



An experimental study on bio-oil production from co-pyrolysis with potato skin and high-density polyethylene (HDPE)

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ABSTRACT

In order to investigate the synergistic effect of high dense polyethylene (HDPE) addition to potato skin (pS) during co-pyrolysis, pure HDPE was pyrolysed as a model compound for determination of the optimum process conditions. Thermal decomposition of pure HDPE was performed at constant heating rate of 5 °C min⁻¹ under various pyrolysis temperatures (400, 420, 450, 470, 500 and 550 °C) and sweeping gas flow rates (100, 200, 400 and 800 cm³ min⁻¹). The maximum bio-oil yield was 56% at 500 °C under sweeping flow rate of 400 cm³ min⁻¹. Then, co-pyrolysis of pure HDPE-pS and waste HDPE-pS mixtures were pyrolysed with various proportions such as 1:0, 1:1, 1:2, 2:1 and 0:1. The yield of liquids produced during co-pyrolysis enhanced with increasing weight ratio of HDPE in mixtures. Obtained bio-oils were analyzed in detail with various spectroscopic and chromatographic methods. Co-pyrolysis oil had higher carbon and hydrogen contents, lower oxygen contents with higher heating value than those of pyrolysis. It was concluded that addition of HDPE improved the liquid yields in terms of both quality and quantity.

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1. Introduction

The increasing consumption of polymeric materials in modern daily life causes loss of natural resources, the environmental pollution, and the depletion of landfill space [1]. Nevertheless, the non biodegradable polymeric waste materials such as plastics, tires require the main difficult disposal methods. Presently, the most common solution to deal with organic wastes, namely land filling and incineration do not appear to be the most suitable ones since they present various problems related with the environment. For instance; landfill areas are limited. Also, land filling could pollute environment such as phthalates and various dyes found in plastic additives leak into ground water. Incineration is an alternative to landfill. However, this process causes formation of unacceptable emissions of gases such as nitrous oxide, sulfur oxides, dusts, dioxins and toxins [1,2].

The utilization of such waste materials is indeed of importance from economical and environmental aspects. Especially, packing materials make up the 50–70% of the total plastic disposal, containing mainly 89% polyolefins (polyethylene, polypropylene, polystyrene, polyvinyl chloride). Nevertheless, decomposition of polyethylene and polypropylene do not give high yields of ethylene and propylene with the ordinary recovery techniques [3,4]. Pyrolytic processes are suitable to convert polyolefins and cellulose (or lignin) derived materials into

valuable feedstock and the specific benefits of these methods potentially include: the reduction of the volume of waste, the recovery of chemicals, and the replacement of fossil fuels [5].

The aim of mixing polymers with biomass wastes is to improve the liquid fraction of the products, and to evaluate the H-donor effect of polymers. There are several studies about co-pyrolysis of biomass-polymers which has indicated the synergistic effect on liquid production [5–15]. According to these studies, the composition and the nature of the biomass and synthetic polymer as well as the pyrolysis conditions have a great influence on the yield, the chemical structure and the physical properties of the products. The addition of polymer to biomass has a positive effect on the yield and basic physical properties of bio-oil.

Potato skin is a promising biomass candidate. According to our previous study, resultant oil from pyrolysis of potato skin has a high aliphatic content which is very beneficial for artificial fuel production. Potato is an essential nutrition in the world. In Turkey, potato is grown on 200 thousand ha, and 4.5 million tons of potato is produced every year. Revealed residue amount is 495,000–594,000 tons/yr. Converting the organic matters in residues such as polymers and food industry waste into more valuable, concentrated forms of energy by pyrolysis will be a sustainable way for waste management [16].

The thermal degradation of the organic materials, the product distribution and consequently the economics of the process are strongly influenced by the experimental conditions used. In the present work, co-pyrolysis of pS with pure and waste HDPE was investigated for the first time to optimize the experimental conditions for bio-oil production. Obtained bio-oils were analyzed in detail with various spectroscopic and

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chromatographic methods. As a result, the addition of HDPE caused an increase of yields and also improvement of fuel properties.

