



## Characterization of bio-oil obtained from fruit pulp pyrolysis

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### ABSTRACT

Apricot pulps was pyrolyzed in a fixed-bed reactor under different pyrolysis conditions to determine the role of final temperature, sweeping gas flow rate and steam velocity on the product yields and liquid product composition with a heating rate of 5 °C/min. Final temperature range studied was between 300 and 700 °C and the highest liquid product yield was obtained at 550 °C. Liquid product yield increased significantly under nitrogen and steam atmospheres. For the optimum conditions, pyrolysis of peach pulp was furthermore studied. Liquid products obtained under the most suitable conditions were characterized by FTIR and <sup>1</sup>H-NMR. In addition, gas chromatography/mass spectrophotometer was achieved on all pyrolysis oils. Characterization showed that bio-oil could be a potential source for synthetic fuels and chemical feedstock.

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### 1. Introduction

Recently, increasing attention has been focused on biomass as renewable source of fuels and chemicals due to environmental reasons and the problem of energy assurance [1]. Biomass resources that can be used for energy production cover a wide range of materials such as forestry residues, energy crops, organic wastes, agricultural residues, etc. [2,3].

Pyrolysis of biomass has been a major commercial interest with hopes of producing new fuels, intermediate compounds for the chemical industry, as well as controlling the products produced from obligatory pyrolysis processes. Products from the pyrolysis of biomass include residue chars, tars, and volatile gaseous components [4]. For many biomass systems, the products of pyrolysis can be controlled by regulating the pyrolysis conditions. Parameters that affect the decomposition of biomass are heating rate, gas flow rate, pressure, sample size, and inorganic salts [5].

Biomass pyrolysis liquid product, bio-oil, has the potential to be used as a fuel oil substitute. Bio-oils, also known under the names of pyrolysis oils or pyrolysis liquids, are usually dark-brown organic liquids. Bio-oils are comprised of different size molecules derived from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose, and lignin. Therefore, the elemental composition of bio-oil resembles that of biomass. In contrast to petroleum fuels, bio-oils contain a large amount of oxygen, usually 45–50 wt%. This

oxygen is present in most of the compounds that have been identified in the oils [6].

The distribution of the compounds in bio-oil mostly depends on the type of biomass used and on the process severity (temperature, residence time, and heating rate profiles). The single most abundant bio-oil component is water. The other major groups of compounds identified are hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. Most of the phenolic compounds are present as oligomers having a molecular weight ranging from 900 to 2500 [7,8].

In this study, apricot and peach pulps generated by the fruit juice factories—a food industry waste—is taken as the biomass sample for pyrolysis experiments. Apricot (*Prunus armeniaca* L.) is classified under the prunus species of Prunoideae sub-family of the Rosaceae family of the Rosales group. This type of fruit is cultivated as a type of zerdali (wild apricot) which is produced by inoculation. Turkey is the biggest apricot producer in the world with 538,000 ton production (134,500 ton pit) and contributed to the world production by 20.15%. There are 13,350,000 apricot trees, of which approximately 10,710,000 are fruit-bearing and 2,640,000 are non-bearing. Most of the apricots are produced in Malatya region, in Turkey. This region has a 60% share of fresh apricot production and an 80% share of dried apricot production in Turkey. Peach (*Prunus persica*) is also classified under prunus species. It is a deciduous tree, belonging to the sub-family Prunoideae of the family Rosaceae. Peach trees are the second most commonly cultivated fruit trees in the world after apple trees. Important peach-producing countries are China, USA, Italy, Greece, Spain, French, Turkey, Mexico, and Argentina. Turkey's peach production was about 553,000 ton in 2006 [9–11].

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This present work focuses on two aspects on fruit pulp pyrolysis: (i) effect of pyrolysis conditions on the product yields and (ii) liquid product characterization. The main objective of the study is to identify if the liquid product from fruit pulp pyrolysis could be utilized instead of fuels or could be a potential source for chemical feedstock.

## 2. Experimental

### 2.1. Pyrolysis

The fruit pulps chosen for this study were taken from fruit juice factories around Bursa located in Western Anatolia. Pulp samples were ground to have an average particle size of  $0.85 < D_p < 1.25$  mm. The pyrolysis of the air-dried pulp was carried out in a fixed-bed reactor in three different atmospheres, namely, static, steam and nitrogen as the carrier gas. The 316 stainless steel retort has a volume of  $400 \text{ cm}^3$  (70 mm i.d.) and is externally heated by an electric 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  $400^\circ\text{C}$  to avoid condensation of the bio-oil vapor [10].

For the first part of the pyrolysis experiments, 10 g sample of apricot pulp was placed into the reactor and pyrolyzed at 300, 400, 450, 500, 550,  $700^\circ\text{C}$  with a heating rate of  $5^\circ\text{C min}^{-1}$ . In the second part of the experiments, the sample was pyrolyzed at  $550^\circ\text{C}$  under nitrogen atmosphere with a flow rate of 50, 100, 200,  $400 \text{ cm}^3 \text{ min}^{-1}$  and with a heating rate of  $5^\circ\text{C min}^{-1}$ . In the third part of the experiments, the pyrolysis process was carried out under water vapor atmosphere with a flow rate of  $2.5 \text{ cm}^3 \text{ min}^{-1}$  and a heating rate of  $5^\circ\text{C min}^{-1}$  to the final temperature of 300, 400, 450, 500, 550,  $700^\circ\text{C}$ . Pyrolysis of peach pulp was then carried out under optimum conditions.

The liquid products were collected in a glass liner located in a cold trap maintained at  $0^\circ\text{C}$ . At the end of the experiment, the liquid phase consisting of an aqueous and an oil phase were separated and weighed. The total liquid product (oil+water) was weighed in a dry-ice cooled trap and recovered in dichloromethane for analysis. Water was determined by refluxing the toluene solution in a Dean-Stark apparatus. The bio-oils were then recovered from the toluene solutions. Char yield was determined from the overall weight losses of the reactor. Gas yield was determined by overall material balance. All the yields were calculated on a dry-ash-free (daf) basis and product yields were determined by the average of at least three experiments, and experimental errors were lower than 5%.

