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Steam pyrolysis of an industrial waste for bio-oil production

Eylem P. Önal [b], Başak Burcu Uzun [a], Ayşe Eren Pütün [a,*]

[a] *Anadolu University, Dept. of Chemical Engineering, Iki Eylul Campus, 26555, Eskisehir, Turkey*
[b] *Bilecik University, Faculty of Engineering, Chemical and Process Engineering, Bilecik, Turkey*

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ABSTRACT

Potato skin, a food industry waste, was pyrolysed under three different atmospheres namely static, nitrogen, and steam to produce bio-oil and its derivatives. The oil yield obtained at 550 °C was 24.77% in static atmosphere, whereas it reached to 27.11% in nitrogen atmosphere. Moreover, the use of steam caused a sharp increase of oil yields up to 41.09% with a steam velocity of 1.3 cm s^{-1}. TG-DTA analyses were applied on the raw material to investigate the thermal degradation. Liquid products obtained under the most suitable conditions were characterized by elemental analyses, FT-IR and ^{1}H NMR. In addition, column chromatography was employed to separate the bio-oil into its derivatives. Asphaltene fraction of bio-oil is decreased under steam atmosphere. Gas chromatography was also used to investigate the C distributions. The characterization has shown that the bio-oil obtained under steam atmosphere was more beneficial than those obtained under both static and inert atmospheres. Further comparison of H/C ratios of pyrolysis oils 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. It can be concluded that potato skin could be evaluated as a promising biomass candidate of bio-oil production.

1. Introduction

Considering the fact that energy consumption is increasing and limited fossil fuels are nearly exhausted, with increasing population and economic developments, renewable energy should be widely explored in order to renovate the energy sources structure and keep sustainable development safe. Among the technologies concerning clean energy generation, the energy exploitation of biomass is an interesting challenge due to being clean (zero net CO_2 emission) and unlimited, also these technologies minimize the disposal problems associated with the generation of agricultural wastes. Moreover, biomass exploitation allows the possibility of generating added value products such as chemicals or activated carbons (ACs) which means an attractive economic and technological solution. The feasibility of using agricultural by-products as renewable source of energy by means of pyrolysis and gasification processes has been widely reported. Due to its low cost and large availability, lignocellulosic biomass is being studied worldwide as a feedstock for renewable liquid bio-fuels. The energy crisis and fuel tension made biomass pyrolysis liquefaction a more important area of research and development [1–4].

The thermal degradation characteristics of lignocellulosic materials are profoundly influenced by their chemical composition (cellulose, hemicellulose and lignin), and TG and DTG curves provide semi quantitative understanding of the thermal degradation processes occurring during thermochemical conversion under various atmospheres. Thus, the comparative thermogravimetric study of different materials can provide useful information about the differences associated to their lignocellulosic composition. On the other hand, three phases are produced when biomass is subjected to pyrolysis processes: char, liquid and gas. The most interesting one from the energetic point of view is the gas (mainly composed by H_2, CO, CO_2, CH_4, etc.) which has a higher heating value (HHV), high enough to be used for the total energy requirements of a biomass waste pyrolysis plant and might also be employed in internal combustion engines, gas turbines and other operating devices. The liquid phase generated (known as tar) is the oil mainly composed of oxygen-containing structures and can be used directly as fuel for boilers or added to the petroleum refinery as feedstock. The char is a solid carbonaceous residue with a high content in fixed carbon (>75%), which can be used directly as fuel, and briquettes or as precursor for the activated carbon production [5,6].

Many pyrolysis parameters such as particle size, temperature, heating rate, residence time, different atmospheres, biomass type, catalyst, and so on, strongly affect the yield and properties of the products [7]. There is an extensive literature on the pyrolysis of biomass. The objective of most of those studies, were obtaining alternative liquid fuels by the decomposing of the biomass samples,

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* Corresponding author. Tel.: +90 2223350580/6504; fax: +90 222 3239501.
E-mail address: aeputun@anadolu.edu.tr (A.E. Pütün).

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the optimization of process conditions and the chemical characterization of bio-oils by various instrumental techniques [1–20].

The pyrolysis of biomass under steam is a promising method for the simultaneous production of liquid and gaseous fuels, valuable chemicals and activated carbon. The presence of steam in the pyrolysis favors the formation of high yield liquid products, while the almost simultaneous pyrolysis and gasification of the fuel result in the formation of solid products with a high surface area and well-developed porous structure. In the literature, the effect of the steam flow on the yield and the properties of the products obtained in the pyrolysis activation of the selected samples of the agricultural and forestry wastes are investigated by Minkova et. al. The results are compared with those obtained in the atmosphere of nitrogen. The presence of steam has increased significantly the yield of liquid pyrolysis products at the expense of the gaseous and solid products. It is found that the liquid products consist predominantly of water-soluble polar compounds. Large part of the volatiles is found in the water phase condensed along with the tar [13]. Moreover, the activated carbon production in argon atmosphere from potato peel was investigated for the removal of heavy metal copper (II) from aqueous solutions. The activated carbons (ACs) were prepared by pyrolysis of the potato peel in the presence of zinc chloride for chemical activation. It is concluded that well-developed pore structure surface areas as high as 1078 m^2 g^{-1} and pore volumes as large as 0.97 cm^3 g^{-1} could be achieved from the potato peel pyrolysis with zinc chloride impregnation [21].

