of bio-oils in the presence of natural expanded perlite, MgO, and K_2CO_3 was investigated.

bioresources.com

EXPERIMENTAL

Feedstock

The medlar fruits were purchased from a local market in Karabük. The seeds were separated from the fruits and washed several times. The seeds were air-dried for 2 days at room temperature, ground, and sieved to achieve a homogeneous mixture with a particle size of less than or equal to 1 mm. Then the ground seeds were air-dried for 2 days at room temperature again. The proximate and ultimate analysis of the medlar seeds were shown in Table 1.

Table 1. Proximate and Ultimate Analysis of the Medlar Seeds

Proximate Analysis (wt%)		Ultimate Analysis (%)	
Moisture	6.34	C	43.210
Volatile matter	81.78	H	6.634
Fixed carbon	10.90	N	0.514
Ash	0.98	O[a]	49.64
		HHV[b] (MJ/kg)	15.22
[a] by difference			
[b] by Dulong formula: HHV = 0.338C + 1.428(H - O/8) + 0.095S			

Pyrolysis Experiments

The pyrolysis experiments were performed at 350, 450, 550, and 650 °C in a 250-mL stainless steel fixed bed reactor under nitrogen atmosphere. In a typical pyrolysis experiment, 10 g of medlar seeds (dry basis) were placed in the reactor. Before heating the reactor to the set temperature, the nitrogen gas passed through the system for 30 min, and nitrogen gas continued to pass through the system throughout the entire pyrolysis process. Then, the reactor was heated (10 °C/min) to the set temperature. After the reactor reached the set temperature, the system was held at that temperature for 1 h. There have been some studies regarding the pyrolysis of biomass at long holding time (30 min<) (Abnisa *et al.* 2011; Güngör *et al.* 2012; Fan *et al.* 2014; Ling *et al.* 2015); thus the justification for selecting a pyrolysis holding time of 1 h was to ensure entire pyrolysis vapors flowed to the collection flasks. The pyrolysis vapors were passed through the collection flasks by nitrogen gas flow, and they were collected in the collection flasks that were cooled with an ice-water mixture. Liquid product, which includes water, was collected in the collection flasks and it was labeled as "bio-oil". The bio-oil was subjected to extraction with dichloromethane (20 mL), and after evaporating dichloromethane from the organic phase, the resulting product was labeled as dichloromethane extract. The same procedure was used in the catalytic experiments with the addition of catalyst (10 wt% of the biomass) into the reactor. All experiments were repeated three times. No investigation regarding the yield and composition of the gas product was performed in this study.

Analysis Procedure

The compounds in the bio-oils were determined by gas chromatography-mass spectrometry analysis (GC-MS). The analysis was performed using an Agilent GC-MSD-7890B+5977MSD with HP5-MS column (Agilent Technologies, Santa Clara, CA, USA). The temperature program for the GC oven was as follows: started at 40 °C and held at that temperature for 1 min, raised to 250 °C with 5 °C/min, and held for 15 min; finally raised

to 270 °C with a heating rate of 5 °C/min and held for 20 min. The elemental composition of the bio-oils and the raw material was determined by using a LECO CHNS 932 (LECO Corporation, St. Joseph, MI, USA).

RESULTS AND DISCUSSION

Effect of the Pyrolysis Temperature on Product Yields

Bio-oil, dichloromethane extract, and biochar yields that were obtained from the pyrolysis of medlar seeds at different temperatures (350 °C, 450 °C, 550 °C, and 650 °C) at a heating rate of 10 °C/min are shown in Fig. 1. The pyrolysis temperature had a noticeable effect on the product yields. The highest bio-oil yield (49.9 wt%) was obtained at 550 °C. Increasing the temperature from 350 to 550 °C led to an increase in the bio-oil yield from 44.5 wt% to 49.9 wt% and led to a decrease in biochar yield from 36.6 wt% to 30.1 wt%. At the highest temperature, the bio-oil yield decreased to 47.2 wt% while the biochar yield remained almost the same. This may be due to the formation of secondary cracking of pyrolysis vapors (Yorgun and Yildiz 2015). A similar trend was observed in the case of dichloromethane extract yields. However, the highest dichloromethane extract yield was 6.70 wt% at 450 °C. A further increase in the pyrolysis temperature resulted in a decrease in the dichloromethane extract yield.
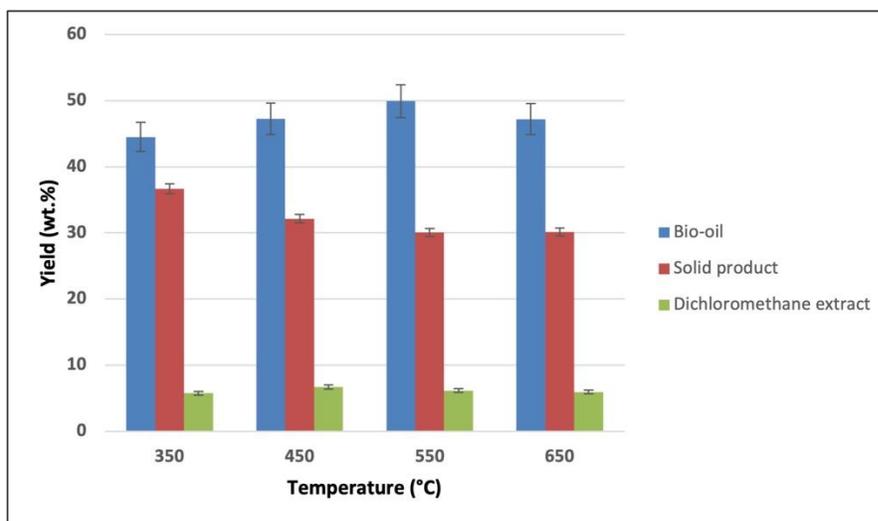
Fig. 1. Product yields obtained from the pyrolysis of medlar seeds at different temperatures

