Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene

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Abstract

A comparison of waste and virgin polypropylene (PP) plastics under slow pyrolysis conditions is presented. Moreover, mixtures of waste PP with wastes of polyethylene (PE) and polystyrene (PS) were pyrolyzed under the same operating conditions. Not only the impact of waste on degradation products but also impacts of the variations in the mixing ratio were investigated. The thermo-gravimetric weight loss curves and their derivatives of virgin and waste PP showed differences due to the impurities which are dirt and food residues. The liquid yield distribution concerning the aliphatic, mono-aromatic and poly-aromatic compounds varies as the ratio of PP waste increases in the waste plastic mixtures. In addition to this, the alkene/alkane ratio of gas products shows variations depending on the mixing ratio of wastes.
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1. Introduction

Consumption of plastics has increased dramatically over the last 50 years. In 1940, the consumption of plastics was around 0.04 million tons; in 1962, the consumption increased to around 1 million tons per year; for 1992, it was 86 million tons; and for 2002, it was assumed to be approximately 110 million tons in the world (Jorgensen, 1992). Plastic wastes constituted 18 million tons of the 2.8 billion tons of total wastes in Western Europe for 1996 (Warmington, 1997). The consumption of plastics has been increasing rapidly which will no doubt put pressure on crude oil and natural gas usage for production of plastics, since the world deposits are declining.

In the USA, among the types of plastic packaging material, polypropylene (PP) ranked fourth after Low Density (LD) and High Density (HD) polyethylene (PE) and polystyrene (PS) (Anon., 1996). The consumption figures indicate that waste plastics are always a potential environmental hazard and a great burden on resources.

There still exists the necessity for the development of an appropriate plastic waste management policy.

One of the desired methods of plastic waste management is the reuse of products in their original structure. However, this is possible for some wastes and there is also an obvious limit on the number of cycles for each material. The recycling of material, the incineration with and without heat recovery and the use of landfills are among many ways of processing waste plastics. Pyrolysis is one of the well-known processes for the chemical and resource recycling of plastics (Bisio et al., 1994). The output products from the degradation of the plastics by the application of heat under oxygen-deficient conditions can be used in petrochemical and chemical industries or they can be combusted and used for heating.

Pyrolysis processes are generally classified into low, medium and high temperatures based on the range of temperatures used to destroy the plastic structure (Brophy et al., 1996). The corresponding temperatures defining the pyrolysis states are with the following temperature ranges 600 °C $\geqslant$, 600–800 °C and 800 °C $<$ (Kaminsky et al., 1989). The products obtained from pyrolysis of plastics depend on the type of plastics, feeding arrangement, residence time, temperatures

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employed, reactor type and condensation arrangement (Shelley et al., 1992; Kaminsky, 1992).

Low temperature processes generally enhance liquid products and high temperature processes enhance gaseous products. Some polymers such as PS and poly (methymethacrylate) give high monomer yields approaching 100% when pyrolyzed. Whereas PP yields only about 2% of its weight as its monomer (Kaminsky, 1992). Although pyrolysis is not an economic system for monomer recovery from the point of PP reprocessing, under optimum pyrolysis process operating parameters, the concentration of certain compounds other than propene produced from PP pyrolysis processes with substantial market price may qualify pyrolysis as a feasible recovery process (Ratcliffe, 1994). These kind of polymers undergo pyrolysis process to produce valuable hydrocarbons (Duryodhan, 1996).

In this study, Gray–King Assay pyrolysis of virgin and waste samples of PP were carried out. Moreover, same pyrolysis process was performed in the case of mixtures of PE:PP and PS:PP plastic wastes. The differences between virgin and waste PP and PE and PS plastics are considered. In addition to this, the results of PE:PP and PS:PP mixtures were compared with PP wastes. 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

The virgin PP plastics were atactic PP and labeled with a code of MH418 by the producer; PETKIM Turkish State Monopoly Petrochemical Company. The waste atactic PP samples were obtained in the form of plastic bowls from Green Plastic Inc; the wellknown plastic recycling company. These waste PP plastic bowls that were used for food packaging were manufactured from the same atactic PP that has the label of MH418. The plastics that were in the shape of bowls were shredded by machines and then they were cut into size of approximately 3 cm in diameter manually. The PE and PS waste plastics that were used for food and bevarage packaging were also supplied from Green Plastic Inc.