2. Experimental procedure

2.1. Raw material

Potato chips industry waste was obtained from the Kar Chips Factory in Turkey. As reasoned waste was dried in air and then ground in a rotary cutting mill to obtain a grain size lower than 2 mm. After milling, biomass sample was screened to obtain seven different particle sizes (D_p), namely $1.8 > D_p > 1.25$ mm; $1.25 > D_p > 0.85$ mm; $0.85 > D_p > 0.6$ mm; $0.6 < D_p < 0.425$ mm; $0.425 < D_p < 0.224$ mm. Average particle size range was found to be as 0.81 mm. Pure and waste High Density Polyethylene (HDPE) were brought from a petrochemical company (PETKİM Aliağa, Turkey) and Nur Plastic Factory (Eskişehir, Turkey), respectively.

Proximate analysis was performed on the samples to determine the weight fractions of volatile, ash and fixed carbon contents. The ultimate analysis was performed in an elemental analyzer (Carlo Erba, EA 1108). The results are given in Table 1.

Thermo Gravimetric Analysis (TGA) was applied by using Linseis Thermowaage L 81 thermo gravimetric analyzer coupled with Differential Thermal Analyzer (DTA) to evaluate the thermal behavior of potato skin and HDPE. Conditions 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 and HDPE recorded from room temperature to 900 °C are shown in Fig. 1.

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 control by a thermocouple inside the bed. The experiments were carried out in three groups. The first group was performed in the retort, in order to see the effect of residence time of pyrolysis vapors evolved during the reaction in the media on the yields of pure HDPE. Sweeping gas flow rates were varied of 100, 200, 400 and $800 \text{ cm}^3 \text{ min}^{-1}$. In this part, the final pyrolysis temperature, and the heating rate were kept constant as 5 °C min^{-1} and 400 °C , respectively.

The second group was performed to determine the effect of pyrolysis temperature on the yields of pure HDPE. The samples were placed into the retort and the temperature was raised to 400, 420, 450, 470, 500 and 550 °C with a constant heating rate of 5 °C min^{-1} and the sweeping gas flow rate of $400 \text{ cm}^3 \text{ min}^{-1}$ and then the system was 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 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 last group of experiments, the biomass: polymer mixtures both pure and waste were prepared at various weight ratios such as 1:0, 1:1, 1:2, 2:1 and 0:1 for co-pyrolysis experiments at constant pyrolysis temperature of 500 °C , sweeping gas flow rate of $400 \text{ cm}^3 \text{ min}^{-1}$ and the heating rate of 5 °C min^{-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 analyzed in this study were 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 raw material were determined.

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, ester and polar fractions with eluting 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 sub-fractions were recorded using a Mattson 1000 Infrared Spectrophotometer.

GC/MS (Gas Chromatography Mass Spectroscopy) analyses of the aliphatic sub-fractions 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. Thermal analysis

The TG and DTG curves for potato skin (pS) and HDPE recorded from room temperature to 900 °C are shown in Fig. 1. The initial slight mass loss occurs up to $180\text{--}200 \text{ °C}$ due to the evaporation of moisture from pS. Second weight loss occurred between 200 and 575 °C corresponds to main pyrolysis process, devolatilization. DTG data of biomass showed that initial mass loss gives its maximum peak at 95.8 °C . Second major weight loss starts at about 175 °C , having its maximum point at 293 °C , finishes at about 350 °C . Biomass sample decomposed at lower temperature than HDPE while HDPE begins to decompose 430 °C and showed the maximum mass loss around 470 °C (this can be seen from DTG of HDPE). At the final temperature of TG measurements (650 °C), HDPE degrades completely, leaving no residue behind, whereas the residue for pS is 13.21 wt.% from the initial sample mass. This is related to the high content of ash and fixed carbon in biomass, which is not decomposed at this temperature. Considering these results, in order to achieve highest amount of liquid and gaseous products, temperature range for co-pyrolysis can be chosen from 470 to 520 °C since most of the weight loss is due to devolatilization.