Effect of the Catalysts on the Product Yields at Different Temperatures

Figure 2 shows the product distribution from the pyrolysis of medlar seeds at different temperatures in the presence of 10 wt% perlite. The use of perlite noticeably affected the product yields. The bio-oil yield increased in the presence of perlite at all pyrolysis temperatures. However, the rate of increase was less at 550 °C, which was the optimum temperature for the non-catalytic experiments, when compared to other temperatures. The bio-oil yield increased from 44.5 wt% to 46.3 wt% and from 47.2 wt% to 49.0 wt% at 350 and 450 °C, respectively. The highest bio-oil yield (50.3 wt%), which was also higher than the maximum bio-oil yield in the non-catalytic runs, was obtained at the highest temperature.

bioresources.com
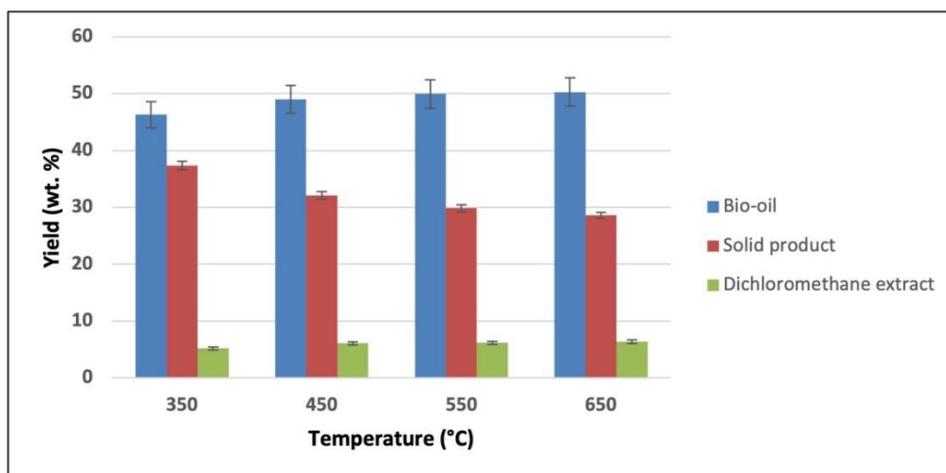
Fig. 2. Product yields from the pyrolysis of medlar seeds at different temperatures in the presence of perlite (10 wt%)

The dichloromethane extract yield increased, and the biochar yield decreased when increasing the pyrolysis temperature in the catalytic experiments, and the dichloromethane extract yield reached the maximum (6.38 wt%) at the highest pyrolysis temperature. When compared to non-catalytic runs, the use of perlite resulted in a decrease in dichloromethane extract yields at below 550 °C. The use of perlite had no noticeable effect on the dichloromethane extract yield at 550 °C. The only pyrolysis temperature at which the dichloromethane extract yield (6.38 wt%) from the experiment in the presence of perlite was higher than dichloromethane extract yield (5.95 wt%) from the non-catalytic experiment at the same temperature, was 650 °C. The biochar yields in the catalytic runs with perlite were lower than the biochar yields from the non-catalytic runs at 450 °C and at higher temperatures.

Product yields obtained from the pyrolysis of medlar seeds in the presence of MgO are shown in Fig. 3. The dichloromethane extract and bio-oil yields obtained from the catalytic runs were lower than that of non-catalytic runs at all pyrolysis temperatures. The highest bio-oil yield (45.3 wt%) and dichloromethane extract yield (5.67 wt%) were obtained at 450 and 550 °C, respectively.
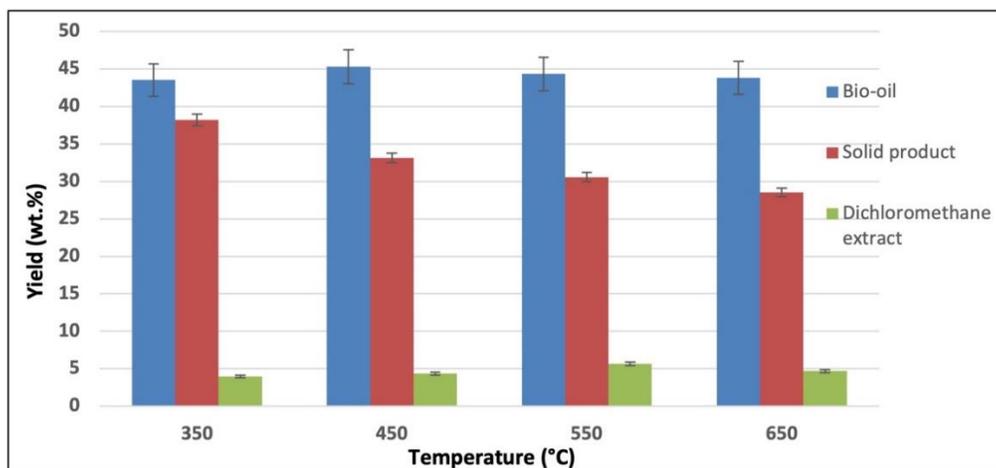
Fig. 3. Product yields from the pyrolysis of medlar seeds at different temperatures in the presence of MgO (10 wt%)

The biochar yields were higher than the yields from the non-catalytic experiments at all temperatures except 650 °C. Increasing the temperature from 350 to 650 °C led to a decrease in biochar yields from 38.2 to 28.5 wt%, respectively.