Pütün et al. conducted the fixed bed pyrolysis of *Euphorbia rigida*, sunflower presses bagasse and hazelnut shell, at different temperatures and constant heating rate of 7 °C min^{-1}. While comparing three biomass samples in the temperature intervals between 400 and 500 °C the increase of the bio-oil from *E. rigida* was greater than those for the others. Similar results were obtained on increasing the N_2 flow rate [15]. The obtained bio-oil product yields were compared with that of the produced in different conditions by Pütün et.al. [16–18]. In these studies, the bio-oil yield obtained under three different atmospheres (static, inert and steam) were compared and the results showed that the highest bio-oil yield was obtained under steam atmosphere.

Although there are several studies like obtaining activated carbons by pyrolysis of the potato peel and to investigate the influence of the potato starch in flash pyrolysis as a biopolymer, this study is the first one to evaluate the potato chips industry wastes for the production of bio-oil [19–21]. Potato is a major carbohydrate (starch) supplier in the diet of millions of people. Potato which has a global importance as a food crop, ranks number four after wheat, maize, rice with an overall annual production of nearly 327 million tons and about 19 million ha planted. In Turkey, potato is grown on 200 000 ha, and 4.5 million tons of potato is produced every year. Revealed residue amount is 495,000–594,000 t [22,23]. Converting the organic matters in residues into more valuable, concentrated forms of energy will be beneficial to developing countries. Pyrolysis is an advantageous method to obtain liquid fuels from waste or industrial disposals. It could be a promising way for waste management to convert them to bio-oils which have more advantages in production and marketing.

The objectives of this study are: (i) effect of pyrolysis conditions on the product yields; (ii) liquid product characterization and (iii) evaluate the various industrial disposals as a biomass source.

2. Experimental

2.1. Raw material

Potato skin samples investigated in this study have been taken from a chips factory around İzmit, located in Western Anatolia of Turkey. Air-dried potato skins were grounded in a high speed rotary cutting mill and screened to obtain six different particle sizes (Dp), namely $Dp<0.224$, $0.224<Dp<0.425$, $0.425<Dp<0.85$, $0.85<Dp<1.25$; $1.25<Dp<1.8$, $Dp>1.80$ mm. The average particle size was found to be as 0.80 mm. Proximate analysis was performed on the potato skin sample to determine the weight fractions of moisture, volatile, ash and fixed carbon contents. The ASTM Standard Test Method for Proximate Analysis of Wood Fuels (E 870-82) was used. Then, the fixed carbon was obtained by subtracting the percentages of volatile matter, moisture and ash from 100%. The average bulk density of this raw material was found at 250 kg m^{-3} according to ASTM 321-D.

The ultimate analysis was performed in an elemental analyzer (Carlo Erba, EA 1108). As being the main constituents of potato skin, cellulose, lignin, hemicellulose, extractives, oil, starch and protein were determined [7,24]. The protein content of potato skin was determined by the Kjeldahl method (ASTM E-258-67) using with Labcanco Rapid still −2 and N × 6.25 as conversion factor. All of these main characteristics of potato skin are given in Table 1.

The chemistry of biomass is very complicated. In general, biomass has three major constituents; hemicellulose, cellulose and lignin. It is known from previous studies that thermal decomposition of hemicellulose and cellulose have the first weight-loss (150–350 °C) and the second weight-loss (275–350 °C) steps for lignocelluloses after the initial weight loss (30–150 °C) associated with the moisture loss. However, lignin undergoes gradual decomposition over a wide temperature interval (275–500 °C) [25–29]. To evaluate the thermal behavior of potato skin, Thermo Gravimetric Analysis (TGA) was applied by using LINSEIS Thermowaage L 81 thermo gravimetric analyzer coupled with Differential Thermal Analyzer (DTA). Experiments were applied working with 25 mg sample, 100 mL min^{-1} nitrogen flow with 10 °C min^{-1} heating rate. The TG and DTG curves for potato skin recorded from room temperature to 900 °C are shown in Fig. 1. The initial slight mass loss is due to the evaporation of moisture from potato skin. The second weight loss that occurred between 200 and 575 °C corresponds to the main pyrolysis process, devolatilisation. After this major weight loss, there is essentially no further loss of weight. The final residue corresponds to ash and fixed carbon. DTG data showed that initial mass loss gives its maximum peak at 95.8 °C. The second major weight loss starts at about 175 °C, having its maximum point at 293 °C, and finishes at about 350 °C. According to these results, it can be said that since most of the weight loss, related to the volatilization of hydrocarbons, happens at

Table 1
Main characteristics of potato skin.

