



Recycling of plastic wastes via pyrolysis

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Abstract

Pyrolysis for the simultaneous generation of oils and gases can be convenient to obtain hydrocarbons and even to recover crude petrochemicals or to generate energy from waste plastics. A Gray–King apparatus has been used to pyrolyze waste polyethylene (PE), polystyrene (PS), both separately and with different compositions. Thermogravimetric analysis of waste plastics indicated the critical temperatures, which should be effective for pyrolysis. The chosen heating rate was low in order to achieve higher liquid yields. The results showed that waste PS yielded higher liquid, and waste PE yielded higher gaseous products. The dominant liquid product of PS waste was styrene whereas for waste PE, propenylbenzene was the dominant pyrolysis product. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

As a result of the increase in the consumption of plastics, the wastes generated from their production, transportation and consumption create various environmental problems. The problem of waste plastic management can be solved if economic, political, technological, energetic, material and environmental dimensions are all considered [1].

Since plastics are generally high calorific value products ranging approximately from 18 000 to 38 000 kcal/kg, utilization for their energy alone or for related

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chemical production may be an alternative option [2]. The two main processes exploring these options are incineration and pyrolysis. Incineration is a destructive process in which hydrocarbons are converted to their combustion products whereas pyrolysis may convert them to other hydrocarbons, which may be utilized as fuel, new material and monomer [3].

Pyrolysis processes are generally classified into low, medium and high temperatures based on the range of temperatures used to destroy the plastic structure [4]. The corresponding temperatures defining the pyrolysis states are with the following temperature ranges less than or equal to 600°C, 600–800°C and greater than 800°C [5]. The products obtained from pyrolysis of plastics depend on the type of plastics, feeding arrangement, residence time, temperatures employed, reactor type and condensation arrangement [6,7].

Low temperature processes generally enhance liquid products and high temperature processes enhance gaseous products. Some polymers such as; polystyrene and poly(methylmethacrylate) undergo to produce monomers and other mono-aromatics besides other hydrocarbons [8–10]. However, polyethylene and polypropylene having 0 and 2% monomer yield should not be used for monomer production processes. These kind of polymers undergo pyrolysis process to produce valuable hydrocarbons [9].

In this study where low temperature pyrolysis process is implemented, thermal cracking experiments are carried out in a fixed bed reactor; Gray–King Assay. Prior to this, it is aimed to investigate the thermal degradation of waste plastics by using Thermogravimetric Analysis to determine the basics of decomposition mechanism and kinetics.

2. Experimental section

Two types of waste plastics were used in this study. One of them was polyethylene (PE) wastes with a diameter of 13 mm, and was obtained from Green Plastic Inc. (a company for plastic waste recycling) as shredded shampoo bottles. Polystyrene (PS) wastes were collected from landfill in the form of cattery. They were shredded into 5-mm size.

In order to assess the thermal behavior of the plastic samples, thermogravimetric analysis (TGA) and Gray–King Pyrolysis runs were performed. The products were analyzed mainly in liquid state using gas chromatography, gas chromatography-mass spectroscopy (GC-MS) and nuclear magnetic resonance (NMR) spectroscopy. Some chromatographic analysis of the gaseous products was also made.

For thermogravimetric analysis, a Perkin Elmer TGA 7 type instrument was used. Isothermal conditions and a controlled heating program of 5°C/min were used. The heating was carried out from ambient to 700°C in nitrogen.

Gray–King Assay was originally developed for coal pyrolysis, a modified version for biomass and plastics was used in this study [11]. A schematic representation of the apparatus used is shown in Fig. 1. The horizontal reactor was 30 mm in length and 20 mm in internal diameter. The quartz system was partially inserted in a stone

furnace of 300 mm length, 50 mm internal diameter. At the end of the Gray–King apparatus a trap was used for condensing the liquid and tar products. This trap was connected to the reactor with side arm and has a volume of approximately 100 ml. The other end of the trap was connected to an evacuated Teflon bag for gas sample collection. Samples of 5 g were heated up to 600°C at a heating rate of 5°C/min. The system was held there for 15 min and was left to cool down for 2 h. The degradation products were collected within three different groups as non-condensable gaseous products, condensables as tar and wax degradation products and residue.