Figure 4 shows the bio-oil, biochar, and dichloromethane extract yields obtained from the pyrolysis experiments with the use of K_2CO_3. The use of K_2CO_3 noticeably decreased the dichloromethane extract and bio-oil yields when compared to non-catalytic runs. The highest bio-oil yield (43.2 wt%) was obtained at 550 °C while the highest dichloromethane extract yield (3.97 wt%) was obtained at 450 °C. However, the yields of all products (dichloromethane extract, biochar, and bio-oil) were lower than that of the product type obtained from the non-catalytic runs. The yield of biochar decreased from 33.8 wt% to 26.4 wt% by increasing the pyrolysis temperature from 350 to 650 °C, respectively. Increasing the temperature from 350 to 450 °C led to an increase in the dichloromethane extract yield from 2.59 to 3.97 wt%. However, an increase in temperature from 550 to 650 °C had no noticeable difference on the dichloromethane extract yields.
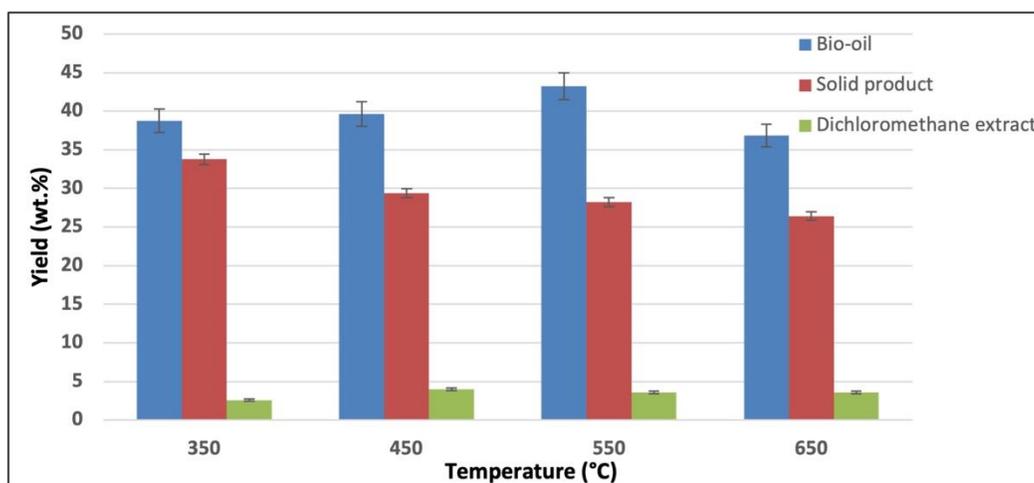
Fig. 4. Product yields from the pyrolysis of medlar seeds at different temperatures in the presence of K_2CO_3 (10 wt%)

Characterization of Bio-oils

The identified compounds in the bio-oils obtained from the non-catalytic pyrolysis of medlar seeds are listed in Table 2. Bio-oils from the non-catalytic pyrolysis mainly consisted of phenolic compounds. The pyrolysis temperature had a noticeable effect on the composition of bio-oils. The compound 2,6-dimethoxyphenol was the major component in the bio-oils at all tested temperatures, while it was followed by 2,6-dimethoxy-4-methylphenol at lower temperatures (350 and 450 °C). Increasing the pyrolysis temperature from 450 to 550 °C had a noticeable effect on the relative concentrations of both compounds as the area percentages of compounds decreased from 18.7% to 11.1% and from 12.1% to 7.66% for 2,6-dimethoxyphenol and 2,6-dimethoxy-4-methylphenol, respectively. However, the relative concentrations of 2-methoxyphenol, 4-ethyl-2-methoxyphenol, and 2-methoxy-4-methylphenol increased when increasing the temperature from 350 to 550 °C. The second major compound was 2-methoxy-4-methylphenol in the bio-oil obtained at 550 °C. The pyrolysis of medlar seeds resulted in production of bio-oils with rich phenolic content which can be used as a chemical source and/or production of phenolic resins.

Table 2. Composition of Bio-oils Obtained from the Non-Catalytic Pyrolysis Experiments

