

# Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene



Eylem Önal<sup>b</sup>, Başak Burcu Uzun<sup>a</sup>, Ayşe Eren Pütün<sup>a,\*</sup>

<sup>a</sup> *Anadolu University, Dept. of Chemical Engineering, İki Eylül Campus, 26555 Eskisehir, Turkey*

<sup>b</sup> *Bilecik Şeyh Edebali University, Faculty of Engineering, Chemical and Process Engineering, Bilecik, Turkey*

## ARTICLE INFO

### Article history:

Received 23 April 2013

Accepted 13 November 2013

Available online 20 December 2013

### Keywords:

Bio oil

Co-pyrolysis

HDPE

Almond shell

## ABSTRACT

Biomass from almond shell (aS) was co-pyrolyzed with high density polyethylene (HDPE) polymer to investigate the synergistic effects on the product yields and compositions. The pyrolysis temperature was selected as 500 °C, based on results of TGA-DTG. Co-pyrolysis of HDPE-biomass 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 23%, as the weight ratio of HDPE in the mixture was doubled. Obtained bio-oils were analyzed with using column chromatography, <sup>1</sup>H NMR, GC/MS, and FT-IR. According to analyses results, produced liquids by co-pyrolysis had higher carbon (26% higher) and hydrogen contents (78% higher), lower oxygen content (%86 less) with a higher heating value (38% higher) than those of biomass oil.

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## 1. Introduction

Plastics are used in many aspects of human life, but their mass consumption has caused severe environmental pollution, with a great loss of resources from their disposal. Much attention has been paid to solve these problems, with the production of fuel or recycling of valuable chemicals from pyrolysis having been intensively studied as a potential solution. The pyrolysis (or thermal cracking in an inert atmosphere) of waste plastics, particularly polyolefins, arouses great interest for the valorization of these wastes, as it allows high yields of fuels and raw materials to be obtained for the benefit of the petrochemical industry. Moreover, the pyrolysis process has few environmental issues [1,2]. Having a high hydrogen-to-carbon ratios and convenient molecular chain structures, waste commodity plastics such as low and high density polyethylene, polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC) are very suitable for liquid production [3].

Biomass (plant materials) has been recognized as a major world renewable energy source to supplement declining fossil fuel resources. It is composed mainly of cellulose, hemicelluloses, lignin and minor amounts of other organics, which are determined as the elements of carbon, hydrogen and oxygen with high energy content [4]. Biomass energy is destined to play an important role in the future energy systems of the world. Furthermore, it has the advantage of reducing global warming since it uses carbon dioxide through photosynthesis. Biomass could also be sources of energy and raw chemical feedstock because it produces various

biochemical materials. Meanwhile, biomass is typically converted to energy through thermochemical conversion, such as gasification, combustion and pyrolysis. Pyrolysis of biomass has received strong interest in recent decades when the awareness on limited amounts of fossil resources called for alternative solutions based on renewable materials [5]. However, biomass bio-oil has very unstable fuel properties compared with conventional oils. Due to its higher oxygen and acid content; its water content is also too high (over 20 wt.%). Therefore, these shortcomings should be overcome for its use as a regular fuel. To improve the fuel suitability of bio-oil, co-pyrolysis of biomass and organics containing higher hydrogen contents can be considered. Therefore, plastics could potentially be a beneficial feedstock due to their higher hydrogen content and small amount of water in their pyrolysis derived oil. When plastic and biomass are simultaneously pyrolyzed, the stability of the oil product would be expected to be greatly improved compared with that from single biomass pyrolysis, because plastic can provide plenty of hydrogen to the biomass pyrolysis [1].

There are many studies about thermal decomposition of PE, PP, tyre, PS etc. with biomass [5–15]. Data obtained in these studies demonstrated that the co-pyrolysis of plastic and biomass resulted in a high oil yield with an acceptable quality. Nevertheless except for a few studies in the literature, pyrolysis of HDPE with biomass has not been sufficiently investigated [16–18]. For example, Rotliwala and Parikh studied co-pyrolysis of HDPE with de-oiled cake of jatropha (JC) in a batch reactor at 450 °C, under nitrogen flow and at the atmospheric pressure. The yield of liquid product was found to be as 63%. They characterized the liquid phase obtained from co-pyrolysis by gas chromatography–mass spectrometry and ASTM D86 (boiling point distribution) analyses.

\* Corresponding author. Tel.: +90 222 335 05 80 6514; fax: +90 222 3239501.