3. Results and discussion

Thermogravimetric curves for PE and PS wastes are displayed in Fig. 2. The qualitative behavior of PE and PS shows one main distinct weight loss step, which shows that both of them have a constant degradation behavior at the involved temperature range. In order to have quantitative comparison between the two samples onset temperature of weight loss occurs T_{onset} , temperature for 50% weight loss T_{hl} , temperature at which maximum rate of weight loss T_{max} and temperature at which final constant weight is observed T_{end} were determined and displayed in Table 1. All of the four characteristic temperatures (T_{onset} , T_{hl} , T_{max} , T_{end}) are highest for PE and lowest for PS. Degradation finished between 440 and 475°C for both plastics.

The differences in thermal behavior could obviously be attributed to the molecular structure and degradation mechanism. PE thermal degradation consists of free radical formation and hydrogen abstraction steps whereas for PS thermal degradation is a radical chain process including initiation, transfer and termination steps

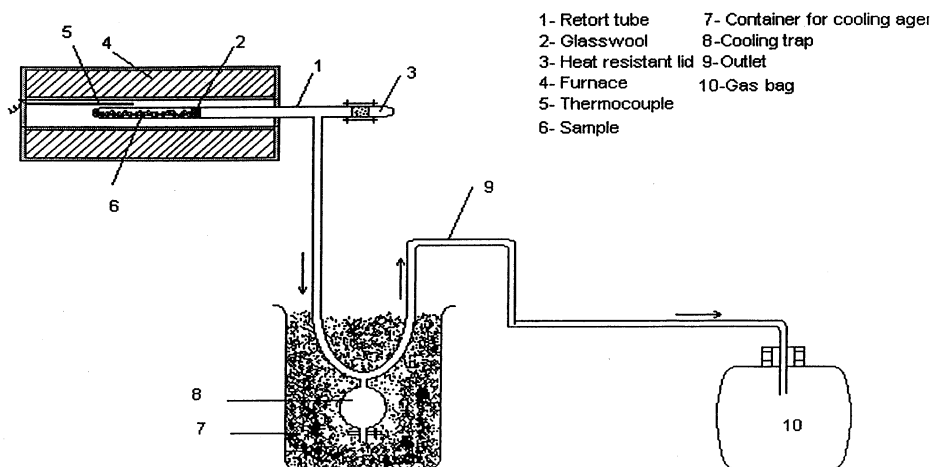


Fig. 1. Schematic illustration of experimental apparatus.

