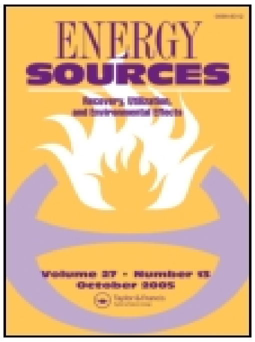

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

ISSN: 1556-7036 (Print) 1556-7230 (Online) Journal homepage: www.tandfonline.com/journals/ueso20

Pyrolysis of Peach Pulp: Effect of Chemical Additives

N. Özbay & A. E. Pütün

To cite this article: N. Özbay & A. E. Pütün (2014) Pyrolysis of Peach Pulp: Effect of Chemical Additives, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 36:23, 2546-2554, DOI: 10.1080/15567036.2011.569841

To link to this article: https://doi.org/10.1080/15567036.2011.569841

Energy Sources, Part A, 36:2546–2554, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1556-7036 print/1556-7230 online
DOI: 10.1080/15567036.2011.569841

Pyrolysis of Peach Pulp: Effect of Chemical Additives

N. Özbay[1] and A. E. Pütün[2]
[1]*Department of Process and Chemical Engineering, Bilecik University, Bilecik, Turkey*
[2]*Department of Chemical Engineering, Anadolu University, Eskisehir, Turkey*

Peach pulp and impregnated sample have been investigated as an alternative feedstock to obtain fuels and chemicals. The effect of a series of operation variables was studied. The maximum oil was obtained as 23.24% at the final temperature of 550°C. The maximum char yield was obtained as 48.7% by H_3PO_4 impregnated samples. The liquids products obtained under the most suitable conditions were characterized by elemental analysis, Fourier transform-infrared, 1H NMR. In addition, gas chromatography/mass spectrophotometer was achieved on all pyrolysis oils. According to the experimental results, it showed that bio-oil could be a potential source for synthetic fuels and chemical feedstock.

Keywords: characterization, peach pulp, pyrolysis

1. INTRODUCTION

Biomass is a renewable energy that has social, political, and economic advantages. Indeed, pyrolysis of these materials produces oils that can be used for energy production and value added chemicals, such as phenolics, levoglucosan, octane enhancers, and fertilizers. Gases utilizable as fuels in the same plant are also obtained. The third product, solid char, can be used as fuel or as a feedstock to prepare activated carbons (Blanco Lopez et al., 2002; Meier and Faix, 1999; Uzun et al., 2007).

Vegetable residues exhibit a high degree of heterogeneity as a function of their origin, and thus the proportion of different products formed during pyrolysis (oil, gas, char) varies widely among materials. The distribution of the compounds in bio-oil mostly depends on the type of biomass used and on the process severity (Raveendran et al., 1996).

In this study, peach pulp, a food industry waste generated by the fruit juice factories, is taken as the biomass sample for pyrolysis experiments. Peach (*Prunus persica*) is classified under Prunus species. It is a deciduous tree belonging to the sub-family Prunoideae of the family Rosaceae. Important peach-producing countries are China, United States, Italy, Greece, Spain, France, Turkey, Mexico, and Argentina. Turkey's peach production was about 553,000 tons in 2006 (Turkish Statistical Institute, 2007).

Address correspondence to Nurgül Özbay, Department of Process and Chemical Engineering, Bilecik University, Bilecik, Turkey. E-mail: nozbay@anadolu.edu.tr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/ueso.

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

2. EXPERIMENTAL

2.1. Feed Stocks

Peach pulp used in this work was obtained from fruit juice factories around Bursa, located in Western Anatolia. Air-dried pulps were ground to obtain a uniform material of an average particle size ($0.600 < D_p < 1{,}250$ mm). On the other hand, peach pulps were impregnated with analytical grade of $AlCl_3$, NH_4Cl, and H_3PO_4 in aqueous solution. After impregnation, the samples were dried at 110°C for 4 h in air. Impregnation ratios of 10 wt% were used. Raw and impregnated samples with $AlCl_3$, NH_4Cl, and H_3PO_4 are designated as PP, PPA, PPN, and PPH, respectively.