Proximate analysis (wt.%, as received)	
Moisture	10.74
Volatiles	9.69
Fixed C	70.11
Ash	9.46
Elemental analysis (wt.%, daf basis[a])	
Carbon	79.77
Hydrogen	6.86
Nitrogen	2.88
Oxygen (by difference)	10.49
Empirical formula	$CH_{1.03}N_{0.031}O_{1.58}$
H/C molar ratio	1.03
O/C molar ratio	1.58
Calorific value (MJ kg^{-1})	34.99
Component analysis (wt.%, as received)	
Extractives	19.50
Hemicellulose	13.12
Lignin	0.80
Cellulose	46.66
Oil	0.105
Starch	14.28
Protein	4.03

[a] Dry and ash free.

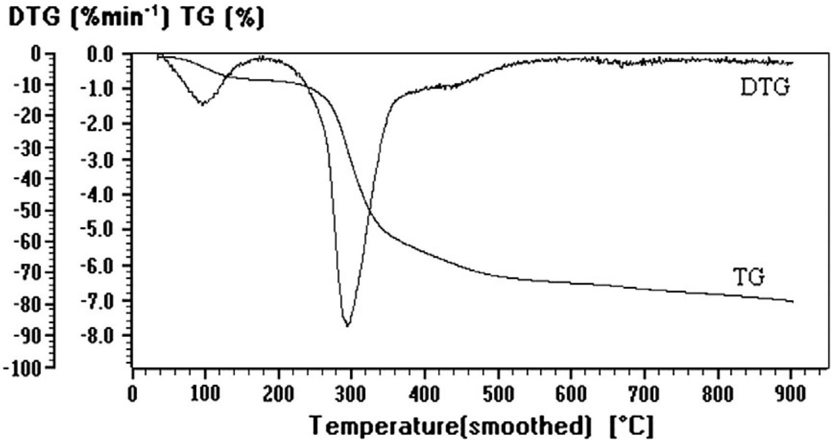

Fig. 1. TG and DTG curves for potato skin.

temperatures lower than 600 °C, choosing pyrolysis temperature as 550 °C is appropriate when the maximum amount of liquid and gaseous products is aimed.

To have information about the chemical structure of the raw material, FT-IR spectrum is taken and given in Fig. 2. It shows that the chemical structure of the potato skin, being a lignocellulosic material, is made up of different atomic groupings and a large number of functional groups. The broad and flat band at about 3244 cm^{-1} is ascribed to OH stretching vibrations in hydroxyl groups which was attributed to the moisture content of the sample. Two very strong bands at 2918 and 2850 cm^{-1} are assigned to C–H stretching vibrations in CH_2 groups and a weak band at 1467 cm^{-1} due to C–H deformation frequencies confirms the presence of these functional groups. The next strong band (1708 cm^{-1}) is ascribed to C=O vibrations probably from esters, ketones or aliphatic acids. At 1615 cm^{-1}, the very strong band is assigned to either C=C conjugated, aromatic conjugated or C=N conjugated or cyclic double bond vibrations. Skeletal vibrations from $(CH_3)_3$–C–R give a strong band at 1272 cm^{-1}. The weaker bands between 880 and 600 cm^{-1} are ascribed to aromatic structures [30,31].

2.2. Pyrolysis experiments

The 316 stainless steel retort used in this study has a volume of 400 cm^3 and externally heated by an electric furnace with the temperature being controlled by a thermocouple inside the bed. The experiments performed in the retort were carried out in three groups; static, nitrogen and steam atmospheres. The first group was performed to determine the effect of pyrolysis temperature on the yields of potato skin pyrolysis. Ten grams of potato skin, having average particle size of 0.81 mm, were placed into the reactor and the temperature was raised to 400, 450, 500, 550, 600, 700 °C with a constant heating rate and held for either a minimum of 30 min or until no further significant release of gas was observed. The flow of gas released was measured using a soap film for the duration of the experiments. The liquid phase was collected in cold traps maintained at about 0 °C using salty ice. The liquid phase consisted of aqueous and oil phases which were separated by decanting at room conditions and then weighed. After pyrolysis, the solid char was removed and weighed, and then gas yield was calculated by the difference.

The second group of experiments was performed in the retort, to see the effect of the residence time of the pyrolysis vapors evolved during the reaction in the media. The experiments were conducted with changing the sweeping gas flow rates of either 50, 100, 200 and 400 cm^{3}min^{-1}. In this part the heating rate, the final pyrolysis temperature, and the particle size were kept constant as 5 °C min^{-1}, 550 °C and 0.81 mm, respectively, based on the results of the first group of experiments.