### 2.2. Characterization of bio-oils

Nuclear magnetic resonance analysis was used to determine the percentage of aromatic, paraffinic and olefinic species in pyrolytic oils. These measurements were performed using Bruker DPX-400, 400 MHz high performance digital FT-NMR instruments. The liquid samples were diluted in TMS-containing deuterated chloroform. The FTIR spectroscopy of the bio-oils was achieved on thin films between KBr plates by using Bruker Tensor 27 Fourier Transform Infrared Spectrophotometer.

Elemental analyses were carried out on the oils obtained under experimental conditions that give maximum oil yield with Carlo Erba, EA 1108. The elemental compositions and the calorific values of the pyrolysis oils were determined.

### 2.3. Oil analysis

All pyrolysis oils were analyzed with an HP 6890 gas chromatograph equipped with 5793 mass selective detector using an HP-5 capillary column supplied from Hewlett-Packard, USA. The following temperature program was used: initial and final temperatures were  $40$  and  $280^\circ\text{C}$ , respectively, retention times at initial and final temperatures were both 10 min and the heating rate was  $8^\circ\text{C min}^{-1}$ . The inlet temperature was set to  $280^\circ\text{C}$  and  $1 \mu\text{l}$  of the sample was injected. The carrier gas was He of 99.999% purity. The MS detector operated in scan mode and its mass-range was 50–550 amu.

## 3. Result and discussion

### 3.1. Biomass characteristics

Proximate analysis of apricot pulp and peach pulp gave 10.3–9.3% moisture, 71.9–70.2% volatile matter (dry basis), 4.7–2.4% ash (dry basis), 13.0–18.0% fixed carbon (dry basis) respectively. Elemental analysis (wt%, dry basis) gave 51.4–45.6% C, 5.7–6.9% H, 2.5–0.9% N and 40.2–46.5% O for apricot and peach pulps respectively [10]. It can be deduced from the elemental analysis that the total organic matter (C, H, O) of the fruit pulp is about 99.8% wt/wt and calorific value of apricot and peach pulps were calculated as 18.4 and  $15.4 \text{ MJ kg}^{-1}$ , respectively using Du-Long's formula with the known values of elemental composition [12].

### 3.2. Pyrolysis yields

#### 3.2.1. Effect of pyrolysis temperature on product yields

Fig. 1 shows the product yields for the pyrolysis of apricot pulp in relation to final temperature of pyrolysis at heating rate of  $5^\circ\text{C min}^{-1}$ . The yield of char increased from 22.6% to 31.4% while the final pyrolysis temperature was increased from 300 to  $700^\circ\text{C}$ . While the oil yield was 18.6% at the pyrolysis temperature of  $300^\circ\text{C}$ , it appeared to go through a maximum of 22.4% at the final temperature of  $550^\circ\text{C}$ . Then at the final pyrolysis temperature of  $700^\circ\text{C}$ , the oil yield decreased to 18.8%. As it can be seen, the increase in temperature leads to a decreased yield of solid and an increased yield of gases. The increase in gas yield was suggested as being due to secondary reactions of the pyrolysis vapors in the reactor. The decrease in the char yield with increasing temperature could either be due to greater primary decomposition of apricot pulp at higher temperatures or through secondary

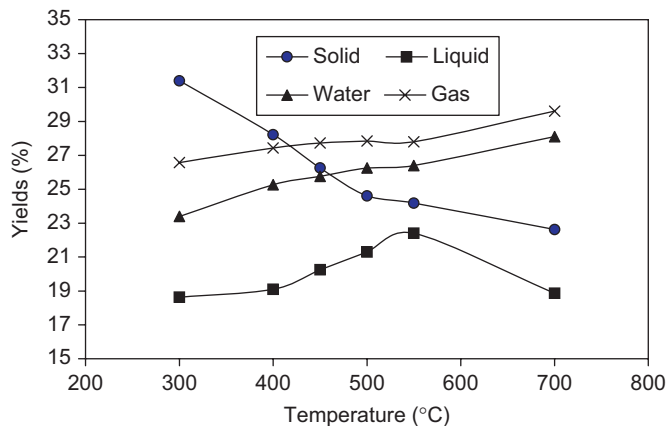


Fig. 1. Yields of apricot pulp pyrolysis products at final temperatures of either 400, 500, 550,  $700^\circ\text{C}$  (heating rate:  $5^\circ\text{C min}^{-1}$ ).

decomposition of char residue. The secondary decomposition of the char at higher temperatures may also give some non-condensable gaseous products, which also contributes to the increase in gas yield, which is parallel with to the increase in temperature of pyrolysis [10].

Indeed, as the temperatures of primary degradation are increased or the residence times of primary vapors inside the cracked particle has to stay shorter, the char yields decrease [13–15].

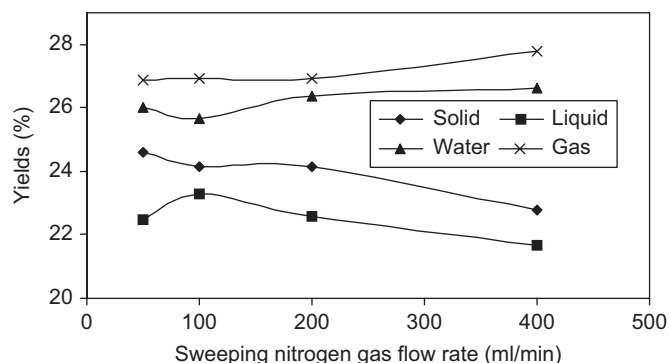


Fig. 2. Yields of apricot pyrolysis products at sweeping gas rates of 50, 100, 200, 400 cm<sup>3</sup> min<sup>-1</sup> (heating rate: 5 °C min<sup>-1</sup>; pyrolysis temperature: 550 °C).