Retention Time (min)	Quality	Compound	Area (%)			
			350 °C	450 °C	550 °C	650 °C
5.447	91	2-furancarboxaldehyde			6.95	
7.299	93	2-methyl-2-cyclopenten-1-one			0.74	
8.940	94	5-methyl-2-furancarboxaldehyde			3.25	
9.543	90	phenol		0.45	2.60	
10.837	96	2-hydroxy-3-methyl-2-cyclopenten-1-one	1.79	1.45	2.73	
11.696	97	2-methyl-phenol		0.61	1.65	
12.328	97	4-methyl-phenol	0.88	1.95	4.03	
12.659	97	2-methoxy-phenol	6.41	6.36	6.85	4.85
13.201	95	2,6-dimethyl-phenol			0.49	
14.436	97	2,4-dimethyl-phenol			1.54	
15.053	93	3,4-dimethyl-phenol			1.31	
15.294	90	1,4-dimethoxy-benzene		0.98		
15.384	95	benzoic acid			1.27	
15.686	97	2-methoxy-4-methyl-phenol	5.69	5.95	8.09	3.43
16.559	93	benzothiazole	2.13	1.79		
18.110	94	4-ethyl-2-methoxy-phenol	4.89	5.12	5.29	3.23
19.058	96	2-methoxy-4-vinylphenol	1.81	1.61	1.94	
20.082	97	2,6-dimethoxy-phenol	18.23	18.73	11.11	12.65
20.232	97	2-methoxy-4-(2-propenyl)-phenol			1.07	
21.362	96	4-hydroxy-3-methoxy-benzaldehyde			0.90	
22.536	93	2,6-dimethoxy-4-methylphenol	10.15	12.12	7.66	7.33
22.596	98	2-methoxy-4-(1-propenyl)-phenol	4.56	3.51	2.69	
23.590	93	1-(4-hydroxy-3-methoxyphenyl)-ethenone			0.83	
24.478	90	1,2,5-trimethoxy-3-methyl-benzene	7.16	8.25	4.44	4.55
24.614	70	methyldopa-M			1.10	
24.659	92	4-hydroxy-3-methoxy-homovanillic acid	0.90	1.06		
25.412	91	2,6-dimethoxy-4-vinyl-phenol	2.04	1.39		
26.285	98	2,6-dimethoxy-4-(2-propenyl)-phenol	1.39	1.53	0.96	0.89
26.436	91	2,6-dimethoxy-4-propyl-phenol	2.50	2.70	1.33	
27.384	96	2,6-dimethoxy-4-(2-propenyl)-phenol	0.79	0.61	0.34	
27.595	97	4-hydroxy-3,5-dimethoxy-benzaldehyde		0.64	1.42	
28.498	94	2,6-dimethoxy-4-(2-propenyl)-phenol	2.64			2.27
29.191	97	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	1.01	1.32	1.67	
32.473	98	Nonadecane				5.70
34.160	98	Eicosane				8.14
33.753	90	5-(6-Methylbenzothiazol-2-yl)furan-2-carbaldehyde				3.11

bioresources.com

Table 3 shows the relative abundance of compounds identified in the bio-oils obtained from pyrolysis of medlar seeds in the presence of perlite. The bio-oils mainly consisted of phenolic compounds, and 2,6-dimethoxyphenol and 2,6-dimethoxy-4-methylphenol were the major compounds in the bio-oils. However, their relative concentrations increased while increasing the temperature from 550 to 650 °C in contrast to non-catalytic runs.

Table 3. Composition of Bio-oils Obtained from the Pyrolysis Experiments in the Presence of Perlite

Retention Time (min)	Quality	Compound	Area (%)			
			350 °C	450 °C	550 °C	650 °C
5.463	94	2-furancarboxaldehyde			9.19	
8.956	94	5-methyl-2-furancarboxaldehyde			2.83	
9.573	93	phenol			1.75	
10.823	97	2-hydroxy-3-methyl-2-cyclopenten-1-one			1.92	
11.711	98	2-methyl-phenol			1.38	
12.343	96	3-methyl-phenol		2.02	2.00	1.91
12.659	97	2-methoxy-phenol	6.60	7.03	5.85	7.95
14.481	97	2,4-dimethyl-phenol			0.73	
15.068	91	3,4-dimethyl-phenol			0.71	
15.686	97	2-methoxy-4-methyl-phenol	4.99	5.86	4.81	7.95
16.559	91	benzothiazole		2.47	0.34	3.15
17.763	90	3-methoxy-1,2-benzenediol			0.95	
18.110	93	4-ethyl-2-methoxy-phenol	4.48	5.36	3.84	5.69
19.058	95	2-methoxy-4-vinylphenol		1.97	1.71	1.96
20.067	97	2,6-dimethoxy-phenol	17.55	17.5	14.08	20.15
20.233	95	2-methoxy-4-(2-propenyl)-phenol			0.78	
21.558	95	2-methoxy-4-(1-propenyl)-phenol			0.69	
22.521	93	2,6-dimethoxy-4-methyl-phenol	10.21	10.43	9.99	11.80
22.596	98	2-methoxy-4-(1-propenyl)-phenol	4.65	4.39	2.55	6.07
24.478	90	1,2,5-trimethoxy-3-methyl-benzene	7.48	7.43	6.19	7.60
24.614	87	methyldopa-m			0.94	
25.397	90	2,6-dimethoxy-4-vinyl-phenol		1.77	1.45	2.54
26.285	98	2,6-dimethoxy-4-(2-propenyl)-phenol	1.25	1.21	1.37	1.63
26.436	91	2,6-dimethoxy-4-propyl-phenol		2.40	1.99	
27.384	97	2,6-dimethoxy-4-(2-propenyl)-phenol		0.86	0.64	1.29
27.595	97	4-hydroxy-3,5-dimethoxy-benzaldehyde			1.61	
28.483	94	2,6-dimethoxy-4-(2-propenyl)-phenol	2.89	2.52	0.75	5.90
29.191	97	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone		0.80	1.65	

The identified compounds obtained from the pyrolysis of medlar seeds in the presence of MgO are shown in Table 4. The use of catalyst noticeably affected the composition of bio-oils. The relative abundance of phenols reduced and the formation of compounds, such as ketones and carboxylic acids, were observed in the bio-oils, unlike the runs without catalyst. However, 2,6-dimethoxyphenol and 2,6-dimethoxy-4-methylphenol still remained as two of the abundant compounds in the bio-oils.