The last group of experiments was established to investigate the effect of steam. Pure steam at 10 psig was sent to the reactor from a

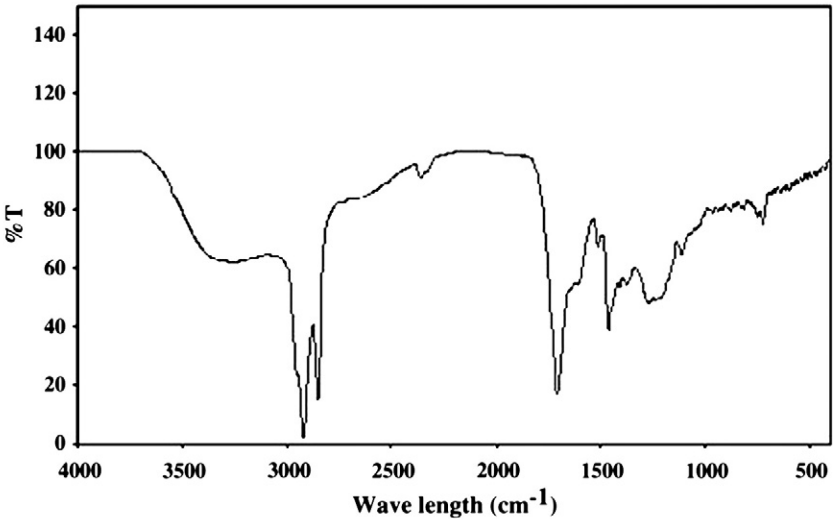

Fig. 2. FT-IR spectra of potato skin.

generator and the linear velocity of the steam is calculated according to the inlet diameter of the reactor (0.63 cm). Keeping all the parameters constant as previous parts, only the steam velocity was changed as 0.6, 1.3 and 2.7 cm s^{-1}.

All the experiments were carried out at least three times in order to determine the variability of the results and to assess the experimental errors. In this way, the arithmetical averages were calculated for all the results.

2.3. Bio-oil characterization

The oils analysed in this study have been obtained under experimental conditions that gave maximum oil yields.

Elemental analyses were carried out with Carlo Erba, EA 1108 and the C, H, O, N, and S contents of the raw material were determined.

For characterization of bio-oils, ^{1}H NMR (Proton Nuclear Magnetic Resonance Spectroscopy) spectra were recorded using a BRUKER DPX-400, 400 MHz High Performance Digital FT-NMR Instrument.

The chemical class compositions of the oils were determined by liquid column chromatographic fractionation. Bio-oils were separated into two fractions as asphaltenes and maltenes using n-pentane as the solvent. Silica gel, the packing material, was pre-treated at 105 °C for 2 h prior to use. Pentane soluble fraction, maltenes, was further separated into aliphatic, aromatic, and polar fractions with eluating 200 mL of n-pentane, toluene, and methanol, respectively. Each fraction was dried and weighed.

The FT-IR (Fourier transform infrared spectroscopy) spectra of the oils and their aliphatic and aromatic sub-fractions were recorded using a Mattson 1000 Infrared Spectrophotometer.

GC/MS (Gas Chromatography Mass Spectroscopy) analyses of the aliphatic subfractions were performed using a Hewlett-Packard 6890 Model gas chromatograph coupled with mass selective detector using HP-1 column.

3. Results and discussion

3.1. Effect of pyrolysis temperature

Fig. 3 shows the product yields for the pyrolysis of potato skin in relation to the final temperature of pyrolysis at a heating rate of 5 °C min^{-1}. While the oil yield was 21.36% at 400 °C, it appeared to go through a maximum of 24.77% at 550 °C. Then at the final pyrolysis temperature of 700 °C, the oil yield decreased to 18.60%. As increasing the temperature, char yields decreased slightly, but gas yields show an opposite trend.

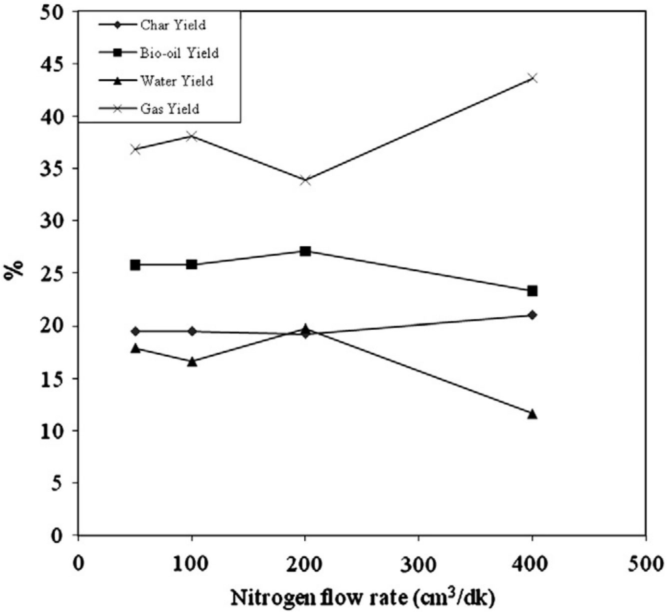

Fig. 4. Pyrolysis of potato at different nitrogen flow rates, product yields.