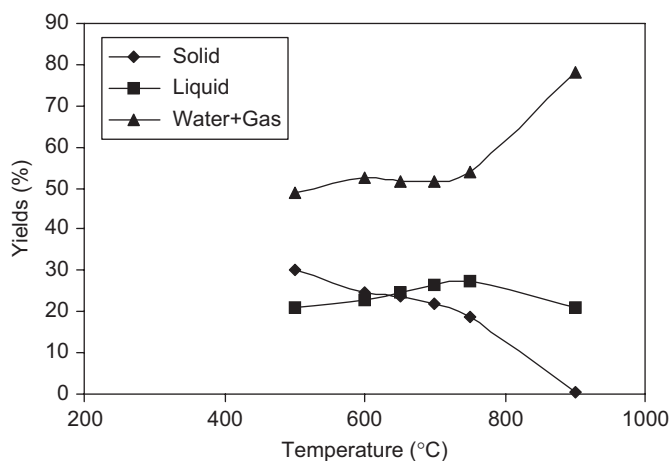


Fig. 3. Yields of apricot pyrolysis products at steam velocity of 2.5 cm<sup>3</sup> min<sup>-1</sup> (heating rate: 5 °C min<sup>-1</sup>; pyrolysis temperature: 400, 500, 550, 700 °C).

### 3.2.2. Effect of sweeping gas flow rate on product yields

The product yields of pyrolysis in relation to the nitrogen flow rate are given in Fig. 2.

An increase in the sweeping gas flow rate did not change pyrolysis conversions essentially. The oil yield reached its maximum of 23.3% with a sweeping gas velocity of 100 cm<sup>3</sup> min<sup>-1</sup> [10]. Pyrolysis vapors are removed instantly by higher sweeping gas flow rates, and if they are quenched sufficiently, the liquid yield should be high. But in the present study, the maximum oil yield was reached at 100 cm<sup>3</sup> min<sup>-1</sup> instead of at the highest velocity of 400 cm<sup>3</sup> min<sup>-1</sup> because of the experimental conditions especially insufficient quenching. Use of sweeping gas caused a 4.0% increase in oil yield.

As reported in the literature, nitrogen flow influences the residence time of the vapor phase produced by pyrolysis and hence, a rapid flow serves to remove the product quickly from the hot zone to cold to minimize the secondary reactions, such as thermal cracking, repolymerization, and recondensation and to maximize the liquid yield. The gas yield rises with increasing nitrogen flow rate; whereas the char yield decreases because uncondensed volatiles are removed from the reaction zone by the nitrogen stream [10,16,17].

### 3.2.3. Effect of steam velocity on product yields

The chemistry of biomass is very complicated. But generally it is assumed that biomass has three major carbon containing constituents: cellulose, hemicellulose, and lignin. Previous studies showed that while the first degradation of the carbon in biomass starts at about 200 °C, volatiles start to be evolved [18,19]. If steam is in the media as an oxidizing agent, it causes some reactions that are occurring on the surface of the biomass sample and/or with the volatile products. Those parallel reactions lead to a higher proportion of H<sub>2</sub> formation. The homolytic cleavage of a hydrogen molecule produces two hydrogen free radicals. Free radicals are usually highly reactive and unstable and often involved in chain reactions leading to a formation of cracked molecules, which favors the production of condensable gases forming light tars. Also, steam removes carbon from the surface thus creating a char with a more porous structure. In this manner, using steam as the oxidizing agent increases formation of liquid products with decreasing char and gas yields when compared with sweeping gas or static pyrolysis [20–24].

Fig. 3 shows the product yields of apricot pulp obtained in the presence of steam velocity at 2.5 cm<sup>3</sup> min<sup>-1</sup> and a heating rate of 5 °C min<sup>-1</sup> to the final temperature of 300, 400, 450, 500, 550, 700 °C. The yield of oil appears to go through a maximum at

Table 1  
Elemental compositions of the bio-oils from pyrolysis under static, nitrogen (N<sub>2</sub>) and steam atmospheres

	Apricot pulp <sup>a</sup>			Peach pulp		
	Static <sup>c</sup>	Nitrogen <sup>d</sup>	Steam <sup>e</sup>	Static <sup>c</sup>	Nitrogen <sup>d</sup>	Steam <sup>e</sup>
C	57.95	61.50	72.17	54.77	59.58	60.75
H	7.44	7.80	9.81	7.27	7.88	8.87
N	1.87	1.74	1.76	0.53	0.58	0.78
O <sup>b</sup>	32.74	28.96	16.26	37.43	31.96	30.60
H/C	1.54	1.52	1.63	1.58	1.58	1.74
O/C	0.42	0.35	0.17	0.51	0.40	0.37
Empirical formula	CH <sub>1.54</sub> N <sub>0.02</sub> O <sub>0.42</sub>	CH <sub>1.52</sub> N <sub>0.02</sub> O <sub>0.35</sub>	CH <sub>1.63</sub> N <sub>0.02</sub> O <sub>0.17</sub>	CH <sub>1.58</sub> N <sub>0.008</sub> O <sub>0.51</sub>	CH <sub>1.58</sub> N <sub>0.008</sub> O <sub>0.40</sub>	CH <sub>1.74</sub> N <sub>0.01</sub> O <sub>0.37</sub>
Calorific value (MJ kg <sup>-1</sup> )	24.44	26.82	35.63	22.27	25.76	27.83

<sup>a</sup> Published in Fuel Processing Technology 87 (2006) 1013–1019 as Table 2.

<sup>b</sup> By difference.

<sup>c</sup> Bio-oil from static atmosphere (550 °C, 5 °C min<sup>-1</sup>).

<sup>d</sup> Bio-oil from nitrogen atmosphere (550 °C, 100 cm<sup>3</sup> min<sup>-1</sup>, 5 °C min<sup>-1</sup>).

<sup>e</sup> Bio-oil from steam atmosphere (550 °C, 2.5 cm<sup>3</sup> min<sup>-1</sup>, 5 °C min<sup>-1</sup>).

550 °C while a decrease in the oil yield was observed at the much higher pyrolysis temperature of 700 °C [10]. This is consistent with the literature [25] which was reporting that steaming of coal at 300–600 °C enabled higher yields of primary tars. The decrease in tar as the pyrolysis temperature increased from 550 to 700 °C is attributed to the secondary reactions occurring at high temperatures: mainly oil vapor cracking into gaseous products. Such results are in full agreement with those reported for different biomass samples and also for oil shales [26].