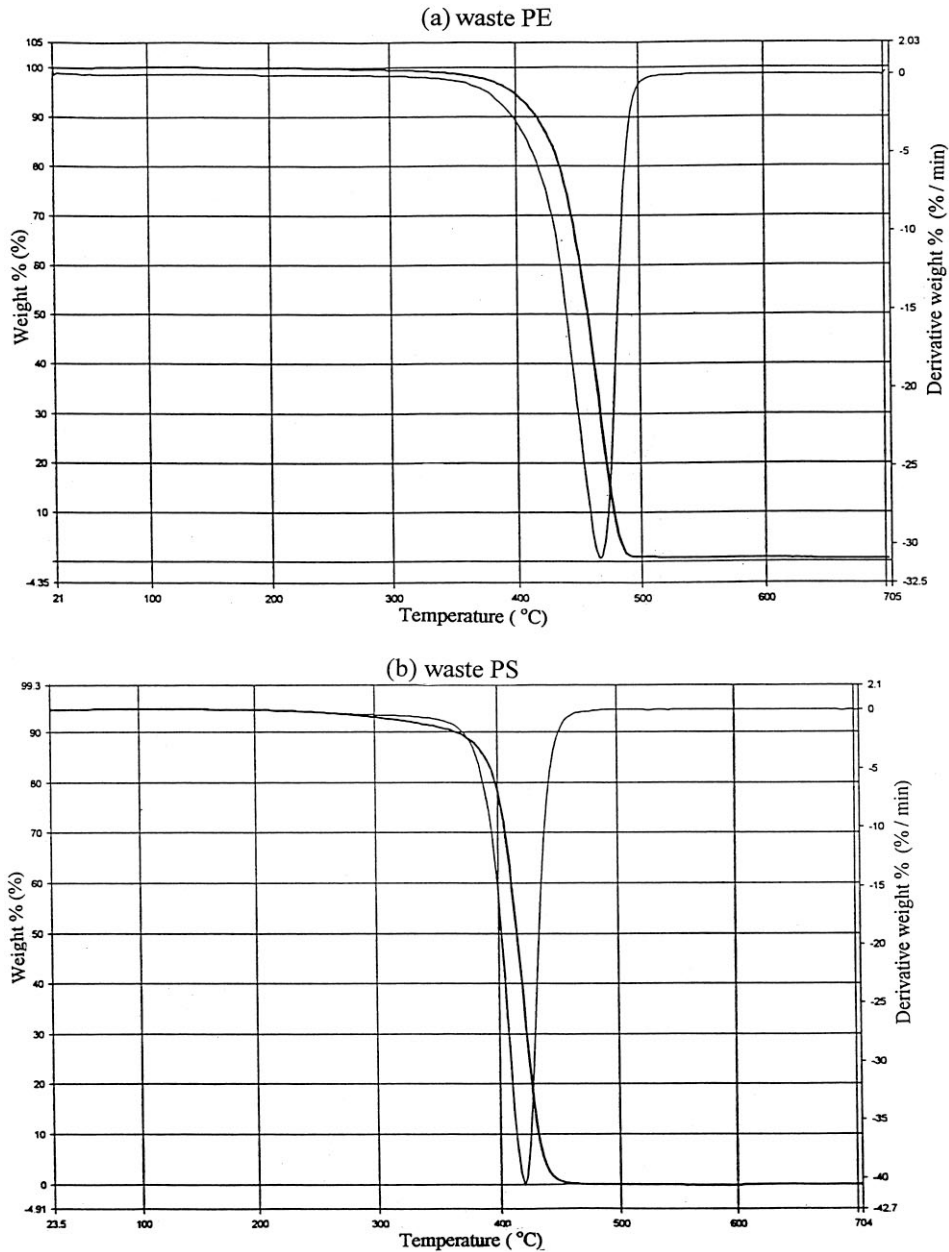


Fig. 2. TGA curves of (a) waste PE, and (b) waste PS in N_2 at a heating program of $10^\circ\text{C}/\text{min}$.

[12,13]. The maximum rate of degradation can influence the production of different types of radicals. The rate at which radicals are formed increases with their stability; therefore the conversion rate is higher if the radicals, which are formed

Table 1
Thermogravimetric analysis results of virgin and waste plastics

Stage	Temperature (°C)	Weight loss (%)	Derivative of weight loss % (%/min)
<i>Waste PE</i>			
Onset	398	90.7	2.4
Half life	449	50.0	
Maximum derivative weight	465	36.7	30.9
End	475	00.0	
<i>Waste PS</i>			
Onset	388	90.9	5.7
Half life	416	50.0	
Maximum derivative weight	419	40	41.46
End	439	00.0	

during thermal volatilization, are more stable. When this consideration is applied to waste plastics, the maximum degradation rate value of 41.46%/min obtained from TGA of PS is considered to be high and this implies the production of stable radicals [12]. For weight loss at the maximum rate of degradation, when the use of waste plastic is evaluated in comparison with virgin plastics, it has been observed that waste leads to a marked enhancement of the process, particularly in the case of waste PE [14].

In order to interpret the TG data, the integral method proposed by Freeman-Carroll is used [15]. The thermal degradation of plastics is not governed by elementary reactions, therefore the significance of these parameters were merely indicative, but they do, however, allow useful internal comparison [16]. The kinetic parameters calculated for T_{\max} using a computer program are compiled in Table 2.

As it appears from the data in Table 2, the activation energy of PE is lower than that of PS. Not every broken bond in the polymer chain leads to the evaporation of the product. Only polymer chain fragments small enough to evaporate at the given reaction temperature will actually leave the polymer sample. This implies that both physical and chemical processes influence the rate of change of the polymer mass and hence the observed pyrolysis kinetics [16,17].

The kinetic parameters for the thermogravimetric analysis of selected virgin polymers in the literature show higher values of activation energies and reaction

Table 2
Kinetic parameters calculated from thermogravimetric data of waste PE and PS

Plastic type	Reaction order	E (kJ/mol)	T_{\max} (°C)	k (1/s)
PE waste	0.9	218	465	0.0002
PS waste	0.7	269	419	0.0321