Table 4. Composition of Bio-oils Obtained from the Pyrolysis Experiments in the Presence of MgO

Retention Time (min)	Quality	Compound	Area (%)			
			350 °C	450 °C	550 °C	650 °C
7.564	90	2-furancarboxaldehyde	9.60	8.83	6.81	
8.482	95	2-furanmethanol	2.26	2.48	1.70	2.27
10.078	94	2-methyl-2-cyclopenten-1-one	0.74		0.75	0.95
13.315	72	phenol	1.66	2.23	1.69	1.23
14.580	94	3-methyl-1,2-cyclopentanedione		1.68		1.46
14.685	93	2-hydroxy-3-methyl-2-cyclopenten-1-one	1.64		1.32	
15.619	95	2-methyl-phenol	1.15	1.34	1.33	1.48
16.341	96	4-methyl-phenol	0.76	1.17	0.90	1.00
16.537	95	2-methoxy-phenol	4.67	4.85	4.12	4.38
17.004	92	2-methyl-benzofuran			0.25	
17.094	90	2,6-dimethyl-phenol			0.19	
17.531	94	3-ethyl-2-hydroxy-2-cyclopenten-1-one	0.50	0.50	0.39	
18.524	95	2,4-dimethyl-phenol	0.86	1.24	0.75	1.13
19.217	90	3,5-dimethyl-phenol			0.80	
19.744	97	2-methoxy-4-methyl-phenol	3.66	4.06	3.49	3.85
20.271	90	2-vinyl-2,3-dihydrobenzofuran		0.47	0.42	0.50
21.009	95	3,4-dimethoxytoluene			0.23	
21.897	94	3-methoxy-1,2-benzenediol			0.83	
22.198	94	4-ethyl-2-methoxy-phenol	3.56	3.74	3.60	3.64
22.514	94	1-methyl-naphthalene		0.24	0.35	
23.147	96	2-methoxy-4-vinylphenol	1.79	1.70	1.83	1.49
23.824	90	(trimethyl-[3-(3-phenylcyclopentylidene)-1-propynyl]silane				0.21
23.839	90	5-methyl-2-phenyl-4,6-diisopropylpyrimidine			0.28	
24.321	96	2,6-dimethoxy-phenol	8.36	8.74	7.85	8.64
25.496	94	1,2,3-trimethoxy-5-methyl-benzene	0.43	0.40		0.46
25.646	95	2-methoxy-4-(1-propenyl)-phenol	0.75	0.55	1.02	0.72
26.790	95	2-methoxy-4-(1-propenyl)-phenol	1.28	1.71		
26.805	90	2,6-dimethoxy-4-methyl-phenol	7.87	8.72	9.44	11.36
27.754	90	1-(4-hydroxy-3-methoxyphenyl)-ethanone			0.36	
28.687	90	1,2,5-trimethoxy-3-methyl-ethanone	4.70	5.34	4.59	5.90
28.718	90	homovanillyl alcohol				1.05
28.808	87	methyldopa-m	0.94		1.00	

bioresources.com

Retention Time (min)	Quality	Compound	Area (%)			
			350 °C	450 °C	550 °C	650 °C
29.546	90	2,6-dimethyl-3-(methoxymethyl)-p-benzoquinone		1.63		
30.434	98	2,6-dimethoxy-4-(2-propenyl)-phenol	1.20	1.28	1.26	1.43
30.584	91	4-propyl-syringol	1.73	1.90	1.80	2.11
31.533	93	2,6-dimethoxy-4-(2-propenyl)-phenol	0.88	0.89	1.11	1.06
31.819	97	4-hydroxy-3,5-dimethoxy-benzaldehyde	1.14	1.02	1.21	1.03
32.692	94	2,6-dimethoxy-4-(2-propenyl)-phenol	2.78	3.15	3.07	3.48
33.415	96	1-(4-hydroxy-3,5-dimethoxyphenyl)- ethanone	1.06	1.00	1.17	1.13
35.312	87	4-propionyl–syringol			0.78	0.78
37.149	98	hexadecanoic acid methyl ester	0.40	0.38	0.41	0.33
38.007	97	n-hexadecanoic acid	0.98	0.84	0.85	1.17
38.459	92	3,5-dimethoxy-4-hydroxycinnamaldehyde	0.40		0.40	
40.341	99	9,12-octadecadienoic acid	0.30	0.30	0.29	0.27
40.461	99	9-octadecenoic acid methyl ester	1.05	1.11	0.96	0.92
40.928	98	octadecanoic acid methyl ester	0.12	0.13	0.10	0.10
41.334	99	9-octadecenoic acid	1.76	1.22	1.26	1.47
41.651	95	octadecanoic acid	0.12			
41.681	90	oleic acid			0.09	
42.027	95	8,11-octadecadienoic acid methyl ester			0.03	

Table 5 shows the composition of bio-oils obtained in the presence of K_2CO_3. The composition of bio-oils was noticeably affected using catalyst when compared to the composition of bio-oils from the non-catalytic runs. 2,6-dimethoxyphenol and 2-methoxyphenol were the major compounds in the bio-oils. The formation of high molecular weight compounds and decrease in the low molecular weight products was observed with the use of catalyst, which can be related to promotion of coking. The pyrolysis conditions and the interactions between bio-oil components strongly affects the formation of coke. It was reported that temperature and heating rate are the pyrolysis parameters which have a noticeable effect on coke formation and high heating rate lowers the coke yields (Xiong *et al.* 2019).