### 3.2.4. Product yields for peach pulp pyrolysis at optimum conditions

Pyrolysis experiments performed with apricot pulp showed that maximum bio-oil yield was attained at 500–550 °C pyrolysis temperature under static atmosphere. When nitrogen was used as the sweeping gas, 100 cm<sup>3</sup> min<sup>-1</sup> flow rate gave the highest bio-oil yield. Using the optimum conditions set above, peach pulp was

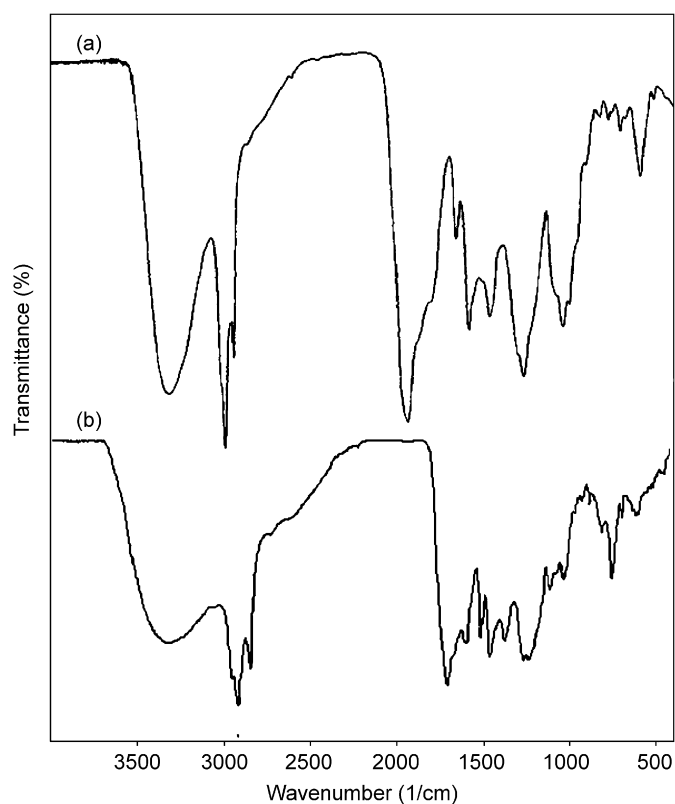


Fig. 4. FT-IR spectra of bio-oils obtained under static atmosphere from (a) apricot pulp and (b) peach pulp.

Table 2  
Results of <sup>1</sup>H-NMR spectra for bio-oils

Type of hydrogen	Chemical shift (ppm)	Apricot pulp <sup>a</sup>			Peach pulp		
		Static <sup>b</sup>	Nitrogen <sup>c</sup>	Steam <sup>d</sup>	Static <sup>b</sup>	Nitrogen <sup>c</sup>	Steam <sup>d</sup>
Aromatics	6.5–9.0	3.96	4.41	6.67	14.27	22.86	15.05
Phenolic OH or olefinic proton	5.0–6.5	0.85	0.81	1.95	6.31	13.69	5.21
Ring joining methylene (Ar–CH <sub>2</sub> –Ar)	3.3–4.5	17.93	3.26	8.54	9.96	13.94	11.75
CH <sub>3</sub> , CH <sub>2</sub> , CH <sub>x</sub> to an aromatic ring	2.0–3.3	19.65	28.84	34.64	36.83	31.07	33.57
CH <sub>2</sub> , CH <sub>β</sub> to an aromatic ring (naphthenic)	1.6–2.0	8.20	2.77	7.14	3.28	4.42	5.57
βCH <sub>3</sub> , CH <sub>2</sub> , and CH <sub>γ</sub> or further from an aromatic ring	1.0–1.6	41.39	46.29	30.42	19.61	22.79	16.75
CH <sub>3γ</sub> or further from an aromatic ring	0.5–1.0	10.25	13.62	10.63	9.74	14.14	12.07

<sup>a</sup> Published in Fuel Processing Technology 87 (2006) 1013–1019 as Table 5.

<sup>b</sup> Bio-oil from static atmosphere (550 °C, 5 °C min<sup>-1</sup>).

<sup>c</sup> Bio-oil from nitrogen atmosphere (550 °C, 100 cm<sup>3</sup> min<sup>-1</sup>, 5 °C min<sup>-1</sup>).

<sup>d</sup> Bio-oil from steam atmosphere (550 °C, 2.5 cm<sup>3</sup> min<sup>-1</sup>, 5 °C min<sup>-1</sup>).

also pyrolyzed to obtain yields for it. When static pyrolysis was applied at about 550 °C peach pulp gave solid and bio-oil yields as 26.7% and 21.8%, respectively. Under nitrogen gas flow (with a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>), bio-oil yield increased with 6.7% and reached a value of 23.2%; on the other hand, char yield was decreased to 25.7%. Like apricot pulp, peach pulp gave the highest bio-oil yield when steam was used. Char and bio-oil yields were calculated to be 25.2% and 27.7%, respectively at 550 °C and with a steam flow rate of 2.5 m<sup>3</sup> min<sup>-1</sup>.

### 3.3. Bio-oil composition

The main objective of this study is to characterize bio-oils obtained under different atmospheres and to investigate the effect of pyrolysis atmosphere on bio-oil quality.

Elemental compositions of apricot pulp bio-oils and their sub-fractions from static, sweeping gas (N<sub>2</sub>) and steam atmospheres are given in the previous study [10]. Table 1 gives the results for these bio-oils and peach pulp bio-oils. Generally all bio-oils obtained under three different conditions have low oxygen content and high H/C ratios than original feedstock. Comparison of H/C ratios with conventional fuels indicates that the H/C ratios of the oils obtained in this study lie between those of light and heavy petroleum products [12].

From Table 1, it could be noted that the calorific value of the apricot and peach pulp bio-oils presents a maximum value of 35.63 and 27.83 MJ kg<sup>-1</sup> respectively under steam atmosphere, the same as the maximum for bio-oil yield. This fact can be related with the presence of steam, and radical formation during pyrolysis. Steam acts as an oxidizing agent, causing some more reactions that lead the formation of more carbonaceous products [13]. Other four bio-oils have similar calorific values indicating that presence of sweeping gas improves the quality a little [10].