2.2. Pyrolysis Procedure

The pyrolysis of samples was carried out in a tubular reactor. The 316 stainless steel tubular reactor was 61.4 cm in height and has an internal diameter of 3.64 cm. A stream of nitrogen was introduced at the top of the reactor. To determine the effect of the pyrolysis temperature on pyrolysis yields, a 10-g air-dried raw sample was placed into the reactor and a sweep gas velocity of 100 cm^3 min^{-1} was controlled and measured with a rotameter. The sample was heated with a heating rate of 70°C min^{-1} up to the selected final pyrolysis temperatures of 400, 450, 500, 550, and 700°C and held at that temperature for 10 min or until no further significant release of gas was observed. The second group of experiments was performed to determine the impregnation effect on pyrolysis yields by taking into account the highest oil yields of the first group of experiments. Liquid products were condensed in traps and the aqueous layer was separated from the organic layer by use of dichloromethane in a separating funnel. The solvent was removed in a rotary evaporator at 40°C and the residual was weighed as the oil. The residual solid in the reactor was weighed as char. The gas yield was then calculated by taking the difference.

2.3. Characterization

The elemental analyses of bio-oils were performed by using Carlo Erba EA 1108-type equipment for C, H, and N. Oxygen was determined by difference. The liquid fractions were characterized in the transmission mode between 4,000 and 400 cm^{-1} using a Bruker Tensor 27 Model Fourier transform infrared spectrometer.

Nuclear magnetic resonance (NMR) analysis was used to determine the percentage of aromatic, paraffinic, and olefinic species in bio-oils. These measurements were performed using Bruker DPX-400, 400 MHz high performance digital FT-NMR instruments. The liquid samples were diluted in tetramethyl silane-containing deuterated chloroform.

All pyrolysis oils were analyzed with an HP 6890 gas chromatograph equipped with a 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°C, respectively; retention times at initial and final temperatures were both 10 min; and the heating rate was 8°C min^{-1}.

3. RESULT AND DISCUSSION

3.1. Biomass Characteristics

Proximate analysis of peach pulp [wt% dry basis (db)] gave 9.3% moisture, 2.6% ash, and 70.2% volatile matter. Biopolymer analysis (wt%, db) gave 35.0% cellulose, 38.7% lignin, and 3.5% extractive. The elemental analysis of raw and impregnated materials is given in Table 1. It can be deduced from the elemental analysis that the impregnated materials with H_3PO_4 had lower carbon and nitrogen content than the other materials. Calorific value of PP, PPH, PPN, and PPA were calculated as 16.79, 10.56, 12.50, and 13.98 MJ kg^{-1}, respectively, using Du-Long's formula with the known values of elemental composition.

3.2. Pyrolysis Yields

To determine the effect of pyrolysis temperature on pyrolysis products yields, the experiments were conducted with a heating rate of 70°C min^{-1}, sweeping gas flow rate of 100 cm^3 min^{-1}, and at final temperatures of 400, 450, 500, 550, and 700°C. Results of the experiments are given in Figure 1. As can be seen, the char yield decreased from 38.56 to 25.38% when the final pyrolysis temperature was raised from 400 to 700°C. On the contrary, gas yield increased from 13.11 to 30.69% with the same temperature increase. Bio-oil yield was 17.01% at the pyrolysis temperature of 400°C; it appeared to go through a maximum of 23.24% at the final temperature of 550°C. At temperatures higher than 550°C, the oil yield again decreased to a value of 20.54%. Therefore, the optimum temperature for peach pulp pyrolysis was obtained to be 550°C.

To determine the effect of impregnation on pyrolysis products yields, the experiments were conducted with a heating rate of 70°C min^{-1}, sweeping gas flow rate of 100 cm^3 min^{-1}, and final temperature at 550°C. The yields of pyrolysis products are given in Figure 2. It was shown that