From previous studies, it is known that the pyrolysis temperature has a great influence on product distributions. The kinetics of pyrolysis reactions shows that the primary pyrolysis reactions take place in the temperature range of 200–400 °C which results in the formation of solid product, char. Temperatures above 400 °C solid residue slowly undergoes further chemical and physical transformations which lead to the formation of liquid and gas products. Pyrolysis temperature up to 600 °C maximizes the production of bio-oils and temperatures above 700 °C maximize gaseous products while minimizing char formation. For different biomass samples, the pyrolysis temperatures that have given the highest liquid product yield were determined to be the temperatures between 500 and 550 °C. These results are consistent with literature [32–38].

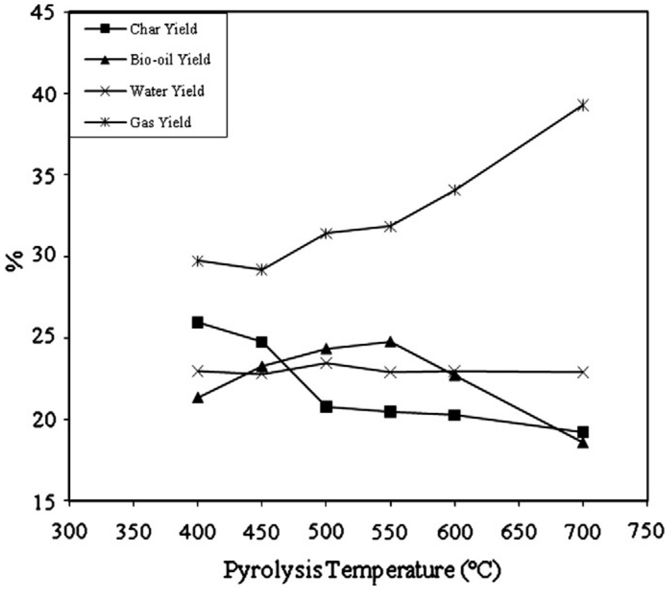

Fig. 3. Pyrolysis of potato skin at different temperatures, product yields.

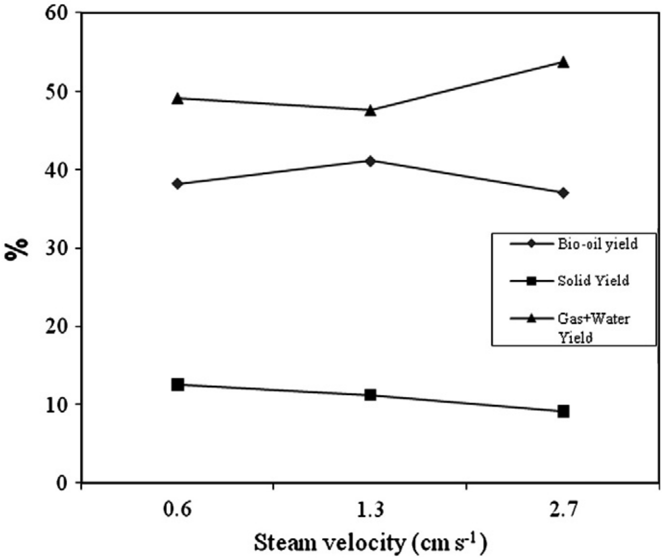

Fig. 5. Pyrolysis of potato skin at different steam velocities, product yields.

Table 2
Elemental compositions and calorific values of bio-oils obtained under different atmospheres at 550 °C.

Component	Static (%)	Nitrogen (%)	Steam (%)
C	69.67	58.82	72.04
H	9.31	8.54	11.31
N	2.59	1.22	1.24
O[a]	18.43	31.41	15.41
H/C	1.60	1.74	1.88
O/C	0.20	0.40	0.16
Molar formula	$CH_{1.60}N_{0.032}O_{0.20}$	$CH_{1.74}N_{0.018}O_{0.40}$	$CH_{1.88}N_{0.015}O_{0.16}$
Calorific value (MJ kg^{-1})	33.61	32.00	37. 91

[a] Difference.

3.2. Effect of sweeping gas flow rate on product yields

The nitrogen gas flow rate affects the residence time of the volatiles produced as a result of the pyrolysis reactions and the high flow rate minimizes the secondary reactions such as recondensation, repolymerisation and char formation by the fast removal of volatiles before these reactions proceed [37–39]. The product yields of pyrolysis in relation to the nitrogen gas flow rate are given in Fig. 4 at the constant heating rate of 5 °C min^{-1} and pyrolysis temperature of 550 °C. The highest bio-oil yield of 27.11% was achieved with a nitrogen gas flow rate of 200 cm^3 min^{-1}. Taking into account the bio-oil yield under the static atmosphere, the bio-oil yield increased about 9.5% under the nitrogen atmosphere. In present reaction conditions, the maximum oil yield reached sweeping gas flow rate of 200 cm^3 min^{-1} instead of 400 cm^3 min^{-1}.