E-mail address: [aeputun@anadolu.edu.tr](mailto:aeputun@anadolu.edu.tr) (A.E. Pütün).

HDPE co-processing with JC significantly increased the proportion of gasoline like ( $C_6$ – $C_{12}$ ) fraction to 45% with comparing the HDPE pyrolyzed alone [16] Berruenco et al., studied co-pyrolysis of HDPE/sawdust mixtures in a fluidized bed reactor at five temperatures: 640, 685, 730, 780 and 850 °C. They showed that the gas yield increased and gas composition changed drastically when the temperature was increased for both pure components and the mixture. In addition, average heating value of produced gases by co-pyrolysis of biomass and HDPE are found greater than that of obtained biomass alone [18].

HDPE is the fourth-largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. HDPE has accounted for a major share of ethylene consumption structure over the recent years. The demand for HDPE had an increase of 3.6% in a year to 31.3 million MT in 2011 [19]. In the case of Turkey, according to the Turkish State Statistical Institute's database, 25.28 million tones of municipal waste was collected in 2010 and 33,637 tones of this municipal wastes are plastics. All plastics and other kind of wastes are recovered by methods such as incineration, composting or controlled landfilling [20]. By the way the conversion of waste plastics to valuable chemicals or fuels is more advantageous than the methods mentioned above. Plastics recycling by thermal and chemical methods of conversion of scrap polymers, as gasification, liquefaction, hydrolysis, pyrolysis, and thermo-catalytic degradation, are well known and environmentally accepted. They reduce the impact of waste plastics on the environment and may be a cheap source of energy and useful raw materials [21,22].

Almond is a crop of major importance throughout the world's temperate growing regions with the worldwide almond production in 2011 being approximately 2.00 million ton according to FAO (Food and Agriculture Organization). Turkey is one of the important almond producers among Spain, Greece and Italy in EU. Turkey has a share of 3.5% in the world shelled almond producing and 44,366 tons of almonds and 23,205 tons of almond shells are produced annually. One of the wastes which can be considered to have a good potential as a biomass feedstock is fruit shells. Between the outer hull and the nutritious kernel lies the shell, primarily composed of cellulose, hemicelluloses and lignin. The valorization of such by-product could be an important way to add value to a low value product. Despite the existence of a number of published papers that have been reported the production of activated carbons from such by-product using different methodologies, adsorption applications, gasification of almond shells etc. [23,24,26]. There are a few studies about bio-oil production from this lignocelluloses source. Moreover, there are quite few studies about thermal degradation of HDPE in a pyrolysis reactor. According to our previous work, pyrolysis of aS gives 21% of bio-oil which can be considered as a low amount with compared to other biomass sources such as olive residues and cotton seed cake [23–26]. This study aims to increase the oil yield of aS pyrolysis with addition of a widely used polymeric waste (HDPE), a difficult thermally degraded disposal with compared to PP, LDPE [2,27,28].

In this study, HDPE is selected as a widely used plastic sample for the co-pyrolysis with a well-known lignocellulosic biomass source (aS) to investigate the synergistic effect on bio-oil yield and composition and understand the chemical transformations which could have taken place during the co-pyrolysis. Moreover, the co-pyrolysis of biomass and HDPE bio-oil was characterized in detail to determine its possibility of being a potential energy source and chemical feedstock.

## 2. Experimental

The almond shell (aS) taken from the city Mugla-Datca located in Aegean region, western part of Turkey was used as a biomass

sample, while HDPE was considered as a representative synthetic polymer. HDPE samples used in the experiments were supplied from a petrochemical company (PETKİM Aliğa, Turkey). The particle size of polymer sample was  $D_p = 10 \mu\text{m}$ . Air-dried biomass samples were ground in a high speed rotary cutting mill and screened to give fractions of  $D_p > 1.8 \text{ mm}$ ;  $1.8 > D_p > 0.85 \text{ mm}$ ;  $0.85 > D_p > 0.425 \text{ mm}$ ;  $D_p < 0.425 \text{ mm}$ ,  $0.425 < D_p < 0.224$ ,  $0.224 < D_p$ . Average particle size was found to be as 1.67 mm.

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 aS and HDPE. Experiments were applied to 25 mg sample,  $100 \text{ mL min}^{-1}$  nitrogen flow with  $10 \text{ }^\circ\text{C min}^{-1}$  heating rate. The TG and DTG curves for aS and HDPE recorded from room temperature to 1100 °C are shown in Fig. 1.