TABLE 1
Elemental Analyses (wt%) of Raw Materials and Bio Oils

	Raw Materials					
	C	*H*	*N*	*O*	*H/C*	*Calorific Values, Mj/Kg*
PP_R[a]	45.60	5.70	0.90	47.80	1.27	16.79
PPH_R[b]	37.50	5.61	0.90	56.68	1.79	10.56
PPN_R[c]	40.43	5.60	2.67	51.30	1.66	12.50
PPA_R[d]	43.64	5.52	2.38	48.46	1.52	13.98
	Bio Oils					
	C	*H*	*N*	*O*	*H/C*	*Calorific Values, Mj/Kg*
PP_B[a]	57.47	7.98	1.34	33.21	1.66	24.96
PPH_B[b]	55.92	6.80	0.66	36.62	1.45	22.11
PPN_B[c]	57.51	7.38	1.77	33.34	1.54	20.08
PPA_B[d]	58.26	8.08	0.86	32.80	1.55	25.45

[a] Peach pulp.
[b] Impegrenated peach pulp with H_3PO_4.
[c] Impegrenated peach pulp with NH_4CI.
[d] Impegrenated peach pulp with $AlCI_3$.

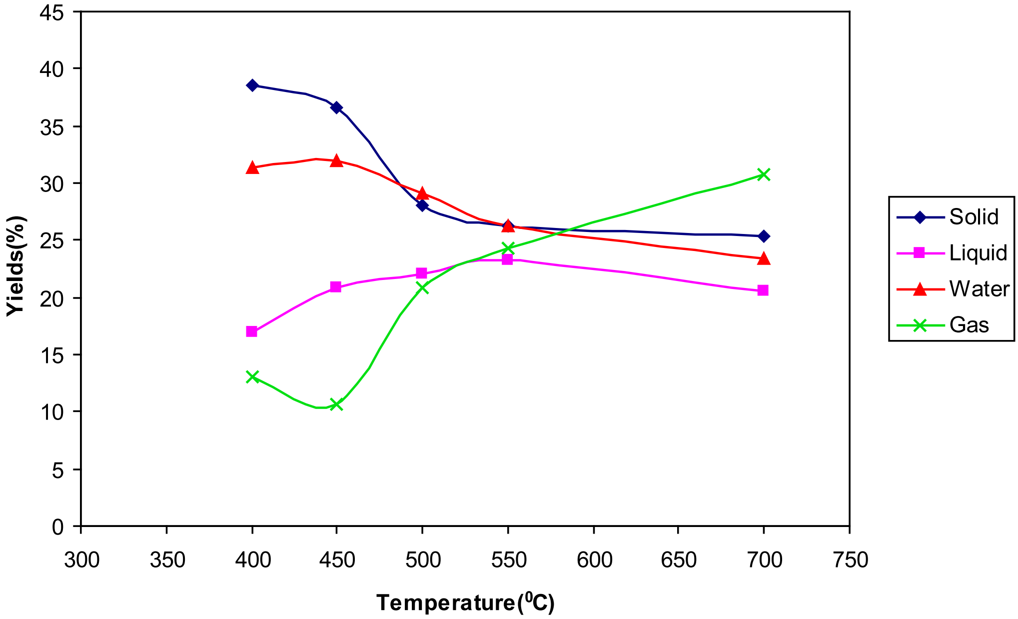

FIGURE 1 Effect of temperature on pyrolysis products yields.