Table 5. Composition of Bio-oils Obtained from the Pyrolysis Experiments in the Presence of K_2CO_3

Retention Time (min)	Quality	Compound	Area (%)			
			350 °C	450 °C	550 °C	650 °C
8.452	94	2-furanmethanol	1.55	1.86		1.34
10.078	93	2-methyl-2-cyclopenten-1-one	0.88	1.19		
12.216	92	3-methyl-2-cyclopenten-1-one	1.79	2.02	1.90	2.02
14.565	93	3-methyl-1,2-cyclopentanedione		0.76		
14.655	93	2-hydroxy-3-methyl-2-cyclopenten-1-one		0.42		
14.775	78	2,3-dimethyl-2-cyclopenten-1-one	1.25	1.28	1.96	1.68
15.453	74	3,5-dimethyl cyclopentenolone	0.66		0.79	
15.694	94	2-methyl-phenol	1.51	2.29	1.94	2.58
16.357	96	4-methyl-phenol	0.82	1.32		1.97

16.537	94	2-methoxy-phenol	7.28	6.78	10.10	7.61
17.109	95	2,6-dimethyl-phenol		0.50		
17.531	95	3-ethyl-2-hydroxy-2-cyclopenten-1-one		0.58		
18.615	96	2,4-dimethyl-phenol	1.82	2.35	2.97	3.41
19.112	94	3,5-dimethyl-phenol	1.42			2.9
19.202	90	2,3-dimethyl-phenol	0.28	2.85		0.89
19.548	81	2,4-dimethyl-phenol			2.19	
19.729	97	2-methoxy-4-methylphenol	2.62	2.91	3.58	3.33
19.880	95	3,4-dimethyl-phenol		0.80		
20.060	90	2,3,5-trimethyl-phenol	0.32	0.58		
20.919	89	2-ethyl-6-methyl-phenol		0.45		
20.933	89	2,3,6-trimethyl-phenol	0.84	0.53	0.73	1.19
21.114	93	4-ethyl-3-methyl-phenol	0.28	0.40		0.56
21.235	93	3-ethyl-5-methyl-phenol		0.63		
22.018	96	2,3,5-trimethyl-phenol				0.89
22.033	87	2,4,5-trimethyl-phenol	0.51	0.78	0.76	0.91
22.213	93	4-ethyl-2-methoxy-phenol	4.35	4.66	6.31	4.74
22.996	90	2-methyl-naphthalene		0.28		
23.147	94	2-methoxy-4-vinylphenol	1.79	1.78		1.43
23.342	90	5-methyl-2-(1-methylethyl)-phenol	0.49			
24.231	97	2,6-dimethoxy-phenol	11.47	11.49	9.25	12.78
25.556	90	1,2,5-trimethoxy-3-methyl-benzene	0.35	0.54	0.46	0.47
25.556	81	2,4-dimethyl-3-(methoxycarbonyl)-5-ethylfuran			0.46	
25.616	91	2-methoxy-4-(2-propenyl)-phenol	0.53			
26.700	94	2,6-dimethoxy-4-methyl-phenol	5.96	7.16	7.90	
26.836	90	2-methoxy-4-(1-propenyl)-phenol	1.42	1.18		
27.904	90	pentadecane			0.34	
28.657	90	1,2,5-trimethoxy-3-methyl-benzene	5.56	5.44	8.11	5.95
29.561	78	1,4-dihydrophenanthrene		1.32		
30.464	96	2,6-dimethoxy-4-(2-propenyl)-phenol	1.12	1.05	1.07	1.25
30.615	91	4-propyl-syringol	2.52		3.40	2.53
31.518	90	2,6-dimethoxy-4-(2-propenyl)-phenol	0.56	0.64		
31.789	97	4-hydroxy-3,5-dimethoxy-benzaldehyde	0.72	0.78		
32.527	91	heptadecane	0.23	0.26	0.26	0.35
32.692	93	2,6-dimethoxy-4-(2-propenyl)-phenol	0.61	1.00	1.66	0.62
33.385	94	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	0.40	0.52		0.43
35.282	74	4-propionyl-syringol	0.32	0.38		
37.134	97	hexadecanoic acid methyl ester	0.27			
37.149	96	14-methyl-pentadecanoic acid methyl ester		0.28		0.21
37.977	99	n-hexadecanoic acid	0.76	0.89		0.65
40.341	99	9,12-octadecadienoic acid methyl ester	0.18	0.14		0.16
40.461	99	9-octadecenoic acid methyl ester	0.34	0.31		0.31
41.304	99	9-octadecenoic acid	1.10	1.52		0.66

Elemental compositions of bio-oils obtained from the experiments with and without catalysts are shown in Table 6. The pyrolysis process led to deoxygenation, as the oxygen content of the bio-oils were noticeably lower than that of the raw material. The higher heating values of the bio-oils were higher than the HHV of raw material, while the bio-oil with maximum HHV (27.4 MJ/kg) was obtained at 450 °C in the non-catalytic runs. The highest higher heating value was 30.4 MJ/kg from the pyrolysis of medlar seeds in the presence of perlite at 450 °C. The use of MgO noticeably reduced the carbon content and HHV of bio-oils when compared to non-catalytic experiments. The higher heating value of bio-oils increased from 23.5 to 24.7 MJ/kg when the temperature was increased from 350 to 450 °C, respectively. A further increase in temperature resulted in a slight decrease in HHV of bio-oils. For K_2CO_3, the higher heating values of bio-oils were between 26.1 and 29.0 MJ/kg. The higher heating values of bio-oils obtained with the use of K_2CO_3 at 350 °C (27.9 MJ/kg) and 550 °C (29.0 MJ/kg) were found to be higher than that of the bio-oils from other experiments at the related temperatures.