The pyrolysis experiments were performed using a fixed bed reactor (Heinze Retort). All detailed information about the system could be found in our previous studies [29,30]. The experiments were conducted at the atmospheric pressure. HDPE, aS and their mixtures (1:1; 1:2; 2:1) were placed in the reactor. Prepared 10 g of samples were put into the reactor. The reactor was heated from room temperature to the final pyrolysis temperature of 500 °C with a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . The sweeping gas nitrogen is passed through the reactor at the gas hourly space velocity (GHSV) of  $0.015 \text{ h}^{-1}$ . The flow of gas released was measured by a rotameter for the duration of experiments. Experimental apparatus was held at adjusted temperature for 30 min. The liquid products were collected in ice-cooled traps. At the end of the experiments, the liquid product consisting of aqueous and oil phases were separated and weighed. All bio-oil yields were given water free basis. Char yield was determined from the overall weight losses of the reactor. The liquid product was weighed and recovered in dichloromethane for the further analyses. Water was determined by a separating funnel. Gas yield was determined by overall material balance.

All the yields were calculated on a dry-ash-free (daf) basis and each experiment was performed. The reproducibility of the experiments is acceptable and experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out three times within the experimental error of less than  $\pm 0.5$ .

The main analyses methods used to reveal the composition of bio-oil are elemental analysis, column chromatography, proton nuclear magnetic resonance spectroscopy ( $^1\text{H NMR}$ ), Fourier transform infrared (FT-IR), column chromatography, and gas chromatography/mass spectrometry (GC/MS). This procedure that we used is illustrated in Fig. 2 and detailed about the analyses were given in our previous studies [29].

## 3. Results and discussion

### 3.1. Thermal gravimetric analysis of raw materials

The normalized weight loss (TG curve) and rate of weight loss (differential thermogravimetric curve (DTG)) for the aS and HDPE are shown in Fig. 1. The results show that the major weight losses of the aS and HDPE occur at  $288.9 \text{ }^\circ\text{C}$ – $345.4.6 \text{ }^\circ\text{C}$  and  $470 \text{ }^\circ\text{C}$ , respectively. It can be seen that biomass sample decomposed at lower temperature than polymers while polymers begin to decompose  $430 \text{ }^\circ\text{C}$  and showed the maximum mass loss around  $470 \text{ }^\circ\text{C}$  (this can be seen from DTG of polymer) and about  $500 \text{ }^\circ\text{C}$ , HDPE degraded completely without leaving any residue. As a consequence of TG/DTG curves of both materials, the optimum co-pyrolysis temperature was selected as  $500 \text{ }^\circ\text{C}$ .

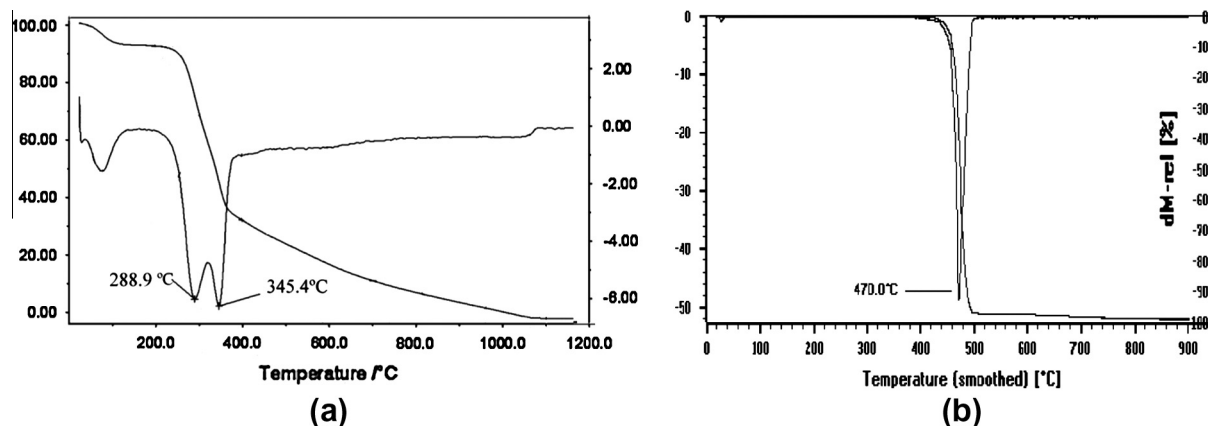


Fig. 1. TG and DTG curves AS (a) and HDPE (b).