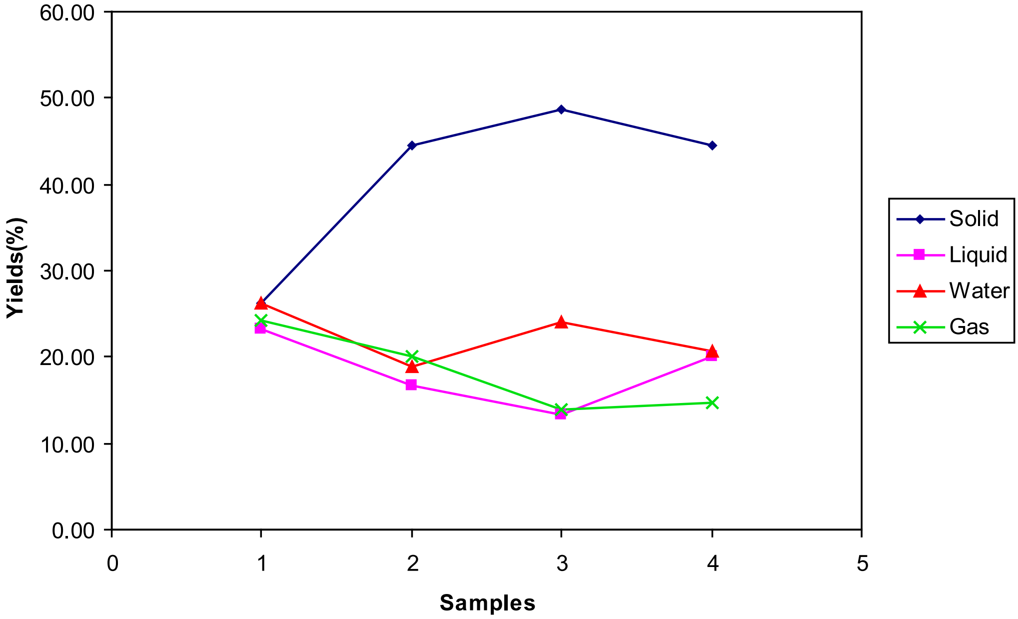

FIGURE 2 Effect of impregnation on pyrolysis products yields. 1: Bio oil obtained at 550°C; 2: Bio oil from impregnated samples with NH_4Cl; 3: Bio oil from impregnated samples with H_3PO_4; 4: Bio oil from impregnated samples with $AlCl_3$.

impregnation is strongly influenced by product distribution. The yield of solid product obtained from PP was lower than that of the other feedstocks. The maximum char yield was obtained as 48.7% by H_3PO_4 impregnated samples. H_3PO_4 has two important functions: it promotes the pyrolytic decomposition of the initial material and the formation of the cross-linked structure. The decomposition is promoted by the catalytic effect of phosphoric acid on the bond cleavage reactions (Budinova et al., 2006).

3.3. Bio-oil Characterization

Biomass pyrolysis oils contain a very wide range of complex organic chemicals (Bridgewater and Grassi, 1991; Antal, 1983; Mohan et al., 2006).

The elemental compositions of the oil characterized and calorific values are listed in Table 1. As seen in the tables, the bio-oils have more carbon and lower oxygen content than raw materials. Comparison of H/C ratio 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. From Table 1, it could be noted that the calorific values of oils from PP, PPH, PPN, and PPA are 24.96, 22.11, 20.08, and 25.45 MJ/Kg, respectively. Calorific values indicate that the energy contents of the oils are very close to that of petroleum products (Pütün et al., 2005).

3.3.1. Fourier Transform Infrared (FTIR) Analysis of Bio-oils

Table 2 shows the FTIR spectra, representing functional group compositional analysis of all pyrolysis oils. The O–H stretching vibrations between 3,245 and 3,334 cm^{-1} of the bio-oils indicate the presence of phenols and alcohols. The low frequency values for these bands suggest that the hydroxyl groups are involved in hydrogen bands. It can be seen from Table 2 that the O-H vibration band is not appearing in only bio-oils from PPH.

TABLE 2
FTIR Spectrum of the Bio Oils

Band Position, cm^{-1}	*Assignment*	*PP*[a]	*PPH*[b]	*PPN*[c]	*PPA*[d]
3,415–3,406	υ (O–H)	+	−	+	+
3,003	υ (C–H), aromatic ring stretching	+	+	+	+
2,926–2,863	υ (C–H)	+	+	+	+
1,710	υ (C=O)	+	+	+	
1,661–1,626	υ (C=C)	+	+	−	+
1,558, 1,517	υ (C=C), aromatic ring	+	+	+	+
1,463	δ_{as} (CH_3, CH_2)	+	+	+	+
1,424	δ_s (OH)	−	−	+	−
1,383–1,377	δ_s (CH_3)	+	+	+	+
1,256	δ_{as} (=C–O–C)	+	+	+	+
1,155	δ_{as} (C–O–C)	+	−	−	−
1,052–1,029	δ (C–O), OH primary	−	−	+	+
755–738	γ (C–H)	+	+	+	+
625	γ (=CH)	+	−	−	−

[a] Peach pulp.

[b] Impegrenated peach pulp with H_3PO_4.

[c] Impegrenated peach pulp with NH_4CI.

[d] Impegrenated peach pulp with $AlCI_3$.