3.3. Effect of steam velocity on product yields

Previous studies on steam pyrolysis show that the presence of steam as the atmosphere in which the pyrolysis reactions take place influences the distribution of products and favors the formation of liquid products at the expense of solid and gaseous products. Steam does not only sweep the primary products from the pyrolysis reactions, but also reacts with the products and helps the evaporation of oils from the biomass and this reduces the formation of solid char [40–42].

Experimental results, given in Fig. 5, show that the bio-oil yield of the steam pyrolysis is significantly higher than that of the pyrolysis under the static and nitrogen atmospheres. As seen, bio-oil yield increases with increasing steam velocity. This result is explained with the inhibition of secondary reactions by steam at high velocities [41]. The char yield decreased from 16.99% to 14.66% while steam velocity increased from 0.6 to 2.7 cm s^{-1}. Pyrolysis vapors were removed instantly by higher sweeping gas velocity, and in cases where they were quenched sufficiently, the liquid yield should have been high [42]. Maximum oil yield was attained at the final pyrolysis temperature of 550 °C and steam velocity of 1.3 cm s^{-1}.

Table 4
Results of column chromatography for three bio-oils.

Bio-oil[a]	Pentane solubles	Subfraction (wt.%)		
		Aliphatic	Aromatic	Polar
Static	57.28	18.64	25.42	55.94
Nitrogen[b]	62.62	20.89	22.39	56.72
Steam[c]	73.50	25.71	15.64	58.65

[a] Bio-oil obtained at 550 °C under static atmosphere.
[b] Bio-oil obtained at 550 °C under nitrogen flow of 200 cm^{3}min^{-1}.
[c] Bio-oil obtained at 550 °C under steam velocity of 1.3 cm s^{-1}.

3.4. Bio-oil characterisation

The elemental compositions, calorific values and the average chemical compositions of the oils characterized under static, nitrogen and steam atmospheres are listed in Table 2. Produced bio-oils have higher H/C ratio than that of raw material (potato skin). Moreover, bio-oils under static and nitrogen atmospheres seem to have a lower H/C ratio than the oil obtained under steam atmosphere. Due to indirect hydrogen introduction to the retort, steam acts as a reactive agent that reacts with the pyrolysis products and stabilize the radicals obtained in the thermal decomposition of the fuel with increasing the yield of volatiles. Moreover, steam reduces the amount of the oxygen in the oils. It can be concluded that calorific values indicate that the energy contents of the oils are very close to that of petroleum [43].

The FT-IR spectra of the oils under three atmospheres and their corresponding aliphatic and aromatic, polar sub-fractions are given in Table 3. The O–H stretching vibrations between 3244 and 3400 cm^{-1} indicate the presence of phenols and alcohols. The figures show that no peaks exist between these wave numbers for the aliphatic sub-fractions of the bio-oils and this indicates that aliphatic sub-fractions do not contain oxygenated compounds like bio-oils. The C–H stretching vibrations between 2849 and 2856 cm^{-1} and C–H deformation vibrations between 1375 and 1465 cm^{-1} indicate the presence of alkanes. The C H stretching vibrations with absorbance between 1650 and 1717 cm^{-1} indicate the presence of ketones or aldehydes. The absorbance peaks between 1590 and 1625 cm^{-1}

Table 3
Results of FTIR spectra for bio-oils and their subfractions.

Band position (cm$-^1$)	Assignment	Static				Nitrogen				Steam			
		Bio-oil	Aliphatics	Aromatics	Polars	Bio-oil	Aliphatics	Aromatics	Polars	Bio-oil	Aliphatics	Aromatics	Polars
3600–3400	υ(O–H)	+	−	+	+	+	−	+	+	+	−	+	+
3040–3000	υ(C–H) aromatic ring	−	−	+	−	−	−	+	−	−	−	+	−
2980–2930	$υ_{as}$(C–H)	+	+	+	+	+	+	+	+	+	+	+	+
2870–2850	$υ_s$(C–H)	+	+	+	+	+	+	+	+	+	+	+	+
1720–1770	υ(C=O)	+	+	+	+	+	+	+	+	+	−	+	+
1625–1590	υ(C=C)	−	+	−	−	−	+	−	−	+	+	−	−
1600, 1580, 1450	Aromatic ring	+	−	+	+	+	+	+	+	+	−	+	+
1460	$δ_{as}$ (CH_3, CH_2 scissor)	+	+	+	+	+	+	+	+	+	+	+	+
1375	$δ_s$(C−-H)	+	+	+	+	+	+	+	+	+	+	+	+
1275–1200	$υ_{as}$(=C–O–C)	+	−	+	+	+	−	+	+	−	−	+	+
1150–1070	$υ_{as}$(C–O–C)/OH secondary, OH primary	+	−	+	+	+	−	+	+	+	−	+	−
900–700	Substituents of aromatic ring	+	−	+	−	−	−	+	+	−	−	+	+
740–720	γ(C–H)	+	+	+	+	+	+	+	+	+	+	+	+
730–675	γ(=CH)	+	+	+	+	+	+	−	+	+	+	+	+
720–725	Rocking band	−	+	−	−	−	+	−	−	−	+	−	−