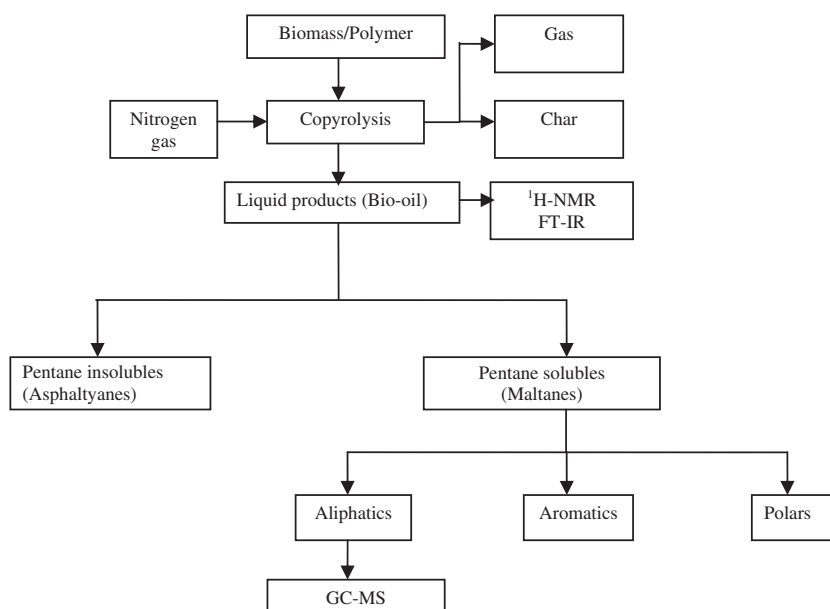


Fig. 2. Flow chart of experimental methodology.

### 3.2. Product yields and synergetic effect

The role of carrier gas during pyrolysis is to evaluate the effect of the residence time of the gaseous products as a result of pyrolysis reactions by removing the products from the reactor. It is an essential parameter for maximizing the oil obtained. Increasing the gas flow rate favors reduction of the secondary reactions, like repolymerization and recondensation [6]. A series of HDPE and aS experiments were carried out under the different nitrogen flow rates in our previous study [30]. According to these results, it is decided to achieve the co-pyrolysis experiments at a constant gas hourly space velocity of  $0.015 \text{ h}^{-1}$ .

In this part, the experiments were conducted to determine the effect of HDPE/aS ratio on the pyrolysis yields for biomass samples. During experiments 10 g of mixtures of aS was mixed with HDPE in various portions (1:1, 1:2, 2:1 w/w) and then placed into the reactor. The product yields obtained from thermal degradation (pyrolysis) of individual aS, HDPE, and of their binary mixtures of aS and HDPE are given in Table 1. The HDPE ratio is a main factor that affects the product yields of the gas, liquid, and solid from the blends of biomass and HDPE. As seen in Table 1, the liquid and solid yield is between 37–51 wt.% and 9–20 wt.%, respectively. At 1:1 weight

Table 1  
Effect of the blending ratio HDPE and aS product yield at 500 °C.

HDPE/aS	Solid (%)	Liquid (%)	Water (%)	Gas (%)
1:0	0.00	56.00	0.00	44.00
1:1	15.58	41.39	10.01	33.02
1:2	20.04	37.93	13.88	28.16
2:1	9.25	50.88	15.42	24.45
0:1	28.23	21.12	18.03	32.63

Table 2  
Synergetic effects obtained for bio-oil after co-pyrolysis of HDPE/aS.

HDPE/aS ratio (w/w)	The percentage of synergetic effect
1:2	7.34
1:1	13.22
2:1	14.36

ratio of mixture, the oil, gas and solid yields were obtained as 41.39%; 33.02% and 15.58%, respectively. With increasing the HDPE ratio in mixtures, the oil yield gradually increases, but the gas and