3.2. Optimization of pyrolysis conditions

The reaction temperature and residence time have a great influence on the pyrolysis product distribution [17]. The effect of residence time on pyrolysis vapors can be investigated by changing the flow rate of the sweeping gas while pyrolysis temperature is kept constant [18]. In this study, the pyrolysis of pure HDPE at 450 °C was studied under various sweeping gas flow rates of 100, 200, 400 and $800 \text{ cm}^3 \text{ min}^{-1}$ and the oil yields obtained were 35.3, 45.8, 48.3 and 36.4 wt.%, respectively.

Table 1
Main characteristics of pS and HDPE.

	pS	HDPE
Proximate analysis (wt.%, as received)		
Moisture	10.74	0.69
Volatiles	9.69	99.05
Fixed C	70.11	–
Ash	9.46	–
Elemental analysis (wt.%, daf basis)		
Carbon	79.77	86.21
Hydrogen	6.86	13.79
Nitrogen	2.88	–
Oxygen (by difference)	10.49	–
Empirical formula	$\text{CH}_{1.03}\text{N}_{0.031}\text{O}_{1.58}$	$\text{CH}_{1.92}$
H/C molar ratio	1.03	1.92
O/C molar ratio	1.58	–
Calorific value (MJ/kg)	34.99	49.06

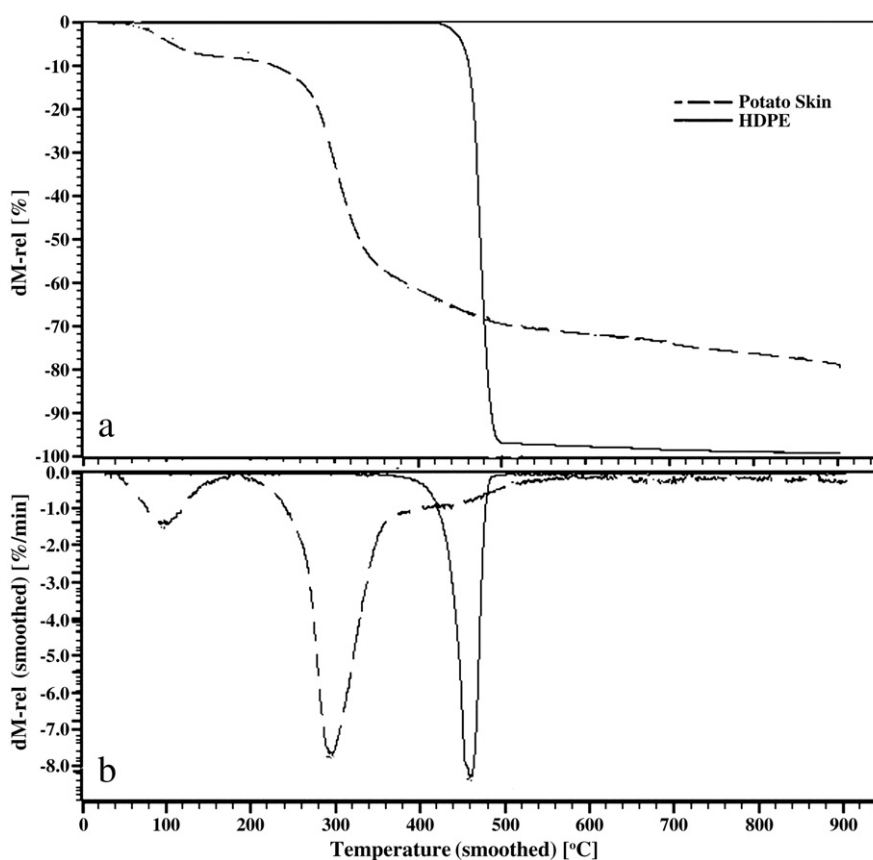


Fig. 1. TG (a) and DTG (b) curves of pS and HDPE.