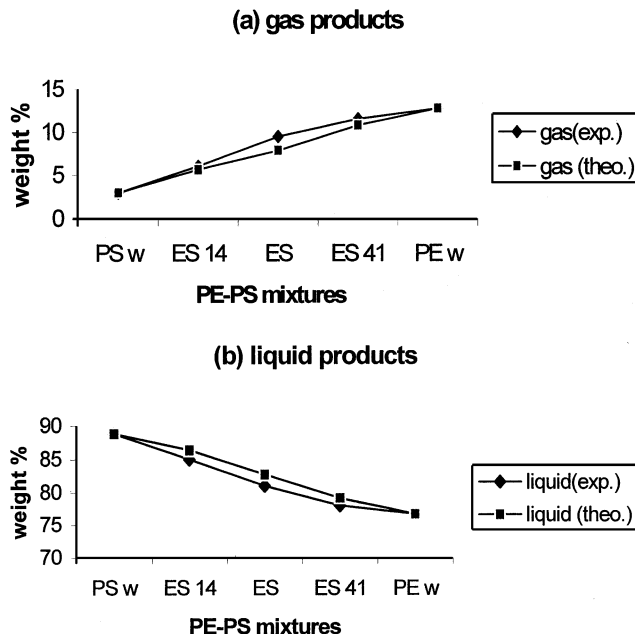


Fig. 3. Variation in experimental waste PE-PS production in comparison with theoretical values: (a) gas products, and (b) liquid products.

constants and show lower values for reaction orders in comparison with waste plastics [14,18].

The amounts of the gaseous and liquid products and the residue obtained from the pyrolysis of waste PE and PS in the Gray King apparatus are shown in Fig. 3.

For the pyrolysis run of PE, two main products, namely a green wax with a melting point of about 80°C and gas were obtained. During its pyrolysis, the most serious operating problem was the plugging of the product lines and condenser tubes by the waxes formed. The pyrolysis of PS gave one main product, a brown colored oil fraction with a weight percentage of 88.8%, which collected in the condenser. Besides this, gas products, which were stripped of the liquid products constituted only a small portion [19]. Primary pyrolysis takes place at low temperatures through a free-radical transfer that leads to low yields of gases, including ethylene and high yields of waxes. Since, PS pyrolysis is controlled by intramolecular transfer section for producing oil compounds, liquid yield formation is higher than that of PE [20].

As depicted in Fig. 3, for the ratios of 20:80, 50:50, 80:20 of waste PE:PS, the total oil production decreases almost linearly with the increase in the PE content of the feed but the total gas production is increased. The residual char was little affected by different mixing ratios of PE and PS in the input mix.

Theoretically calculated and experimental results for copyrolysis show that the gas and residue yields have a synergistic behavior. Thus for all mixtures, higher

yields are obtained. Under the conditions of the present study, the presence of contaminants, which have some catalytic activity, will no doubt have an effect on the product distribution [14]. As medium and high hydrocarbons are volatilized, the catalytic activity becomes a more dominant factor, enhancing char forming reaction and increasing the residue with a concurrent decrease in liquid yield.

Fig. 4 summarizes, the aromatic compound distribution for different polymer waste mixtures. The identification of mono-aromatics from the GC-MS chromatograms shows variations between 35 and 75% by weight, for different PE:PS mixtures. Hydrocarbons with high molecular weight, especially the fraction of poly-aromatics apparently have the lowest values for PS pyrolysis. For PS, mono-