**Table 3**  
Elemental compositions of bio-oils.

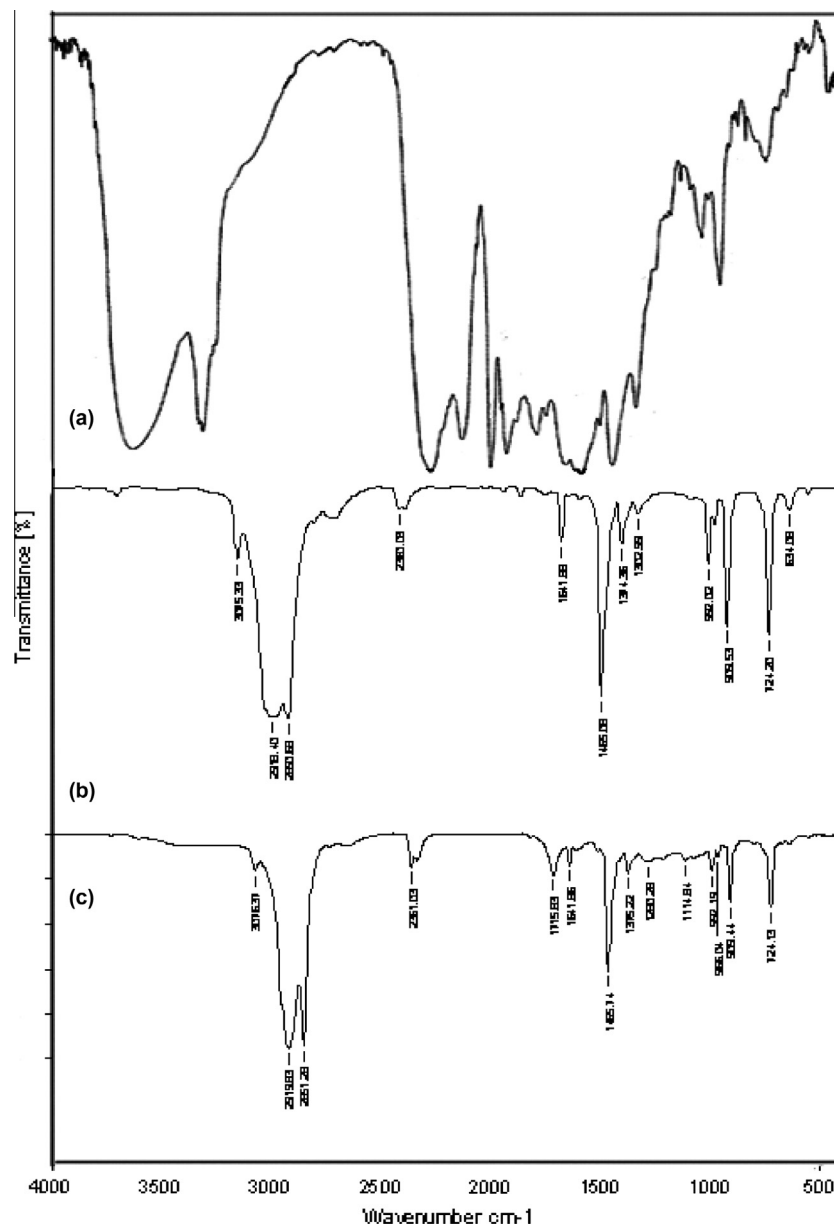
Component	HDPE (%)	aS (%)	HDPE/aS (1:1) (%)
C	85.72	63.85	80.62
H	14.28	8.60	15.32
N	–	0.17	0.33
O (difference)	–	27.75	3.74
H/C	2.00	1.62	2.28
O/C	–	0.33	0.035

solid yields sharply reduces. At 2:1 weight ratio of mixtures, the liquid yield reaches to its maximum, which is about 51 wt.% in our experimental conditions. Due to no ash and fixed carbon present in the HDPE sample (0 wt.%), the quantity of solid residue was not observed.

In literature, there are many studies about the addition of various plastics (PP, PS, PLA etc.) to biomass before the pyrolysis [7–9,13,31]. Abnisa et al. indicated that the ratio of feed was the most important variable on liquid yields in the co-pyrolysis of palm shell

and polystyrene waste mixtures to synthesis liquid fuel [7]. According to this study, maximum liquid yield of ~68.3% was obtained under the optimum conditions. They found that liquid mainly consisted of aliphatic and aromatic hydrocarbons. Cornelissen et al. pyrolyzed biomass together with polylactic acid (PLA) and investigated the bio-oil yield and composition. Flash co-pyrolysis of willow and PLA resulted in an enhanced bio-oil yield with a lower water content. Synergistic effects were observed to addition of PLA to willow caused an increase of 28% in bio-oil yield and a decrease of 37% in water content [31].