Generally, increasing the sweeping gas flow rates increases the liquid yields. This is due to instant removal of pyrolysis vapors by higher sweeping gas flow rates, and in cases where they were quenched sufficiently, the liquid yield should have been high [18]. However, the maximum oil yield was reached as 48.3 wt.% at the sweeping gas flow rate of $400 \text{ cm}^3 \text{ min}^{-1}$ instead of $800 \text{ cm}^3 \text{ min}^{-1}$. Increasing the sweeping gas flow rate from $100 \text{ cm}^3 \text{ min}^{-1}$ to $400 \text{ cm}^3 \text{ min}^{-1}$ resulted in a 37% increase in oil yield.

The polyolefinic polymers can be thermally decomposed to gaseous and liquid hydrocarbons [19]. Therefore pyrolysis of pure polymer did not give any solid. There is no water evolved after pyrolysis as well. This result confirm with previous studies [6,8,9,11]. In one of these studies, the thermal decomposition of polyolefins and in particular, HDPE was carried out, especially under vacuum or inert atmospheres. Polyolefinic materials such as high density poly ethylene (HDPE) show a different behavior to lignocellulosic materials. Under pyrolysis conditions, HDPE decomposition starts at approximately $400 \text{ }^\circ\text{C}$ and progresses very rapidly up to $450\text{--}470 \text{ }^\circ\text{C}$ without producing any solid residue [13].

After determination of optimum sweeping gas flow rate as $400 \text{ cm}^3 \text{ min}^{-1}$, pyrolysis of HDPE was achieved at various temperatures of $400, 420, 450, 470, 500$ and $550 \text{ }^\circ\text{C}$ and resultant bio-oil yields were 41.0, 42.0, 48.3, 54.2, 56.0, 47.8%, respectively. Maximum oil yield was obtained at $500 \text{ }^\circ\text{C}$ with yield of 56 wt.%. It can be suggested that liquid yields increased with the increasing temperature of degradation, and nearly completed cracking at $500 \text{ }^\circ\text{C}$. Remedio et al. studied effect of temperature in the pyrolysis of HDPE in a pyroprobe equipment. It was found that an increase of liquid compounds with temperature, consequently the yield of solid product decreased with this variable [20]. Mastral et al. studied pyrolysis of HDPE in a fluidized bed reactor. At temperatures above $730 \text{ }^\circ\text{C}$ only gas and oil were obtained, the gas yield reaching 79 wt.% at this temperature. The highest amount of gas was obtained at $780 \text{ }^\circ\text{C}$ with yields of 86.4 wt.%. Above this temperature ($850 \text{ }^\circ\text{C}$), the

gas yield decreased due to cyclization reactions that formed aromatic hydrocarbons [21].

3.3. Co-pyrolysis

In the last part, pure and waste HDPE was mixed with biomass (pS) with various portions (1/2, 2/1, 1/1). The experimental results are given in Fig. 2a and b. The results of co-pyrolysis of pure and waste HDPE are similar. The ingredients of the polymers are nearly the same, but waste HDPE consists of dye. Compared to single biomass (pS) pyrolysis, the co-pyrolysis resulted in an increase of liquid yields. The yield of bio-oil obtained from the co-pyrolysis of 1:1 mixture of pS/HDPE was 41.39%. When weight ratio of biomass/HDPE was increased to 1:2, the yield of bio-oil increased to 50.88% and solid yields decreased from 21% to 9.16%. Consequently, the addition of HDPE to the mixture seemed to have increased the liquid production and decreased the gas formation.

Polyolefinic materials contain ~14 wt.% of hydrogen; these materials could provide hydrogen during thermal co-processing with biomass and can lead to an increase of liquid yields. This explains the reason why liquid fraction increases with addition of polymers into biomass before pyrolysis. Similarly, many researchers studied co-pyrolysis of biomass with synthetic polymer mixtures. The results showed that there was a synergistic effect on the co-pyrolysis of biomass–plastic mixtures in the form of enhanced oil yields. The decrease in char yields can be explained by that the hydrogen partly inhibited the recondensation reactions leading to formation of char [21].