The presence of methyl and methylene groups is shown by a spectral appearance of ν (C–H) and δ (C–H) absorption bands. The presence of detection of two such bands at 2,852 and 2,927 cm^{-1} are connected with ν_{as} (C–H) and δ_s (C–H) vibrations. A further band due to δ_{as} (C–H) vibrations should appear at 1,460 cm^{-1}. Since stretching vibrations in aromatic rings also produces absorptions between 1,450 and 1,500 cm^{-1}, the occurrence of band overlapping in this region of the spectrum seems likely. Other bending vibrational modes for the CH_2 groups (i.e., rocking, wagging, twisting) gives rise to bands at lower frequencies. These bands are usually weak, and therefore of little practical utility (Gomez-Serrano et al, 1996; Suarez-Garcia et al., 2002).

The υ (C=C) absorptions occur between 1,700 and 1,400 cm^{-1}. Especially, olefinic υ (C=C) vibrations could be the cause of the band at 1,645 cm^{-1} and skeletal C=C vibrations in aromatic rings band in the 1,660–1,430 region of the spectrum (Gomez-Serrano et al., 1999, 2002). The stretching vibration of alkenes (C=C) bio-oils from PP, PPH, and PPN are observed in 1,650 cm^{-1}. Additionally, this band is as well compatible with the result of GC and GC/MS of bio-oils.

The C–H stretching vibrations of aliphatic bonding to the aromatic ring at 2,900 and 2,960 cm^{-1} are important evidence of the aromatic compounds. According to some previous works (Pütün et al., 1999), single ring aromatic and alkylated aromatic compounds, such as benzene, toluene, and polycyclic aromatic compounds, were previously identified in biomass-derived pyrolysis oils. Indeed absorption peaks between 698–900 and 1,420–1,610 cm^{-1} indicate mono and polycylic substituted aromatic groups.

3.3.2. ^{1}H-NMR Analysis of Bio-oils

^{1}H-NMR spectra were applied to the bio-oils from PP, PPH, PPN, and PPA, and the results are given in Table 3. ^{1}H-NMR spectra of the bio-oils indicates that the aromaticity of bio-oil from PP was higher than the other bio-oils. The protons in the α positions to an aromatic ring of the bio-oils from PPA and PPN and bio-oils from PPH and PP are in very similar amounts. CH_2 and CH β to an aromatic ring (napthenic) proton are very close to each other in amount for all bio-oils. β-CH_3, CH_2, and CH γ or further from an aromatic ring proton (centered at 1.25 ppm) of the bio-oils from PPN are greater than that of the other bio-oils. CH_3 γ or further from aromatic ring protons are seen for all bio-oils but in different amounts (Table 3).

3.3.3. Gas Chromatography/Mass Spectroscopy (GC/MS) Analysis

GC/MS analyses were carried out with the bio-oils obtained from PP, PPH, PPN, and PPA. 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 them. The distribution of compounds in bio-oils was determined using a semi-quantitative study by means of the percentage area of the chromatographic peaks.

Table 4 indicates the tentative compounds assigned for every identified peak. Every compound has been classified as aromatic (Ar), non-aromatic (NAr), oxygenated aromatic (ArO), or oxygenated non-aromatic (NArO). It can be seen that, as expected, PP pyrolysis oils are a very complex mixture of organic compounds of 6–30 carbons. There are such a great number of compounds in PP bio-oils that the peak is very low. It can be seen in Table 4 that there are an important proportion of aliphatic compounds, such as *n*-alkanes, alkenes, and branched hydrocarbons. The percentage of totally aliphatic compounds from PP, PPH, PPN, and PPA are 18.44, 22.21, 17.90, and 11.98%, respectively.

Table 4 also illustrates that there are several polycyclic aromatic compounds (PAH), such as alkylated naphthalenes, phenanthrenes, etc., in the bio-oils. It can be seen that alkylated naphthalenes are present in all of the bio-oils, while phenanthrenes are present only in bio-oils obtained from PPN. Table 4 shows that there are several oxygenated compounds, such as phenols, acids, aldehydes, etc. Phenolic compounds are also the main products obtained by pyrolysis. The