Synergetic effect was investigated on the product yields of HDPE/aS mixtures in our study. That is, two or more discrete influences or agents acting together create an effect greater than that predicted by understanding only the separate effects of the individual agents. The effect of the HDPE on the co-pyrolysis process can be observed by comparing the co-processed oil yields to the predicted values are calculated after the pyrolysis of HDPE and aS alone. According to literature, when the difference between the experimental value and the predicted values is positive, then it can be concluded that addition of HDPE to aS enhances the



**Table 4**  
Relative proportions (area %) of main pyrolysis compounds in the aliphatic sub-fraction of bio-oils.

Compound	% Area		
	aS	HDPE	HDPE/aS (1:1)
Undecane	–	0.89	–
1-Undecene	–	1.49	–
Dodecene	–	1.97	–
1,11-Dodecadiene	–	–	0.35
1-Tridecene	0.97	2.33	–
6-Tridecene	–	–	0.81
1,12-tridecadiene	–	–	0.86
Tridecane	0.97	1.71	–
1,13-tetradecadiene	–	–	0.46
1-Tetradecene	1.94	3.02	1.74
13-methyl-11-tetradecene	–	–	0.50
5-tetradecene	–	0.47	–
Tetradecane	2.91	1.87	1.11
Pentadecene	1.46	3.05	2.05
1,15-pentadecadiene	–	–	0.87
Pentadecane	4.37	2.05	1.36
7-Hexadecene	–	0.68	–
1-Hexadecene	–	2.90	2.46
Hexadecane	2.91	2.22	1.43
11-Hexadecene	–	–	0.39
14-Methyl-8-hexadecene	–	0.63	–
1-Heptadecene	–	2.65	4.20
Heptadecane	2.43	4.10	1.29
1-Octadecene	–	5.59	2.10
9-Octadecene	–	–	1.64
Octadecane	1.94	4.06	1.23
1-Nonadecene	–	8.18	19.03
9-Nonadecene	–	–	4.74
Nonadecane	13.11	2.93	1.30
1-Eicosyne	–	–	1.48
Eicosane	10.19	5.21	3.24
Cycloeoicosane	–	–	2.28
10-Heneicosene	–	2.32	2.30
Heneicosane	19.42	8.27	1.68
Heneicosene	–	–	14.09
Docosane	4.85	2.01	1.69
1-Docosene	–	6.63	11.80
Tricosane	5.34	–	–
9-Tricosene	–	–	2.98
Cyclotetracosane	–	2.34	–
Tetracosane	7.28	2.32	1.66
Pentacosane	9.22	7.61	1.69
Hexacosane	10.67	2.53	1.71
9-Hexacosene	–	–	3.48
Heptacosane	–	2.58	–
Triacotane	–	3.92	–

bio-oil production [32–34]. Table 2 shows the synergetic effects obtained for the bio-oil yields in the co-pyrolysis of HDPE and aS. As shown in Table 2, an increase in the HDPE ratio in the mixture leads to an increase of synergetic effect in the production of bio-oil. As the predicted value of oil yield of the mixture prepared by using 2:1 weight ratio of HDPE/aS mixture was 44.49%, it was obtained as 50.88% in the experimental study. A 14% of increase was

**Table 5**  
Results of <sup>1</sup>H NMR for the bio-oils.

Hydrogen type	Chemical shift (ppm)	aS (%)	HDPE (%)	HDPE/aS (1:1) (%)
CH <sub>3</sub> γ or further from aromatic ring and paraffinic CH <sub>3</sub>	1.0–0.5	–	31.59	29.95
CH <sub>3</sub> ; CH <sub>2</sub> and CH β to aromatic ring	1.5–1.0	4.28	23.69	21.93
CH <sub>2</sub> and CH attached to naphthenes	2.0–1.5	–	2.59	4.24
CH <sub>3</sub> ; CH <sub>2</sub> and CH α to aromatic or acetylenic	3.0–2.0	44.44	9.92	9.43
Total aliphatics	3.0–0.5	48.72	67.79	65.55
Hydroxyl, ring-joining methylene, methine or methoxy	4.0–3.0	27.18	–	2.83
Phenols, non-conjugated olefins	6.0–4.0	8.51	32.21	21.23
Aromatics, conjugated olefins	9.0–6.0	15.58	0.42	10.38

determined in the experimental studies, which means that there is a synergetic effect on the co-pyrolysis bio-oils obtained from HDPE and aS.