The use of co-pyrolytic techniques on biomass/plastic ratios was investigated by other workers as well [5–9,12,15]. One of the important parameters for liquid production is the ratio in the feedstock. Rutkowski et al. studied the co-pyrolysis of cellulose with polystyrene in various ratios (cellulose/polystyrene=3:1, 1:1, 1:3). They were found that biomass/polymer ratio had a great influence on the product yields.

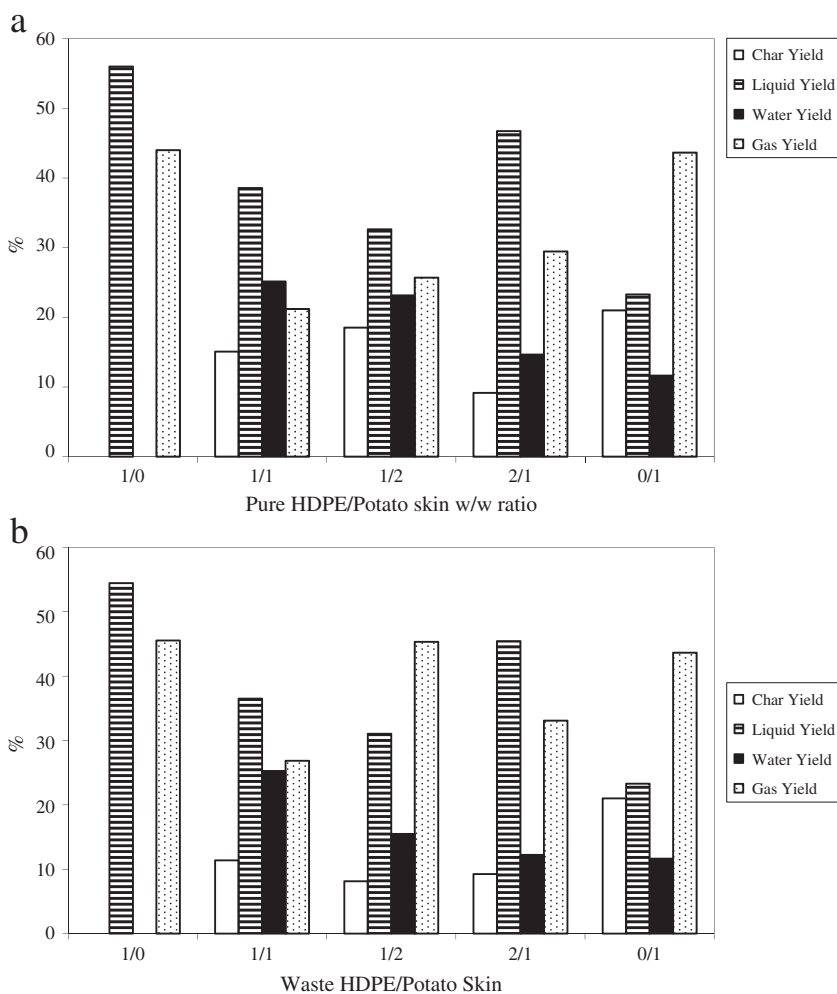


Fig. 2. Results of co-pyrolysis experiments.

The almost linear increase of liquid product yield can be observed as the polystyrene contribution in the C–PS mixture increases, reaching nearly 95 wt.% for the pure polymer. This was accompanied by decreases in both the char and gaseous product yields [7].

3.4. Characterization

The elemental analyses of both pyrolysis and co-pyrolysis oils and their aliphatic fractions are given in Table 2. The carbon content of co-pyrolysis bio-oils (~80 wt.%) is each far greater than that of bio-oil obtained from biomass (58.82 wt.%). The co-pyrolysis oils from pure and waste HDPE/pS contain 14.96 and 12.49% oxygen, respectively, giving them significantly higher energy content than bio-oil obtained from biomass. As known, high oxygen content is regarded as shortcoming of bio-oils obtained via pyrolysis [12]. In the co-pyrolysis of HDPE and biomass, oxygen content in the oils were significantly reduced which can be attributed to influence of the HDPE.