TABLE 3
Results of ^{1}H-NMR Spectra of Bio Oils

Type of Hydrogen	*Chemical Shift, ppm*	*PP*[a]	*PPH*[b]	*PPN*[c]	*PPA*[d]
Aromatics	6.5–9.0	16.54	15.98	11.95	13.24
Phenolic OH or olefinic proton	5.0–6.5	4.28	3.60	3.65	2.60
Ring-join methylene (Ar–CH_2–Ar)	3.3–4.5	8.63	3.85	4.74	4.46
CH_3, CH_2, CH α to an aromatic ring	2.0–3.3	27.99	30.43	24.30	30.99
CH_2, CH β to an aromatic ring (napthenic)	1.6–2.0	4.39	4.30	5.42	5.47
β CH_3, CH_2, and CHγ or further from an aromatic ring	1.0–1.6	26.24	24.68	35.38	27.50
$CH_3\gamma$ or further from an aromatic ring	0.5–1.0	11.93	17.16	14.56	13.24

[a] Peach pulp.
[b] Impegrenated peach pulp with H_3PO_4.
[c] Impegrenated peach pulp with NH_4CI.
[d] Impegrenated peach pulp with $AlCI_3$.

TABLE 4
Tentative GC/MS Characterization of Bio Oil

Tentative Assigment	*Type of Compound*	*Molecular Formula*	*PP*[a]	*PPN*[b]	*PPH*[c]	*PPA*[d]
2-Furan methanol	ArO	$C_5H_6O_2$	0.26	—	0.80	—
5-Methyl furfural	ArO	$C_6H_6O_2$	1.33	—	—	—
Phenol	ArO	C_6H_5OH	3.55	2.29	6.63	4.47
2-Cyclopenten-1-one. -3-methyl	NArO	C_6H_8O	0.33	—	—	—
2-Cyclopenten-1-one. 2-hydroxy-3-methyl	NArO	$C_6H_8O_2$	1.35	—	—	—
2.3-Dimethyl-2-cyclopenten-1-one	NArO	$C_7H_{10}O$	1.64	—	—	—
3-Methyl-cyclopenten-2-one	NArO	C_6H_8O	0.07	—	—	—
Phenol. 4-methyl	ArO	C_7H_8O	1.71	3.23	—	8.33
Phenol. 2-methoxy	ArO	$C_7H_8O_2$	8.31	2.02	7.08	—
Phenol. 2-methyl	ArO	C_7H_8O	2.45	0.70	2.30	3.32
1.2-Dimethyl benzene	ArO	$C_8H_{10}O$	0.38	—	—	—
Phenol. 2.4-dimethyl	ArO	$C_8H_{10}O$	1.03	—	—	—
Phenol. 3-ethyl	ArO	$C_8H_{10}O$	2.80	1.59	—	2.81
Benzaldehyde. 4-methyl	ArO	C_8H_8O	0.64	—	—	—
2-Methoxy-4-methyl phenol	ArO	$C_8H_{10}O2$	4.05	—	1.10	—
2-Methoxy-4-ethyl phenol	ArO	$C_9H_{10}O_2$	4.10	1.25	2.38	2.89
Phenol. 2.4.5-trimethyl	ArO	$C_9H_{11}O_2$	0.55	—	—	—
4-Methyl. 2.5-dimethoxy benzaldehyde	ArO	$C_9H_{10}O_3$	1.56	—	—	—
Vanillin	ArO	$C_8H_8O_3$	—	—	1.54	1.68
1.2.3-Trimethyl cyclohexane	NAr	C_9H_{18}	0.49	—	—	—
Cyclodecane	NAr	$C_{10}H_{20}$	0.51	—	—	—
1-Dodecanol	NAr	$C_{12}H_{26}O$	0.62	—	—	—
Eugenol	ArO	$C_{10}H_{12}O_2$	1.66	—	—	—

(*continued*)

TABLE 4
(*Continued*)