Table 5
Elemental compositions and calorific values of subfractions from column chromatography for the bio-oils obtained at 550 °C.

Component	Static (%)			Nitrogen (%)			Steam (%)		
	Aliphatic	Aromatic	Polar	Aliphatic	Aromatic	Polar	Aliphatic	Aromatic	Polar
C	83.63	78.49	69.90	70.15	79.52	69.00	82.32	77.28	73.17
H	13.05	10.93	10.77	12.00	13.57	10.37	15.71	13.78	12.05
N	1.08	0.70	1.33	1.30	0.53	1.40	–	–	0.72
O[a]	2.25	9.88	18.00	16.54	6.78	19.22	1.97	8.94	14.06
H/C	1.87	1.67	1.85	2.06	1.98	1.80	2.30	2.14	1.98
Calorific value (MJ kg^{-1})	46.72	40.54	35.94	38.06	44.68	34.83	50.16	44.42	39.60

[a] By difference.

represent C C stretching vibrations indicative of alkenes and aromatics. The absorption peaks between 700–900 and 1420–1610 cm^{-1} indicate mono and polycylic and substituted aromatic groups.

The results of the column chromatography of the oils are given in Table 4. Although pyrolysis oils under static and nitrogen atmospheres consist of nearly the same amount of n-pentane solubles (maltenes), steam pyrolysis oil had higher amount of this fraction. In addition to this, the percentage of aliphatic sub-fraction of the steam pyrolysis oil is also significantly higher than that of the bio-oils obtained under both static and nitrogen atmospheres, due to the restrictions to repolymerisation and recondensation. It can be seen that the aromaticity of the steam pyrolysis oil is lower than that of the oils obtained under both static and nitrogen atmospheres.

Elemental analyses were conducted to each sub-fraction and the results are given in Table 5. Calorific values of the aliphatic sub-fractions are significantly higher than that of aromatic and polar sub-fractions. The hydrogen content of the aliphatic sub-fraction of steam pyrolysis oil is very high, when compared with the others. Moreover, the aliphatic sub-fraction of the steam pyrolysis oil has the highest calorific value. As seen from Table 5, H/C ratios are ranging between 1.87 and 2.30 for the aliphatic sub-fractions, nearly the same with gasoline.

The results of the hydrogen distribution of bio-oils obtained by ^1H NMR spectroscopy is given in Table 6. ^1H NMR spectra can be divided into three main regions; aromatic, olefinic and aliphatic, basing upon the chemical shifts of specific proton types. 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. ^1H NMR spectra of the bio-oils indicate that the aromaticity of the bio-oil from steam pyrolysis is lower than that of the bio-oil obtained under static atmosphere. CH_2 and CH_β to aromatic ring protons are higher than the other protons. The results show that larger proportions of the aliphatic structural units exist in the bio-oil from steam pyrolysis.

A gas–liquid chromatogram of the aliphatic sub-fractions of the bio-oils obtained under static and steam atmospheres and their selected ion current chromatograms for the alkenes (m/e = 55) and alkanes (m/e = 57) are obtained. In order to determine the distribution of these hydrocarbons in aliphatic, a semi-quantitative study was made by means of the percentage of areas of the chromatographic peaks and results are presented in Table 7. Three types of compounds were identified in n-pentane sub-fractions: normal alkanes, alkenes and branched hydrocarbons (isoprenoids). While considering the results of GC/MS detailed analysis of the aliphatic sub-fraction of oils obtained under static, nitrogen and steam, the total amounts of n-alkanes are 68%, 56% and 66%, respectively. In the chromatograms mostly doublet peaks were observed. As seen from Table 7, the first ones belong to n-alkenes and the second ones to n-alkane [44]. The straight chain alkanes and alkenes range between CH_{11} and CH_{28} for oil under static atmosphere between CH_{11} and CH_{28} for oil under nitrogen atmosphere and, between CH_{10} and CH_{28} for oil under steam atmosphere. The distribution of straight chain alkanes exhibits a maximum on the range of CH_{13}–CH_{18}, CH_{12}–CH_{18} and CH_{12}–CH_{16} for oils under static, nitrogen and steam atmospheres, respectively. The results of this chromatogram have showed that the aliphatic

Table 6
Results of ^1H NMR for the bio-oils from the pyrolysis of potato skin obtained under three atmospheres at 550 °C.