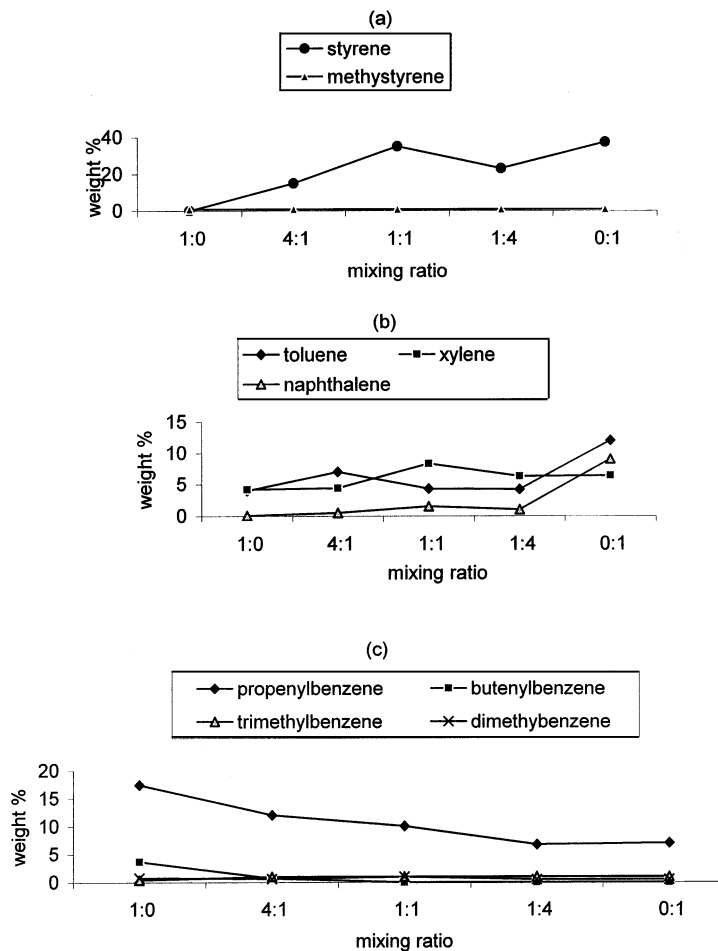


Fig. 4. Weight percentage change of chemicals in the liquid yield at different mixing ratios of waste PE-PS pyrolysis: (a) styrene, methylstyrene; (b) toluene, xylene, naphthalene; and (c) propenylbenzene, butenylbenzene, trimethylstyrene, dimethylbenzene.

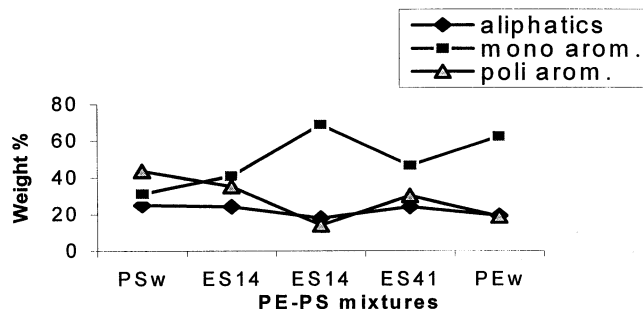


Fig. 5. Variation of: (a) aliphatics; (b) mono-aromatics; (c) poly-aromatics in the liquid yield at different mixing ratios of waste PE-PS pyrolysis.

aromatic production was about 64% of the total aromatics. This value is about 65% for PE:PS 50:50 mixture. The process yields high amounts of styrene monomer (37.1%) for the case of PS. On the other hand, at 500°C the production of styrene dimer and trimers were achieved in the pyrolysis of PS under vacuum [12,14]. Apart from styrene, toluene was evolved in comparable amounts from the degradation of both PS and PE. PE maybe crosslinked after its disposal, since this higher and irregular branching can probably lead to more toluene products [8,21,22].

Moreover, there was an increase in the yield of xylene and styrene in the mixtures of PE:PS in comparison with PE alone. The weight percentage of trimethylbenzene remained relatively constant after PS addition to the feed mixture. In the case of dimethylbenzene, the mixtures of PE:PS performed fluctuations in compound yield not only because of the degradation into different compounds, but also because of contaminants [22]. Propenylbenzene and butenylbenzene are most abundant compounds in case of waste PE. Naphthalene as a poly-aromatic compound is also detected in all mixtures. It can be deduced that, the total mono-aromatics of the oil products for PS and PE wastes were approximately 65 and 30% by weight, respectively.

In order to evaluate the results obtained from ^1H NMR, the products were classified as mono-, poly-aromatics and aliphatics (Fig. 5). The aliphatics cover both the saturated and unsaturated hydrocarbons with C_{7+} . The best results for mono-aromatics are achieved from 50:50 mixture of PE:PS. The high amounts of tar formation in PE led to an increase of poly-aromatics with the addition of PE to the mixture. The weight percentage of aliphatics with C_{7+} is almost constant with the addition of PS to the mixture.

Fractionation of carbon groups show variations from the pyrolysis process of PE:PS mixtures (Fig. 6). A very distinctive increase has to be pointed out in the case of PE for C_{25+} . This was due to the absence of carrier gas, the horizontally designed system and the retention time within the apparatus, which affects the primary pyrolysis reactions [23]. Furthermore, as shown in Fig. 6, C_{25+} group in waste PE decreases as it is mixed with PS. In PE:PS mixtures, PE favors the production of low molecular weight aliphatics as seen in the fraction of C_{7-11} .

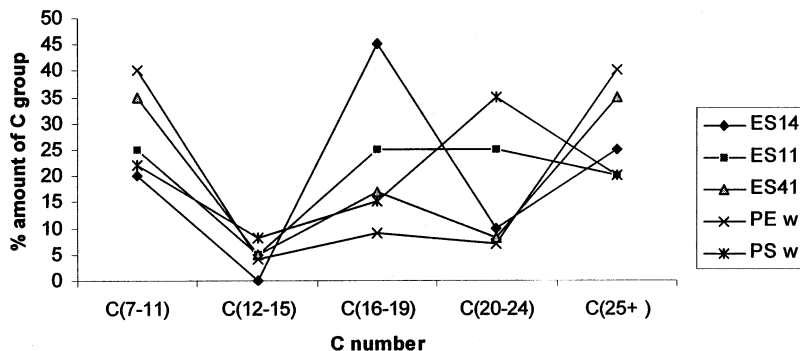


Fig. 6. Variation of aliphatic compounds in the liquid yield at different mixing ratios of waste PE-PS pyrolysis.