Tentative Assigment	*Type of Compound*	*Molecular Formula*	*PP*^{a}	*PPN*^{b}	*PPH*^{c}	*PPA*^{d}
Cis-Isoeugenol	ArO	$C_{10}H_{12}O_2$	2.76	—	—	—
Naphthalene. 1.2.3.4-tetrahydro	Ar	$C_{10}H_{11}$	—	0.83	1.88	0.97
Naphthalene. 1.4-dihydro	Ar	$C_{10}H_{13}$	0.25	—	—	—
1H-Indene. 1-methy	Ar	$C_{12}H_{14}$	0.64	—	1.41	—
2.3-Dimethyl anisole		$C_8H_{10}O$	0.45	—	—	—
Phenanthrene	Ar	$C_{10}H_{10}$	0.14	—	—	—
Naphthalene. 1-methyl	Ar	$C_{11}H_{11}$	1.76	—	1.57	1.85
Buthyl hydroxy toluene	Ar	$C_{15}H_{24}O$	12.63	—	—	—
Benzoic acid. 4-hydoxy-3-methoxy	ArO	$C_8H_8O_4$	—	—	—	1.36
4-Vinyl. 2-methoxy phenol	ArO	$C_9H_{10}O_2$	—	—	—	—
Phenol. 2.6-dimethoxy	ArO	$C_8H_{10}O_3$	0.72	—	—	—
Naphthalene. 2.7-dimethyl	Ar	$C_{12}H_{12}$	0.80	—	—	—
Tridecane	Nar	$C_{13}H_{28}$	1.36	—	—	—
Tridecane. 7-methylene	Nar	$C_{14}H_{30}$	0.89	—	—	—
Tridecadiene	Nar	$C_{13}H_{24}$	—	—	4.90	—
Trimethyl naphthalene	Ar	$C_{13}H_{14}$	—	1.63	0.79	0.98
Cyclotetradecane	NAr	$C_{14}H_{28}$	0.75	—	—	—
1.13-Tetradecadiene	NAr	$C_{14}H_{26}$	0.44	—	—	—
1-Tetradecene	NAr	$C_{14}H_{28}$	0.65	—	—	—
Tetradecane	NAr	$C_{14}H_{30}$	0.53	—	5.96	
Pentadecane	NAr	$C_{15}H_{32}$	0.97	—	—	1.22
1-Pentadecene	NAr	$C_{15}H_{30}$	—	0.69	—	—
Ambrettolide	NArO	$C_{16}H_{28}O_2$	0.30	—	—	—
1-Hexadecene	NAr	$C_{16}H_{32}$	—	0.56	—	—
Hexadecanoic acid	NArO	$C_{16}H_{32}O_2$	0.86	10.06	12.19	—
1-Heptadecene	NAr	$C_{17}H_{34}$	—	0.51	—	0.40
Heptadecane	NAr	$C_{17}H_{36}$	1.93	—	0.48	—
6.8-Heptadecadiene	NAr	$C_{17}H_{32}$	—	—	—	—
Octadecane	NAr	$C_{18}H_{38}$	0.39	—	—	—
Lineloic acid	NArO	$C_{18}H_{32}O_2$	0.35	—	12.47	4.12
Octadecanoic acid	NArO	$C_{18}H_{36}O_2$	—	1.13	2.35	9.47
9.12-Octadecadien-1-ol	NarO	$C_{18}H_{34}O$	—	5.11	—	—
1-Octadecene	Nar	$C_{18}H_{36}$	0.24	—	—	—
Nonadecane	Nar	$C_{19}H_{40}$	0.69	—	1.73	1.98
2-Nonadecene	Nar	$C_{19}H_{36}$	0.57	—	—	—
Eicosane	Nar	$C_{20}H_{42}$	1.85	—	—	—
Heneicosane	Nar	$C_{21}H_{44}$	0.46	—	—	—
Tricosane	Nar	$C_{23}H_{48}$	—	2.84	—	—
Cyclotetracosane	Nar	$C_{24}H_{48}$	—	—	0.82	—
Methyl-Tetracosane	Nar	$C_{25}H_{52}$	—	—	3.21	—
Pentacosane	NAr	$C_{25}H_{52}$	1.97	3.02	2.56	2.43
Heptacosane	NAr	$C_{27}H_{56}$	—	3.13	2.55	2.56
Octacosane	NAr	$C_{28}H_{58}$	—	—	—	3.21
Nonacosane	NAr	$C_{29}H_{60}$	1.77	—	—	—
2.6.10.14.18.22-Tetracosahexaene	NAr	$C_{30}H_{50}$	—	—	—	—

[a] Peach pulp.
[b] Impegrenated peach pulp with H_3PO_4.
[c] Impegrenated peach pulp with NH_4CI.
[d] Impegrenated peach pulp with $AlCI_3$.

main phenolic compounds obtained from all bio-oils are alkyl and methoxy phenols. The presence of these compounds may be explained by the thermal degradation of oxygenated components of the peach pulp.