Hydrogen type	Chemical shift (ppm)	Static (%)	Nitrogen (%)	Steam (%)
CH_3 γ or furter from aromatic ring and parafinic CH_3	1.0–0.5	10	23.17	12.85
CH_3, CH_2 and CH β to aromatic ring	1.5–1.0	70.95	53.69	67.09
CH_2 and CH attached to naphthenes	2.0–1.5	–	–	5.37
CH_3, CH_2 and CH α to aromatic or acetylenic	3.0–2.0	1.87	17.38	10.57
Total aliphatics	3.0–0.5	82.82	94.24	95.87
Hydrokyl, ring-joining CH_2, CH or OCH_3	4.0–3.0	–	–	0.57
Phenols, non-conjugated olefins	6.0–4.0	6.25	2.68	2.08
Aromatics, conjugated olefins	9.0–6.0	10.92	3.09	1.48

Table 7
Relative proportions (area %) of main pyrolysis compounds in the aliphatic sub-fraction of bio-oils.

Compound	Retention time	% Area		
		Static	Nitrogen	Steam
Undecane (C_{11})	6.16	–	–	1.30
1-Dodecene	7.47	0.20	–	3.51
1-Hexadecene	12.65	–	–	2.28
Cyclopropane	12.78		0.63	–
Dodecane (C_{12})	12.95	0.25	0.40	2.24
1-Tridecene	14.25	0.40	0.51	5.93
Tridecane (C_{13})	14.40	0.71	0.59	2.82
1-Tetradecene	15.66	1.43	1.63	3.75
N-Tetradecane (C_{14})	15.81	0.98	1.04	3.17
1-Pentadecene	17.13	0.78	–	–
Pentadecane (C_{15})	17.32	2.02	1.30	5.18
7-Hexadecene	18.78	1.00	–	–
Hexadecane (C_{16})	18.95	0.71	0.81	2.28
9-Tricosene	19.61	–	–	1.15
Heptadec-8-ene	20.40	0.47	0.26	1.84
1-Heptadecene	20.65	0.33	2.99	1.51
Heptadecane (C_{17})	20.87	0.75	0.63	2.23
1-Octadecene	22.85	0.77	2.15	2.59
Octadecane (C_{18})	23.07	0.38	0.38	1.45
9-Hexacosene	23.79	–	–	7.30
Nonadecane (C_{19})	25.60	2.98	0.32	15.41
5-Eicosene	28.17	0.51	–	–
N-Eicosane (C_{20})	28.44	0.33	0.35	1.88
10-Heneicosene	31.24	0.19	–	–
Heneicosane (C_{21})	31.56	0.61	0.64	6.21
1-Nonadecene	34.54	0.70	1.61	1.60
N-Docosane (C_{22})	34.84	0.40	–	2.48
Cyclotetracosane	41.44	0.30	0.72	4.80
Tetracosane (C_{24})	41.76	0.58	0.51	–
Pentacosane (C_{25})	45.33	1.66	1.61	9.96
1-Docosene	48.46	0.38	0.58	1.72
Hexacosane (C_{26})	48.76	0.78	0.66	3.12
Heptacosane (C_{27})	52.21	1.04	0.91	–
Cyclooctacosane	55.30	0.50	–	–
Octacosane (C_{28})	55.57	0.71	0.64	–

subfraction of the bio-oil has a similar distribution of straight chain alkanes with standard diesel.

According to the results of GC analyses, it can be concluded that the compounds which are obtained during the process of steam pyrolysis are predominantly saturated structures probably due to the conversion of unsaturated hydrocarbons (alkenes) to saturated hydrocarbons (alkanes) while the desorption of low molecular products take place.

4. Conclusion

The experimental results show that pyrolysis conditions have important roles on the bio-oil yield and composition. As it is consistent with the literature, the final temperature of pyrolysis reactions has a great influence on the product yields and steam inhibits the secondary cracking reactions of the products of pyrolysis. In addition, the steam pyrolysis oils are more paraffinic than those of oils obtained under static and nitrogen atmospheres.

When steam was used at the optimum conditions, bio-oil yield increased 65.87% and 51.57% with respect to static and nitrogen atmospheres. The oil yield reached a maximum value of 42.09% with the steam velocity of 1.3 cm s^{-1}.

The results of the spectroscopic analyses are in agreement with chromatography, confirming that the aromaticity of bio-oil under steam atmosphere is significantly lower than that of the bio-oils under static and nitrogen atmospheres. GC/MS and FT-IR results show that the aliphatic sub-fractions are a mixture of alkanes and alkenes. H/C ratios and characterization of the oils confirm that the aliphatic sub-fractions are similar to the currently utilized transport fuels.

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