A comparison of H/C ratios with conventional fuels indicates that H/C ratios of the oils obtained in this study are found as very near to conventional fuels. In particular, H/C ratios of aliphatic sub-fractions were the most appropriate with H/C ratio of 2.08, which is almost as same as the H/C ratio of gasoline. When calorific values of raw material and oils obtained from biomass pyrolysis and co-pyrolysis conditions are compared, pure or waste HDPE addition to the biomass provides bio-oil production with higher calorific value and H/C ratio. Cornelissen et al. and Jeon et al. also reported that the co-pyrolysis of willow/PLA (polylactic acid) and waste wood chip/block polypropylene (PP) showed

synergetic interactions, respectively. Among the blends (10:1, 3:1, 1:1 and 1:2) tested, the 1:2 willow/PLA blend ratio showed the most synergistic effect due to the having the highest bio-oil yield, the lowest oxygen fraction and the highest HHV [15].

After elemental analysis, the bio-oils were separated into two fractions as n-pentane soluble and insoluble compounds (mostly cyclic compounds). The pentane soluble fraction was further separated by adsorption chromatography as aliphatic, aromatic and polar bases. Aliphatic base sub-fraction contains predominantly paraffins and olefins. Aromatic-base sub-fraction contains lower molecular weight aromatics usually benzene or its derivatives, and considering polar base sub-fraction which contains oxygenated compounds. While deasphalted oil (n-pentane soluble fraction) was obtained with pyrolysis of pS is 62%, it was increased to 76 and 73.43% by using pure and waste HDPE, respectively. Considering these results; deasphalted oil in the co-pyrolysis procedure was considerably enhanced by using HDPE compared with biomass pyrolysis.

According to the results of column chromatography of the oil from pS pyrolysis, aliphatic, aromatic and polar fractions are 20.89, 22.39 and 56.72 wt.%, respectively. By addition of HDPE to biomass, aliphatic fractions were increased in bio-oils, whereas aromatic and polar contents were reduced.

The FT-IR spectra of the investigated bio-oils and their aliphatic fractions are presented in Table 3. The spectra of oil from biomass presents some typical bands corresponding to O–H stretching vibrations between 3300 and 3600 cm^{-1} which indicate the presence of phenols and alcohols, C=O stretching vibrations between 1750 and 1650 cm^{-1}

Table 2
Elemental compositions and calorific values of bio-oils and aliphatic sub-fractions of bio-oils.

Component	Bio-oil ¹ (%)	Aliphatic ¹ (%)	Bio-oil ² (%)	Aliphatic ² (%)	Bio-oil ³ (%)	Aliphatic ³ (%)	Bio-oil ⁴ (%)	Aliphatic ⁴ (%)	Bio-oil ⁵ (%)	Aliphatic ⁵ (%)
C	85.72	83.96	81.64	81.33	58.82	70.15	82.80	83.34	80.47	85.98
H	14.28	16.04	13.61	16.33	8.54	12.00	12.66	14.96	12.49	14.79
N	–	–	0.14	0.46	1.22	1.30	0.85	–	0.30	–
O (difference)	–	–	4.61	1.88	31.41	16.54	3.69	–	6.74	–
H/C	2.00	2.29	2.00	2.41	1.74	2.06	1.83	2.10	1.86	2.06
O/C	–	–	0.04	1.77	0.40	0.18	–	–	–	–
HHV (MJ/kg)	49.60	51.55	46.42	50.74	32.00	38.06	45.61	52.03	44.00	50.42

1:1 mixture of biomass–polymer.

Bio-oil¹ and Aliphatic¹: Pure HDPE.

Bio-oil² and Aliphatic²: Waste HDPE.

Bio-oil³ and Aliphatic³: pS.

Bio-oil⁴ and Aliphatic⁴: Pure HDPE/pS.

Bio-oil⁵ and Aliphatic⁵: Waste HDPE/pS.

indicating the presence of aldehydes, ketones and carboxylic acids, and the absorbance peaks between 900 and 650 cm⁻¹ proving existence of single, polycyclic and substituted aromatic groups.