Table 6. Elemental Compositions of Bio-oils Obtained from the Experiments With and Without Catalysts

Bio-oil Type	C (%)	H (%)	N (%)	O[a] (%)	O/C	H/C	HHV[b] (MJ/kg)
Raw material	43.21	6.634	0.514	49.64	0.86	1.84	15.22
350 °C/ -	65.64	6.726	0.484	27.15	0.31	1.23	26.94
450 °C/ -	67.38	6.470	0.584	25.56	0.28	1.15	27.45
550 °C/ -	65.66	6.803	0.470	27.06	0.31	1.24	27.08
650 °C/ -	66.64	6.621	0.679	26.06	0.29	1.19	27.33
350 °C/ Perlite	65.12	6.928	0.470	27.48	0.32	1.28	27.00
450 °C/ Perlite	66.36	8.626	0.549	24.46	0.28	1.56	30.38
550 °C/ Perlite	66.00	7.740	0.598	25.66	0.29	1.41	28.78
650 °C/ Perlite	67.14	7.541	0.601	24.71	0.28	1.35	29.05
350 °C/ MgO	60.29	6.339	0.261	33.11	0.41	1.26	23.52
450 °C/ MgO	60.97	6.847	0.356	31.82	0.39	1.35	24.71
550 °C/ MgO	60.83	6.679	0.388	32.10	0.40	1.32	24.37
650 °C/ MgO	60.64	6.701	0.472	32.18	0.40	1.33	24.32
350 °C/ K_2CO_3	65.89	7.203	0.702	26.20	0.30	1.31	27.88
450 °C/ K_2CO_3	63.73	6.813	0.597	28.86	0.34	1.28	26.12
550 °C/ K_2CO_3	67.21	7.422	1.434	23.93	0.27	1.33	29.04
650 °C/ K_2CO_3	65.39	6.394	0.533	27.68	0.32	1.17	26.29

[a]: By difference
[b]: Higher heating value calculated by Dulong formula (HHV) = 0.338C + 1.428(H - O/8) + 0.095S

CONCLUSIONS

1. The pyrolysis of medlar seeds was performed at different temperatures with and without catalysts. In the non-catalytic experiments, the maximum bio-oil yield was obtained at 550 °C while the maximum dichloromethane extract yield was obtained at 450 °C.

2. The use of K_2CO_3 and MgO noticeably affected the yields and composition of the bio-oils. The maximum bio-oil yields were obtained at 550, 450, and 650 °C in the presence of K_2CO_3, MgO, and perlite, respectively.

3. The higher heating values of the bio-oils obtained from the pyrolysis experiments in the presence of perlite were higher than that of the non-catalytic runs at all tested temperatures. Therefore, bio-oils with increased higher heating values can be obtained with the use of a relatively cheap and an abundant material in the pyrolysis of medlar seeds.

ACKNOWLEDGMENTS

REFERENCES CITED

Abnisa, F., Daud, W. W., Husin, W. N. W., and Sahu, J. N. (2011). "Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in pyrolysis process," *Biomass and Bioenergy* 35(5), 1863-1872.

Al-Rumaihi, A., Shahbaz, M., Mckay, G., Mackey, H., and Al-Ansari, T. (2022). "A review of pyrolysis technologies and feedstock: A blending approach for plastic and biomass towards optimum biochar yield," *Renew. Sust. Energ. Rev.* 167, article ID 112715. DOI: 10.1016/j.rser.2022.112715

Ayaz, F. A., Demir, O., Torun, H., Kolcuoglu, Y., and Colak, A. (2008). "Characterization of polyphenoloxidase (PPO) and total phenolic contents in medlar (*Mespilus germanica* L.) fruit during ripening and over ripening," *Food Chem.* 106(1), 291-298. DOI: 10.1016/j.foodchem.2007.05.096

Aydinli, B., and Caglar, A. (2012). "The investigation of the effects of two different polymers and three catalysts on pyrolysis of hazelnut shell," *Fuel Process. Technol.* 93(1), 1-7. DOI: 10.1016/j.fuproc.2011.07.009

Balat, M., and Balat, M. (2010). "Pyrolysis of black locust wood in the presence of perlite," *Energ. Source. Part A* 33(3), 211-220. DOI: 10.1080/15567030902942655

Chen, H., Liu, Z., Chen, X., Chen, Y., Dong, Z., Wang, X., and Yang, H. (2020). "Comparative pyrolysis behaviors of stalk, wood and shell biomass: Correlation of cellulose crystallinity and reaction kinetics," *Bioresource Technol.* 310, article ID 123498. DOI: 10.1016/j.biortech.2020.123498

Fan, Y., Cai, Y., Li, X., Yin, H., Yu, N., Zhang, R., and Zhao, W. (2014). "Rape straw as a source of bio-oil via vacuum pyrolysis: Optimization of bio-oil yield using orthogonal design method and characterization of bio-oil," *Journal of Analytical and Applied Pyrolysis* 106, 63-70.

Guedes, R. E., Luna, A. S., and Torres, A. R. (2018). "Operating parameters for bio-oil production in biomass pyrolysis: A review," *J. Anal. Appl. Pyrol.* 129, 134-149. DOI: 10.1016/j.jaap.2017.11.019

Güngör, A., Önenç, S., Uçar, S., and Yanik, J. (2012). "Comparison between the "one-step" and "two-step" catalytic pyrolysis of pine bark," *Journal of Analytical and Applied Pyrolysis* 97, 39-48.