4. CONCLUSION

In this study, pyrolysis experiments of peach pulp and impregnated samples were carried out in a well-swept, fixed-bed reactor in order to investigate the effects of pyrolysis temperature and impregnation effect on product yields and chemical compositions. Pyrolysis temperature showed important effects on product yields. While maximum oil yields were obtained at moderate temperatures (500–600°C), on increasing the pyrolysis temperature to 700°C the oil yield was decreased and the gas yield was increased. Various chemical additives ($AlCl_3$, H_3PO_4, NH_4Cl) impregnated on peach pulp at 10 wt% and this result showed that the chemical additives had a greater effect on product distribution. Peach pulp pyrolysis oil is a complex mixture of C_5–C_{29} organic compounds, with a lot of aromatic (Ar), non-aromatic (NAr), oxygenated aromatic (ArO), and oxygenated non-aromatic (NArO). Bio-oil obtained under these conditions can be utilized as either synthetic fuel or chemical feedstock.

REFERENCES

Antal, M. J. 1983. Biomass pyrolysis: A review of the literature. Part 1—Carbohydrate pyrolysis. *Adv. Solar Energy* 1:61–109.

Blanco Lopez, M. C., Blanco, C. G., and Martinez-Alanso, A. 2002. Composition of gases released during olive stones pyrolysis. *J. Anal. Appl. Pyrol.* 65:313.

Bridgewater, A. V., and Grassi, G. 1991. *Biomass Pyrolysis Liquids Upgrading and Utilization*. London: Elsevier Applied Science.

Budinova, T., Ekinci, E., Yardim, F., Grimm, A., Björnbom, E., Minkova, V., and Goranova, M. 2006. Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. *Fuel Proc. Technol.* 87:899–905.

Gomez-Serrano, V., Villegas, J. P., Florindo, A. P., Valle, C. D., and Valenzula-Calohorro, C. 1996. FT-IR study of rockrose and of char and activated carbon. *J. Anal. Appl. Pyrol.* 36:71–80.

Gomez-Serrano, V., Piriz-Almeida, F., Duran-Valle, C. J., and Pastor-Villegas, J. 1999. Formation of oxygen structures by air activation. A study by FT-IR spectroscopy. *Carbon* 37:1517–1528.

Gomez-Serrano, V., Alvarez, P. M., Jaramillo, J., and Beltran, F. J. 2002. Formation of oxygene complexes by ozonation of carbonaceous materials prepared from cherry stones. I. Thermal effects. *Carbon* 40:513–522.

Meier, D., and Faix, O. 1999. State of the art of applied fast pyrolysis of lignocellulosic materials: A review. *Bioresour. Technol.* 68:71–77.

Mohan, D., Pittman, C. U., and Steele, P. H. 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* 20:848–889.

Pütün, A. E., Özcan, A., and Pütün, E. 1999. Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: Yields and structural analysis of bio-oil. *J. Anal. Appl. Pyrol.* 52:33–49.

Pütün, A. E., Uzun, B. B., Apaydin, E., and Pütün, E. 2005. Bio-oil from olive oil industry wastes: Pyrolysis of olive residue under different conditions. *Fuel Proc. Technol.* 87:25–32.

Raveendran, K., Ganesh, A., and Khilar, K. C. 1996. Pyrolysis characteristics of biomass and biomass components. *Fuel* 75:987–998.

Suarez-Garcia, F., Martinez-Alonso, A., and Tascon, J. M. D. 2002. A comparative study of thermal decomposition of apple pulp in absence of phosphoric acid. *Polymer Degrad. Stabil.* 75:375–383.

Turkish Statistical Institute. 2007. *Peach Production of Turkey in 2006.* Available at: /http://www.tuik.gov.tr/VeriBilgi.do?tb_id=45&ust_id=13S.

Uzun, B. B., Putun, A. E., and Putun, E. 2007. Composition of products obtained via fast pyrolysis of olive-oil residue: Effect of pyrolysis temperature. *J. Anal. Appl. Pyrol.* 79:147–153.