Especially, alcohols, phenols and carboxylic acids are not observed in the spectra of the bio-oils obtained from polymers and polymer-biomass mixtures. Bio-oil from pure HDPE is also free of carbonyl groups. In addition, the peaks in this range are less intensive with the HDPE addition to biomass. All the spectra include peaks of alkanes and alkenes. The presence of alkanes is indicated by the absorbance peak of C–H vibrations between 3000 and 2800 cm⁻¹ and by 1460–1350 cm⁻¹ bands due to the C–H bending. The absorbance peaks between 1630 and 1590 cm⁻¹ indicate the presence of alkenes.

Aliphatic fractions of bio-oils were subjected into gas–liquid chromatography. Aliphatic sub-fractions consist of n-alkanes, alkenes and branched hydrocarbons. The abundances of the products are listed and compared in Table 4 by a semi-quantitative study made by means of the percentage of area of the chromatographic peaks. According to the literature, GC/MS chromatograms of HDPE and HDPE/biomass, hydrocarbon chain is randomly broken resulting in a systematic series of “triplets” of peaks corresponding to linear alkane, alkene and diene hydrocarbons with the same carbon atom [10]. When the chromatograms were investigated, the carbon distribution typically was ranged from C10 to C30, aliphatic sub-fraction of bio-oils obtained from both pyrolysis and co-pyrolysis. The C distribution of aliphatic sub-fraction of HDPE pyrolysis yields products with straight-chain hydrocarbon structure with an increase of alk-1-enes, alk-2-enes and alkadienes with comparison to that of biomass pyrolysis. 1-nonadecenes is the most abundant component in aliphatic sub-fraction of oils obtained from co-pyrolysis pure HDPE/pS (35.65%) and waste HDPE/pS (25.33%). It is evident that co-pyrolysis favors the β-scission of primary radicals

(generating alkenes and alkadienes) instead of the intermolecular hydrogen transfer (generating alkanes). The straight chain alkanes and alkenes range between C₁₀–C₂₉ for bio-oil obtained from pyrolysis of biomass, between C₁₁–C₃₀ for bio-oil obtained from co-pyrolysis of biomass–polymer mixtures. Distribution of straight chain alkanes exhibits a maximum on C₁₃–C₁₈ and C₁₄–C₂₀ for oils obtained from pyrolysis and co-pyrolysis, respectively. A significant part of these hydrocarbons is represented by olefins.

4. Conclusions

In this study, co-pyrolysis of pS with synthetic and waste polymers in various proportions was carried out at 500 °C by semi-batch process in an inert atmosphere under fixed bed reactor conditions. The co-pyrolysis of pS/HDPE with ratio of 1:2 is resulted in the most pronounced synergistic effect with the high liquid yield. Results of FT-IR, GC-MS, column chromatography and elemental analyses of bio-oils have showed that HDPE addition into biomass sample in the application of co-pyrolysis changes the chemical composition of resultant pyrolytic liquids. A high content of carbonyls, hydroxyls and aromatics in the oils from biomass declined with co-pyrolysis of pS/HDPE mixtures. High amounts of 2-alkenes, 1-alkenes and alkadienes were obtained in the co-pyrolysis liquid fractions. The bio-oil obtained from co-pyrolysis has improved properties compared with that of oil obtained from the single biomass pyrolysis. The carbon and hydrogen contents were increased, while the oxygen content was decreased. In particular, the co-pyrolysis bio-oils have high calorific values making them attractive for use as a fuel. It is concluded that addition of HDPE improves the quality and quantity of the bio-oil in terms of hydrocarbon distribution.

Table 3
Results of FT-IR spectra for bio-oils and their aliphatic sub-fractions.