Pyrolysis of HDPE resulted in a hydrocarbon mixture, mainly consisting of n-paraffins and n-olefins, in the temperature range of between 400 and 450 °C, whereas products of co-pyrolysis have many other compounds with oxygen, nitrogen, etc. depending on the selected raw materials. As known, the thermal pyrolysis of polymers occurs by a radical mechanism (initiation, propagation and termination). The mechanism of co-pyrolysis is more complex due to the having various chemical species. The following elemental reactions take place during co-pyrolysis of HDPE and biomass could be proposed as follows: initiation, formation of secondary radicals (depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), and isomerization via vinyl groups) and finally termination by disproportionation or recombination of radicals [35].

All these can be summarized as Marin's proposal for the mechanism of co-pyrolysis. The degradation of biomass started at a lower temperature than HDPE degradation. Radicals evolved from biomass degradation were able to initiate the de-polymerization of HDPE. The addition of biomass results in a first step to its independent degradation and lead to a solid formation. Secondly, the assisted degradation of polyolefin occurs. Finally, during the degradation of polymer some interactions between the radicals and the solid are responsible of the formation of 2-alkenes [10]. These reactions accelerate decomposition of biomass in the HDPE, which leaves behind smaller amount of residue. Thus, enhanced rate of thermal decomposition of biomass reduced the residue formation, which leads a synergistic effect [36]. This mechanism is to present the role of evolved and free radicals in stabilization. The reaction of hydrogen transfer from a polyolefinic chain to biomass-derived radicals will stabilize the primary products from cellulose thermal degradation. The stabilization of radicals increases condensable fractions and results in high oil yields. Moreover, scission of polyethylene chains causes an increase of aliphatic fraction of oil [5–13,31].

### 3.3. Pyrolysis oils chemical characterization

Detailed characterization of oils was performed to reveal the effect of HDPE addition to biomass. The results of elemental analysis and heating values of the oils obtained from biomass, HDPE and HDPE/biomass mixtures are given in Table 3. After co-pyrolysis applied, hydrogen content of oil increased. To enhance the H content of the biomass pyrolysis oil, it should be co-pyrolyzed with high H-containing materials to favor the improvement of the oil quality. The heating value of bio-oil from biomass (aS) was very low when compared with liquid products obtained from both HDPE and HDPE/aS. Due to high oxygen content, the oil obtained from biomass pyrolysis has lower calorific value and strong corrosive properties. In addition, the contents of C and H and H/C ratios are

important indicators of the fuel properties [31,37]. As seen in Table 3, the co-pyrolysis oils contain higher contents of C and H, whereas having lower contents of O and N. The addition of HDPE to biomass increases the H/C ratio from 1.62 to 2.28. Liquid products obtained from the pyrolysis of HDPE and co-pyrolysis of biomass/HDPE are likely to have a high energy content, because of their high H/C ratio (Table 3). A further comparison of H/C ratios with conventional fuels indicates that H/C ratios of the oils obtained by the co-pyrolysis lie between those of diesel and gasoline like products.

The results of FT-IR analysis of the obtained oils are shown in Fig. 3. For all spectra, aliphatic hydrocarbon such as alkenes and alkanes were detected at the range of 2926–2856  $\text{cm}^{-1}$ , respectively. In Fig. 3a and c, the strong peaks in the range of 900–700  $\text{cm}^{-1}$  showed the presence of aromatic hydrocarbons. It can be seen that the existence of the HDPE can remarkably reduce the oxygen in the pyrolysis liquid product. When there is no HDPE (pyrolysis-oil of aS alone), the peaks at range of 3400–3244  $\text{cm}^{-1}$  and 1717–1714  $\text{cm}^{-1}$ , which represent –OH and –C=O groups, respectively, perform high intensity. However, these peaks nearly disappear while the HDPE exists. Obviously, polymers can effectively remove the oxygen of pyrolysis products. These results are consistent with the results of elemental analysis.

The results of GC/MS analysis of the aliphatic fraction of bio-oils (from aS, HDPE and co-pyrolysis of aS and HDPE) are given in Table 4. Abundances of the peaks are listed in, as the area (%) related to the total ion intensity. It is clear that co-pyrolysis of HDPE and aS leads to an increase of 75% in alkene fractions comparing with the results obtained from individual biomass pyrolysis. Hence, HDPE addition has a marked impact on both the degradation mechanism and product distribution. As proposed by Jakab et al. [8], and Sharypov et al. [9,10], the formed solid from biomass evolves to act as a radical donor. The evolved radicals from biomass pyrolysis stabilize the free radicals produced from polymers. Stabilization of these radicals is enhanced by progressing the pyrolysis and n-alkenes are generated by  $\beta$  scission.