The results of gas chromatograms show that, since the process was optimized to achieve maximum yield of liquid products, the gas production efficiency was obviously depressed, as it is clearly seen in Fig. 7. Moreover, the absence of carrier gas led to the loss of gas products in the Teflon bag. Mainly C₁₋₄ hydrocarbons were probably left in the tubes. The high yield of methane gas formation in each case is due to the cracking reactions at the end of chain, as it occurs in many pyrolytic processes of hydrocarbons [24].

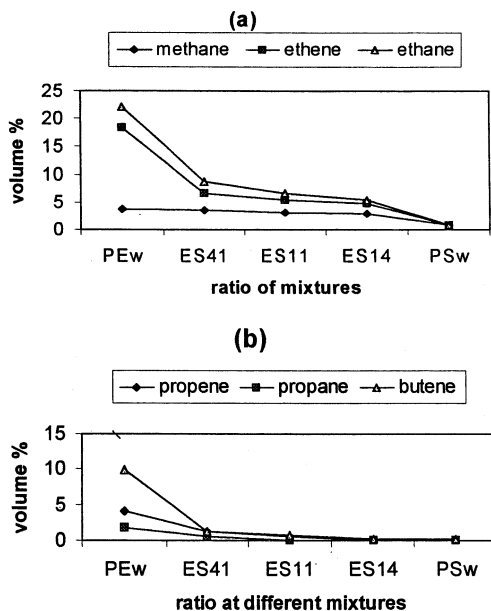


Fig. 7. Variations of: (a) methane, ethene, ethane; and (b) propene, propane, butene for waste PE-PS and their mixtures.

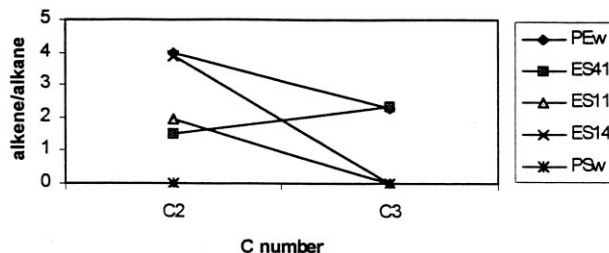


Fig. 8. Variations at the alkene/alkane ratios for: (a) C₂; (b) C₃ production of waste PE and PS pyrolysis and their mixtures.

The PE gas chromatograms showed that ethene, propene and butene are 32% by volume in the gas mixture. The combined yield of ethene and propene produced in the mixture of PE:PS mixtures did not exceed 20%. The total volume of gas products in pyrolysis experiments was 35–40%. The gas yield distribution of PS is significantly lower than those of PE since monomer of polystyrene and other low molecular mono-aromatics are in higher percentage in liquid products.

From Fig. 8, it can be seen that C₂ and C₃ alkene/alkane ratio of PE is quite high because of unsaturated C₂, C₃, C₄. The comparison of the gas fraction obtained from pyrolysis of PS:PE showed that due to poor gas yield from PS, the alkene/alkane ratios show many fluctuations. Gas analysis of PS:PE mixtures with the ratio of 20:80 showed that the ratio of C₃ alkene/alkane was approximately 2.35. However, this ratio is in the range of 1.5 for C₂ alkene/alkane of PE:PS 80:20 mixtures.

4. Conclusions

Liquid yield of PS was found to be higher than waste PE. The dominant product of waste PS was styrene monomer with a percentage of 37% followed by toluene, naphthalene and xylene. The pyrolysate of PE mainly consisted of propenylbenzene followed by butenylbenzene. The pyrolysis results show that gas production is higher in case of PE when compare to PS. The mono-aromatic products, which are economically valuable, were less in the pyrolysis of PE than that of PS. The weight percentage of mono-aromatics is about 63% of the total oil products. This is compensated by the formation of C_{7–11} aliphatics in the case of polyolefins. The absence of carrier gas led to poor sampling of gaseous products. Despite this fact, the formation of methane, ethene, propene and butene were detected in the case of PE and its mixture with PS at different ratios.

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