### 3.3. FTIR analysis

FT-IR spectra of the apricot and peach pulp bio-oils obtained at under static atmosphere are given in Fig. 4.

The presence of a large intense band of intermolecular hydrogen bonds of O–H stretching vibration at 3350 cm<sup>-1</sup>; and, moreover, the in-plane bending at 1246 cm<sup>-1</sup> and out-of-plane bending at 668 cm<sup>-1</sup> are the indications of associated O–H groups. While considering the infrared spectra, it can be seen that the absorption bands between 3100 and 3018 cm<sup>-1</sup> regions (aromatic C–H stretching vibration) indicate the aromaticity of the bio-oils.

The presence of paraffinic compounds are evidenced by the 2918–2850 cm<sup>-1</sup> absorption bands arising from the C–H

stretching vibration, and by the 1450 and 1375  $\text{cm}^{-1}$  bands of C–H bending of the methyl and methylene groups. Paraffinic stretching vibration absorption bands are also acquired in a shape stronger and sharp-edged, in the bio-oil obtained under steam atmosphere. The stretching vibration at 1707  $\text{cm}^{-1}$  is an indication of the ketonic functional group. The presence of the olefinic compounds is confirmed by the band at 1645  $\text{cm}^{-1}$ , represent C=C stretching vibration.

### 3.5. $^1\text{H-NMR}$ analysis

$^1\text{H-NMR}$  spectra were applied to the oils of static, nitrogen, and water vapor atmospheres and hydrogen distribution of  $^1\text{H-NMR}$  is given in Table 2.  $^1\text{H-NMR}$  spectra can be divided into three main regions: aromatic, olefinic, and aliphatic, based on the chemical shifts of specific proton types. As state for the oil shales, aromatic, olefinic, and aliphatic resonances occur in the chemical shift regions of 9.0–6.0, 6.0–4.0, and 3.0–0.5 ppm, respectively [27].

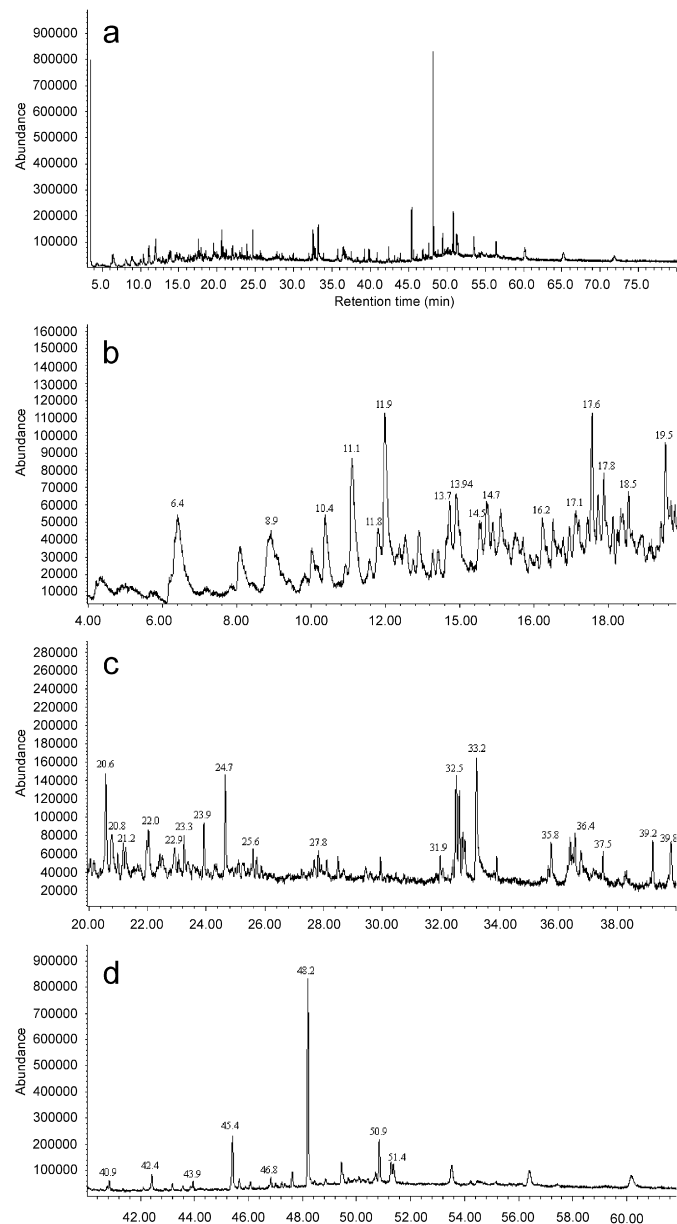


Fig. 5. (a–d) GC/MS chromatogram of bio-oil from apricot pulp obtained under steam atmosphere.

$^1\text{H-NMR}$  spectra of the bio-oils indicates that the aromaticity of the apricot pulp bio-oil of steam pyrolysis was higher than the static and nitrogen atmosphere pyrolysis whereas for peach pulp bio-oil nitrogen atmosphere gave the highest percentage of aromatics.