Band position (cm ⁻¹)	Assignment	pS		Pure HDPE		pS/pure HDPE 1:1		Waste HDPE		pS/waste HDPE 1:1	
		Bio-oil	Pentane	Bio-oil	Pentane	Bio-oil	Pentane	Bio-oil	Pentane	Bio-oil	Pentane
3600–3400	(O–H)	+	–	–	–	–	–	–	–	–	–
3040–3000	(C–H) aromatic ring	–	–	+	+	+	+	+	+	+	+
2980–2930	as(C–H)	+	+	+	+	+	+	+	+	+	+
2870–2850	s(C–H)	+	+	+	+	+	+	+	+	+	+
1720–1770	(C=O)	+	+	–	–	+	–	–	–	+	–
1625–1590	(C=C)	–	+	+	+	–	+	+	+	+	+
1600, 1580, 1450	Aromatic ring	+	+	–	–	–	–	+	–	+	–
1460	δ _{as} (CH ₃ , CH ₂ scissor)	+	+	+	+	–	+	+	+	+	+
1375	δ _s (C–H)	+	+	–	–	+	+	+	+	+	+
1275–1200	as(=C–O–C)	+	–	+	+	–	–	–	–	–	–
1150–1070	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 4
Relative proportions (area %) of main pyrolysis compounds in the aliphatic sub-fraction of bio-oils.

Compound	% Area				
	Waste HDPE/ pS	Waste HDPE	Pure HDPE/ pS	Pure HDPE	pS ^a
Undecane	0.48	0.46	0.74	0.89	–
1-Undecene	–	–	–	1.49	–
Cyclododecane	0.62	0.54	0.58	–	–
Methylcyclododecane	0.71	–	–	–	–
Dodecane	0.55	0.37	0.51	1.47	0.40
Dodecene	–	–	–	1.97	–
1,11-Dodecadiene	–	0.50	0.63	–	–
1-Tridecene	1.41	1.25	1.54	2.33	0.51
Tridecane	1.14	0.97	1.10	1.71	0.59
1,13-tetradecadiene	0.49	1.32	0.64	–	–
1,12-tetradecadiene	–	–	0.65	–	–
1-Tetradecene	2.03	2.21	2.46	3.02	–
13-Methyl-11-tetradecene	1.10	–	–	–	–
5-Tetradecene	–	0.47	–	–	–
Tetradecane	1.31	1.33	1.27	1.87	–
Pentadecene	2.19	2.40	2.56	3.05	–
Pentadecane	1.40	1.47	1.38	2.05	1.30
7-Hexadecene	–	2.34	–	–	–
1-Hexadecene	2.13	–	–	2.90	–
Hexadecane	1.75	1.55	1.38	2.22	0.81
11-Hexadecene	0.50	–	–	–	–
14-Methyl-8-hexadecene	0.48	0.63	–	–	–
1-Heptadecene	4.05	2.26	7.24	2.65	–
Heptadecane	1.31	1.43	1.27	4.10	0.63
Heptadec-8-ene	0.65	–	–	–	0.26
1-Octadecene	4.39	4.71	5.01	5.59	2.15
Octadecane	14.66	5.34	1.24	4.06	0.38
1-Nonadecene	8.66	35.65	25.33	8.18	1.61
Nonadecane	1.25	1.45	2.98	2.93	0.32
1-Eicosyne	–	0.55	1.36	–	–
Eicosane	1.60	1.73	1.59	5.21	0.35
Cycloeicosane	–	3.28	5.15	–	–
10-Heneicosene	2.09	–	–	2.32	–
Heneicosane	1.64	1.82	1.64	8.27	0.64
Heneicosene	2.82	–	5.18	–	–
Docosane	1.73	1.88	1.56	2.01	–
1-Docosene	2.86	8.70	5.18	6.63	0.58
9-Tricosene	2.14	–	–	–	–
Cyclotetracosane	2.13	2.55	5.08	2.34	0.72
Tetracosane	1.68	1.84	1.63	2.32	0.51
Pentacosane	1.90	1.88	1.65	7.61	1.61
Hexacosane	2.23	–	–	2.53	0.66
Heptacosane	–	–	–	2.58	0.91
Cyclooctacosane	2.82	5.14	–	–	–
Octacosane	2.88	–	–	–	0.61
Nonacosane	–	–	4.82	–	–
Triacosane	–	–	–	3.92	–

^a pS: potato skin.

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