The straight chain of n-alkanes are ranging from  $\text{C}_{10}$  to  $\text{C}_{34}$  for HDPE,  $\text{C}_{13}$  to  $\text{C}_{29}$  for aS, and  $\text{C}_{13}$  to  $\text{C}_{33}$  for HDPE/aS in the aliphatic sub-fraction of pyrolysis oils. Products in the range of  $\text{C}_{13}$ – $\text{C}_{20}$ , an indicator of diesel like fraction, formed the major constituent in the liquid product [16]. As seen, in the spectrum of aliphatic sub-fraction of oil from co-pyrolysis of HDPE/aS, heptadecene ( $\text{C}_{17}$ ) nonadecene ( $\text{C}_{19}$ ), heneicosane ( $\text{C}_{20}$ ) and 1-docosene are abundant products in the range of  $\text{C}_{13}$ – $\text{C}_{25}$  like diesel fraction.

Aromatics, olefins, and paraffins content of the obtained oils are determined using  $^1\text{H}$  NMR spectroscopy given in Table 5.  $^1\text{H}$  NMR results indicated that the aromaticity of the oil obtained from co-pyrolysis of the HDPE/aS mixtures is very low compared to that of the oil obtained by pyrolysis of the biomass alone. The olefins in the 4.0–6.0 ppm interval have been observed as the highest percentage in the obtained HDPE oil. The olefinic hydrogen percentage in oil from aS was 8.51% and increased to 21.23% after co-pyrolysis. The aS oil has the highest value of the protons located in carbonyl groups, which were observed in the 2.0–3.0 ppm range; the ether and ester group protons were observed in the 3.0–4.0 ppm range.

Aliphatics (alkanes and alkenes) are essential compounds in bio-oils, since they show the similarity of bio-oil with the gasoline and derivatives. The liquid column chromatographic technique was subjected to separate aliphatics from bio-oil. Oils obtained by pyrolysis were separated into two fractions, as n-pentane-soluble (deasphalted oil) and insoluble (asphaltenes) using n-pentane. The n-pentane-soluble materials were further separated by column chromatography into aliphatic, aromatic, and polar fractions. The yield of de-asphalted oil obtained from the pyrolysis of biomass is 50%. The aliphatic fraction of pyrolysis oil increased from 14% to 68.77% by co-pyrolysis with HDPE. The polar and aromatic

fractions were 34% and 52% in biomass pyrolysis and decreased to 7.77 and 23.46% in the oil obtained by co-pyrolysis of HDPE/aS mixture. This is also consistent with of the result of elemental analysis.

#### 4. Conclusions

In this study, synergic effect on the co-pyrolysis of aS/HDPE was observed both on yields and compositions. It could be attributed to the hydrogen release due to the cracking of polyethylene chains during the thermal decomposition. The conclusions can be drawn as follows:

- The results of elemental analysis show that oil obtained by co-pyrolysis is quite similar to currently utilized transport fuel in terms of H/C ratios and heating values.
- Co-pyrolysis of HDPE/aS decreases oxygen content which makes the oil more stable. The oxygen content aS oil is decreased 86.5% after addition of HDPE (1:1).
- In the spectrum of aliphatic sub-fraction of oil from co-pyrolysis of HDPE/aS, heptadecene ( $\text{C}_{17}$ ) nonadecene ( $\text{C}_{19}$ ), heneicosane ( $\text{C}_{20}$ ) and 1-docosene are abundant products in the range of  $\text{C}_{13}$ – $\text{C}_{25}$  like diesel fraction.
- The addition of HDPE to aS has a positive effect on fuel properties of obtained oil as well.
- The aliphatic contents of the oils obtained by HDPE pyrolysis and co-pyrolysis of HDPE/aS are the highest compared to the oils obtained by aS individual.

In this study, the addition of HDPE to biomass allowed to obtain the bio-liquids by pyrolysis methods with the yield near 40–50% wt. at 500 °C at atmospheric pressure. As a conclusion, the method of biomass co-pyrolysis with synthetic polymer has good prospects for integrated production of engine fuels, chemicals, taking into account a rather high yield of bio-oil. Besides, this process can solve the urgent plastic disposals.

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