The protons in the  $\alpha$  positions to an aromatic ring of the apricot pulp bio-oil from steam pyrolysis are seen to be higher than the other bio-oils.  $\text{CH}_2$  and  $\text{CH}\beta$  to an aromatic ring (naphthenic) protons are very close to each other in amount for bio-oils under

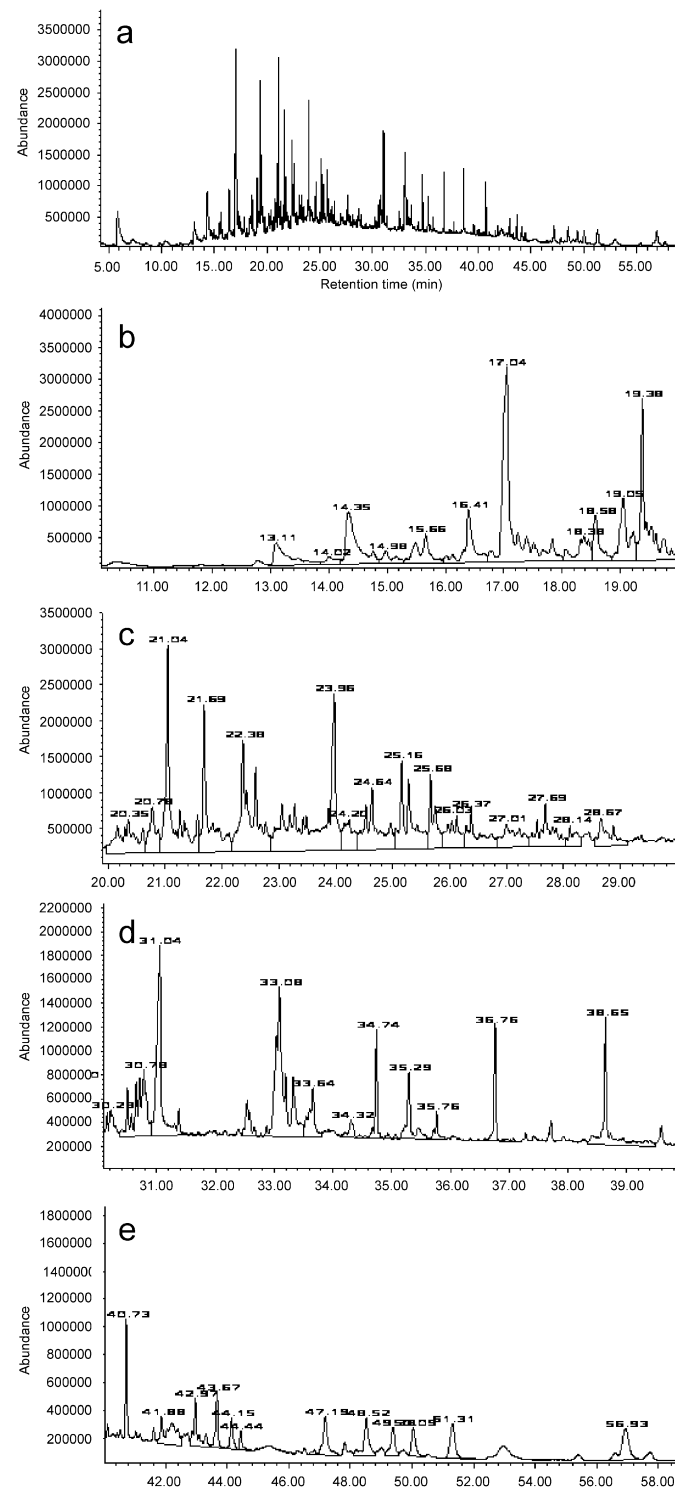


Fig. 6. (a–e) GC/MS chromatogram of bio-oil from peach pulp obtained under steam atmosphere.