Hu, X., and Gholizadeh, M. (2019). "Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage," *J. Energy Chem.* 39, 109-143. DOI: 10.1016/j.jechem.2019.01.024

Islam, M. N., Joardder, M. U. H., Hoque, S. N., and Uddin, M. S. (2013). "A comparative study on pyrolysis for liquid oil from different biomass solid wastes," *Procedia Engineer*. 56, 643-649. DOI: 10.1016/j.proeng.2013.03.172

Kan, T., Strezov, V., and Evans, T. J. (2016). "Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters," *Renew. Sust. Energ. Rev.* 57, 1126-1140. DOI: 10.1016/j.rser.2015.12.185

Kar, Y. (2011). "Catalytic pyrolysis of car tire waste using expanded perlite," *Waste Manage*. 31(8), 1772-1782. DOI: 10.1016/j.wasman.2011.04.005

Kar, Y., and Şen, N. (2012). "Catalytic pyrolysis of the oily seeds of *Styrax officinalis* L. for bio-fuels and valuable industrial chemicals," *Environm. Prog. Sust. Energ*. 31(4), 619-627. DOI: 10.1002/ep.10588

Kim, J. S. (2015). "Production, separation and applications of phenolic-rich bio-oil–a review," *Bioresource Technology* 178, 90-98.

Krutof, A., and Hawboldt, K. (2016). "Blends of pyrolysis oil, petroleum, and other bio-based fuels: A review," *Renewable and Sustainable Energy Reviews* 59, 406-419.

Ling, C., Kyin, E., Hua, L., Chen, L., and Yee, C. (2015). "Yield and calorific value of bio oil pyrolysed from oil palm biomass and its relation with solid residence time and process temperature," *Asian Journal of Scientific Research* 8(3), 351-358.

Liu, X., Yang, S., Zhang, C., Huang, H., and Varodi, A. M. (2023). "Comparative study on slow pyrolysis products of abandoned furniture materials," *BioResources* 18(1), 629-640. DOI: 10.15376/biores.18.1.629-640

Makepa, D. C., Chihobo, C. H., and Musademba, D. (2022). "Advances in sustainable biofuel production from fast pyrolysis of lignocellulosic biomass," *Biofuels* Online, 1-22. DOI: 10.1080/17597269.2022.2151459

Papa, E., Medri, V., Murri, A. N., Laghi, L., De Aloysio, G., Bandini, S., and Landi, E. (2018). "Characterization of alkali bonded expanded perlite," *Constr. Build. Mater*. 191, 1139-1147. DOI: 10.1016/j.conbuildmat.2018.10.086

Pawar, A., Panwar, N. L., and Salvi, B. L. (2020). "Comprehensive review on pyrolytic oil production, upgrading and its utilization," *Journal of Material Cycles and Waste Management* 22, 1712-1722.

Różycka, A., and Pichór, W. (2016). "Effect of perlite waste addition on the properties of autoclaved aerated concrete," *Constr. Build. Mater*. 120, 65-71. DOI: 10.1016/j.conbuildmat.2016.05.019

Solgi, M., Najib, T., Ahmadnejad, S., and Nasernejad, B. (2017). "Synthesis and characterization of novel activated carbon from medlar seed for chromium removal: Experimental analysis and modeling with artificial neural network and support vector regression," *Resource-Efficient Technol*. 3(3), 236-248. DOI: 10.1016/j.reffit.2017.08.003

Tan, S., Zhou, G., Yang, Q., Ge, S., Liu, J., Cheng, Y. W., Yek, P. N. Y., Mahari, W. A. W., Kong, S. H., Chang, J. S., *et al.* (2022). "Utilization of current pyrolysis technology to convert biomass and manure waste into biochar for soil remediation: A review," *Sci. Total Environ*. article ID 160990. DOI: 10.1016/j.scitotenv.2022.160990

Vuppaladadiyam, A. K., Vuppaladadiyam, S. S. V., Awasthi, A., Sahoo, A., Rehman, S., Pant, K. K., Murugavelh, S., Huang, Q., Anthony, E., Fennel, P., Bhattacharya, S., and Leu, S. (2022). "Biomass pyrolysis: A review on recent advancements and green hydrogen production," *Bioresource Technol*. article ID 128087. DOI: 10.1016/j.biortech.2022.128087

Xiong, Z., Syed-Hassan, S. S. A., Hu, X., Guo, J., Qiu, J., Zhao, X., Su, S., Hu, S., Wang, Y., and Xiang, J. (2019). "Pyrolysis of the aromatic-poor and aromatic-rich fractions of bio-oil: Characterization of coke structure and elucidation of coke formation mechanism," *Applied Energy* 239, 981-990. DOI: 10.1016/j.apenergy.2019.01.253

Yorgun, S., and Yıldız, D. (2015). "Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization," *J. Anal. Appl. Pyrol.* 114, 68-78. DOI: 10.1016/j.jaap.2015.05.003

Zhou, Z., Zhu, L., Cui, C., Liu, H., Shen, Y., Yuan, W., and Qi, F. (2022). "Pyrolysis of lignocellulosic biomass: Molecular-level insights with online ultrahigh-resolution mass spectrometry," *Fuel Process. Technol.* 236, article ID 107439. DOI: 10.1016/j.fuproc.2022.107439