**Table 3**  
Tentative GC/MS characterization of bio-oil under static atmosphere

Tentative assignment	Type of compound	Molecular formula	Apricot pulp			Peach pulp		
			Static <sup>a</sup>	Nitrogen <sup>b</sup>	Steam <sup>c</sup>	Static <sup>a</sup>	Nitrogen <sup>b</sup>	Steam <sup>c</sup>
2-Furancarboxaldehyde	ArO	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	–	–	–	–	–	+
2-Furancarboxaldehyde, 5-methyl	ArO	C <sub>6</sub> H <sub>7</sub> O <sub>2</sub>	–	–	–	–	–	+
Phenol	ArO	C <sub>6</sub> H <sub>5</sub> OH	+	–	+	+	+	+
2-Cyclopenten-1-one, 2-hydroxy-3-methyl	NAr	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	+	–	–	–	+	–
1,4-Benzenedicarboxaldehyde	ArO	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	+	–	–	–	–	–
2,3-Dimethyl-2-cyclopenten-1-one	NArO	C <sub>7</sub> H <sub>10</sub> O	+	–	+	+	–	+
Ethanone, 1-(2-furanyl)	ArO	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	+	–	+	–	–	–
Phenol, 4-methyl	ArO	C <sub>7</sub> H <sub>8</sub> O	+	–	–	–	–	–
Phenol, 2-methoxy	ArO	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	+	–	+	+	+	+
Phenol, 2-methyl	ArO	C <sub>7</sub> H <sub>8</sub> O	+	–	+	+	+	+
4-Octanone	NAr	C <sub>8</sub> H <sub>15</sub> O	+	+	–	–	–	–
Phenol, 2,3-dimethyl	ArO	C <sub>8</sub> H <sub>10</sub> O	+	–	+	–	–	–
Phenol, 2,4-dimethyl	ArO	C <sub>8</sub> H <sub>10</sub> O	–	+	+	+	+	+
Phenol, 2,5-dimethyl	ArO	C <sub>8</sub> H <sub>10</sub> O	+	+	+	–	–	–
Phenol, 3-ethyl	ArO	C <sub>8</sub> H <sub>10</sub> O	+	+	–	+	–	+
2-Methoxy-4-methyl phenol	ArO	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	+	+	–	+	+	–
Ethanone, 1-(2,5-dihydroxyphenyl)	ArO	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	+	–	–	–	–	–
Phenol, 2,6-dimethoxy	ArO	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	+	+	+	+	+	+
1,2-Benzenedicarboxylic acid (phthalic acid)	ArO	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	+	–	–	–	–	–
Phenol, 2,3,6-trimethyl	ArO	C <sub>9</sub> H <sub>11</sub> O <sub>2</sub>	–	+	+	–	+	+
Nonane	NAr	C <sub>9</sub> H <sub>20</sub>	+	+	–	–	–	–
Benzene, 1,2,3-trimethyl	Ar	C <sub>9</sub> H <sub>12</sub>	–	–	–	–	–	+
Phenol, 3-ethyl-5-methyl	ArO	C <sub>9</sub> H <sub>11</sub> O	+	+	+	–	–	–
Phenol, 4-ethyl-2-methoxy	ArO	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	+	–	+	–	+	+
2-Methoxy-4-propyl-phenol	ArO	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	–	–	–	–	+	–
3,4-Diethylphenol	ArO	C <sub>10</sub> H <sub>14</sub> O	+	–	–	–	–	–
Carvacrol	ArO	C <sub>10</sub> H <sub>14</sub> O	+	+	–	–	–	–
Thymol	ArO	C <sub>10</sub> H <sub>14</sub> O	+	–	–	–	–	–
Phenol, 2,5-diethyl	ArO	C <sub>10</sub> H <sub>14</sub> O	–	–	+	–	–	–
Cyclopropanoic acid, 2-octyl	NArO	C <sub>10</sub> H <sub>18</sub> O	+	–	–	–	–	–
Eugenol	ArO	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	+	–	–	–	–	–
Cis-isoeugenol	ArO	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	–	–	+	+	+	+
2-Octene, 2,6-dimethyl	NAr	C <sub>10</sub> H <sub>20</sub>	+	–	–	–	–	–
Naphthalene, 1,2,3,4-tetrahydro	Ar	C <sub>10</sub> H <sub>11</sub>	–	+	–	–	–	–
Naphthalene	Ar	C <sub>10</sub> H <sub>8</sub>	–	–	+	–	–	–
Phenol, 2-methoxy-4-(1-propenyl)-	ArO	C <sub>10</sub> H <sub>13</sub> O <sub>2</sub>	+	–	–	–	–	–
2,3,5-Trimethoxytoluene	Ar	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	+	+	–	+	+	+
Phenol, 2-methyl-5-(1-methylethyl)	ArO	C <sub>10</sub> H <sub>14</sub> O	–	+	–	–	–	–
Phenanthrene	Ar	C <sub>10</sub> H <sub>10</sub>	–	+	–	–	–	–
Phenol, 4-butoxy	ArO	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	+	–	–	–	–	–
Naphthalene, 1-methyl	Ar	C <sub>11</sub> H <sub>11</sub>	–	+	+	+	–	–
Undecane	NAr	C <sub>11</sub> H <sub>24</sub>	–	–	–	–	+	–
Benzoic acid, 2,4,6-trimethyl	ArO	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	–	+	–	–	+	–
Phenol, 2,6-dimethoxy-4-(2-propenyl)	ArO	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	–	–	–	–	–	+
Naphthalene, 2,7-dimethyl	Ar	C <sub>12</sub> H <sub>12</sub>	+	+	+	–	–	–
2,7-Dimethylnaphthalene	Ar	C <sub>12</sub> H <sub>12</sub>	+	–	–	–	–	–
1,4-Dimethoxy-4-(2-propenyl)	ArO	C <sub>12</sub> H <sub>18</sub> O <sub>2</sub>	–	–	–	–	–	+
2-Ethyl-4,6-Dimethylindane	Ar	C <sub>13</sub> H <sub>19</sub>	+	–	–	–	–	–
2,3,5-Trimethylnaphthalene	Ar	C <sub>13</sub> H <sub>14</sub>	+	+	+	–	–	+
9H-Fluorene	Ar	C <sub>13</sub> H <sub>10</sub>	–	+	–	–	–	–
9H-Fluorene, 4-methyl	Ar	C <sub>14</sub> H <sub>12</sub>	–	+	–	–	–	–
1,13-Tetradecadiene	NAr	C <sub>14</sub> H <sub>26</sub>	–	+	+	–	–	–
Naphthalene, 1-(1,1-dimethylethyl)	Ar	C <sub>14</sub> H <sub>16</sub>	+	–	–	–	–	+
Tetradecane	NAr	C <sub>14</sub> H <sub>30</sub>	+	–	–	–	–	–
Azulene, 7-ethyl-1,4 dimethyl	Ar	C <sub>14</sub> H <sub>16</sub>	–	+	–	–	–	–
Pentadecane	NAr	C <sub>15</sub> H <sub>32</sub>	–	+	+	–	+	+
Cyclopentadecanone	NArO	C <sub>15</sub> H <sub>28</sub> O	–	+	–	–	–	–
1,1-Diphenylpropane	Ar	C <sub>15</sub> H <sub>16</sub>	+	–	–	–	–	–
Ambrettolide	NArO	C <sub>16</sub> H <sub>28</sub> O <sub>2</sub>	+	+	+	–	–	–
Hexadecane	NAr	C <sub>16</sub> H <sub>34</sub>	+	+	+	–	–	–
Hexadec-7-en-16-olide	NArO	C <sub>16</sub> H <sub>28</sub> O <sub>2</sub>	+	+	+	–	+	–
Hexadecanoic acid	NArO	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	+	+	+	+	+	+
8-Heptadecene	NAr	C <sub>17</sub> H <sub>32</sub>	–	+	–	–	–	–
Heptadecane	NAr	C <sub>17</sub> H <sub>36</sub>	+	+	+	–	–	–
Octadecane	NAr	C <sub>18</sub> H <sub>38</sub>	+	+	+	–	–	–
Linoleic acid	NArO	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	+	–	+	+	+	+
9,12-Octadecadien-1-ol	NArO	C <sub>18</sub> H <sub>34</sub> O	+	–	–	–	–	–
1-Octadecene	NAr	C <sub>18</sub> H <sub>36</sub>	+	+	–	–	–	–
Nonadecane	NAr	C <sub>19</sub> H <sub>40</sub>	–	+	+	+	+	+
1-Nonadecene	NAr	C <sub>19</sub> H <sub>36</sub>	–	+	–	–	–	–
Eicosane	NAr	C <sub>20</sub> H <sub>42</sub>	+	+	–	–	–	+
Heneicosane	NAr	C <sub>21</sub> H <sub>44</sub>	+	+	+	–	+	+
Docosane	NAr	C <sub>22</sub> H <sub>46</sub>	+	+	–	+	+	+

Table 3 (continued)

Tentative assignment	Type of compound	Molecular formula	Apricot pulp			Peach pulp		
			Static <sup>a</sup>	Nitrogen <sup>b</sup>	Steam <sup>c</sup>	Static <sup>a</sup>	Nitrogen <sup>b</sup>	Steam <sup>c</sup>
Docosanol	NArO	C <sub>22</sub> H <sub>46</sub> O	–	+	–	–	–	–
Tricosane	NAr	C <sub>23</sub> H <sub>48</sub>	+	–	+	–	–	–
Cyclotetracosane	NAr	C <sub>24</sub> H <sub>48</sub>	+	–	–	–	–	–
Pentacosane	NAr	C <sub>25</sub> H <sub>52</sub>	–	–	+	–	+	+
9-Hexacosene	NAr	C <sub>26</sub> H <sub>52</sub>	+	–	–	–	–	–
Hexacosane	NAr	C <sub>26</sub> H <sub>54</sub>	+	–	–	–	–	–
9-Hexacosene	NAr	C <sub>26</sub> H <sub>52</sub>	+	–	–	–	–	–
Heptacosane	NAr	C <sub>27</sub> H <sub>56</sub>	+	–	–	+	–	–
Nonacosane	NAr	C <sub>29</sub> H <sub>60</sub>	+	–	–	+	–	+
2,6,10,14,18,22-Tetracosahexaene	NAr	C <sub>30</sub> H <sub>50</sub>	+	–	–	–	–	–

<sup>a</sup> Bio-oil from static atmosphere (550 °C, 5 °C min<sup>-1</sup>).

<sup>b</sup> Bio-oil from nitrogen atmosphere (550 °C, 100 cm<sup>3</sup> min<sup>-1</sup>, 5 °C min<sup>-1</sup>).

<sup>c</sup> Bio-oil from steam atmosphere (550 °C, 2.5 cm<sup>3</sup> min<sup>-1</sup>, 5 °C min<sup>-1</sup>).

static and nitrogen atmosphere while bio-oil under nitrogen atmosphere has a lower value.

$\beta$ -CH<sub>3</sub>, CH<sub>2</sub> and CH<sub>γ</sub> or further from an aromatic ring protons (centered at 1.25 ppm) of the bio-oils from apricot and peach pulps under nitrogen atmosphere are greater than that of the other bio-oils. CH<sub>3γ</sub> or further from an aromatic ring protons are seen as all bio-oils but in different amounts.

### 3.6. Gas chromatography/mass spectroscopy (GC/MS) analysis

GC/MS analyses were carried out with the pyrolysis oils obtained static, sweeping gas (N<sub>2</sub>), and steam atmosphere. The objective was to get an idea of the nature and type of compounds of such oils, in order to establish the possible ways of reusing or treating and reusing them. Figs. 5 and 6 show the GC/MS chromatogram of bio-oil from apricot and peach pulps obtained under steam atmosphere: Fig. (a) shows the whole chromatogram, while Fig. (b)–(e) correspond to enlarged fragments of it and for all figures retention time have been numbered.

Table 3 indicates the tentative compounds assigned for every identified peak. It can be seen that, as expected, fruit pulp pyrolysis oils are a very complex mixture of organic compounds of 5–29 carbons. The most abundant products, with peak areas around or greater than 2%, are pentacosane, octadecane, heneicosane, 2 methoxy phenol, ambrettolide, hexadecanoic acid, 4 octanone, 1,2 benzenedicarboxylic acid, heptacosane, nonacosane, and 2,3 dimethyl phenol. There are such great numbers of compounds but their peak areas are very low, they are not examined in this study.

Every compound in Table 3 has been classified as aromatic (Ar), non-aromatic (NAr), oxygenated aromatic (ArO), and oxygenated non-aromatic (NArO). The aromaticity of apricot pulp pyrolysis oils is due to cyclization of olefin structures followed by dehydrogenation reaction, which take place during the pyrolysis process.

Table 3 also illustrates that there are several polycyclic aromatic compounds such as alkylated naphthalenes, phenanthrenes, fluorenes, etc. in the bio-oils. It can be seen that alkylated naphthalenes are present in all of apricot pulp bio-oils while phenanthrenes and fluorenes are present only in sweeping gas atmosphere.

Table 3 shows that there are several oxygenated compounds, such as phenols, acids, aldehydes, etc. The presence of these compounds may be explained by the thermal degradation of oxygenated components of the fruit pulp. Furancarboxaldehyde, which is due to the presence of hemicellulose in the biomass sample, exists only in the peach pulp bio-oil obtained from steam pyrolysis.

## 4. Conclusions

- This study shows fixed-bed pyrolysis of biomass samples, apricot and peach pulp, under different atmospheres in order to obtain synthetic liquid fuels. The results are compared with those obtained in static, sweeping gas and steam atmosphere. The presence of steam has increased the yield of liquid pyrolysis products at the expense of the gaseous and solid products. The maximum apricot pulp bio-oil yield, 27.2%, was reached under steam atmosphere when steam velocity was 2.5 cm<sup>3</sup> min<sup>-1</sup>. Peach pulp was then pyrolyzed under optimum conditions and its bio-oil yield reached to its maximum, 27.7%, when steam was used as the pyrolysis agent.
- Comparison of H/C ratios with conventional fuels has shown that the H/C ratios of the bio-oils obtained in this work is between those of light and heavy petroleum products.
- Bio-oils obtained under steam atmosphere have the highest calorific value when compared with other bio-oils obtained under static and nitrogen gas atmospheres and raw material.
- According to <sup>1</sup>H-NMR spectra of the bio-oils, it is indicated that the aromaticity of the bio-oils from apricot and peach pulp reached its maximum value under steam and nitrogen atmosphere, respectively.
- Fruit pyrolysis oil are a complex mixture of C<sub>5</sub>–C<sub>29</sub> organic compounds, with a lot of aromatic (Ar), non-aromatic (NAr), oxygenated aromatic (ArO), and oxygenated non-aromatic (NArO). They are an important proportion of polycyclic aromatics such as naphthalenes, phenanthrenes, fluorenes, etc. Significant quantities of valuable oxygenated compounds such as fluorenes, naphthalenes, phenols, acids were obtained.
- Bio-oil obtained under these conditions can be utilized as either synthetic fuels or chemical feedstock.

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