A thermogravimetric analysis was run by using Pelkin-Elmer T.G.A. 7 instrument. A sample (10 mg) was inserted into a small quartz-glass crucible. The crucible was positioned in the TGA instrument connected to a weighing device that registered the weight loss with increasing temperature. All experiments were performed under isothermal conditions at a controlled heating rate of 10 °C/min. The heating was done from ambient temperature to 700 °C in a nitrogen atmosphere under a flow rate of 100 1/min.

The pyrolysis runs were carried out using a modified Gray–King Assay. This pyrolysis system was originally designed for the pyrolysis of coal but later modified to pyrolyze other hydrocarbon minerals, biomass, and plastics (Citiroglu, 1993). A schematic representation of the apparatus used is shown in Fig. 1. The horizontal reactor was 30 mm in length and 20 mm in diameter. The quartz system was partially inserted into a furnace 300 mm length and 50 mm in internal diameter. At the end of the Gray–King apparatus, a trap was used for condensing the liquid and tar products. The 100 ml trap was connected to an evacuated teflon bag for gas sample collection. The samples weighting 5 g were heated up to 600 °C at a heating rate of 5 °C/min. The system was held at the final temperature 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 such as tar, and degradation products and residue under standard conditions.

3. Results and discussion

Typical values for various properties of selected plastics are presented in Table 1. In order to compare the thermal behavior of virgin and waste PP thermogravimetric analyses were made. Fig. 2 presents the standard weight-loss curve and provides the derivative information. For comparison purposes, characteristic temperatures at the onset, half-life, maximum derivative weight-loss, and end point of thermal degradation were determined. The results of these characteristic temperatures are compiled in Table 2. It should be noted that only the data obtained at a heating rate of 10 °C/min are presented.

The waste with its unknown and variable composition can influence the degradation of PP. The weight loss curve and data for virgin PP were relatively simple and showed no differences from the data previously reported in the literature (Day et al., 1995; Audisio et al., 1992). These data and curve form the basis from which the influence of impuritites on the degradation of PP can be evaluated. Also, possible chemical and physical changes

Table 1
Values for various properties of the selected plastics (KOSGEB, 1995)

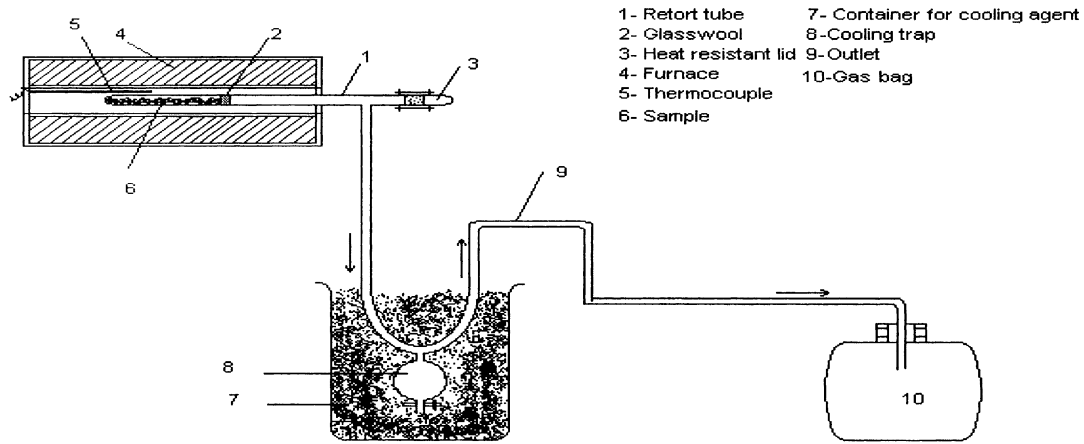| Plastic type/parameter-test method	Density (g/cm^3) TS 1818	Melt flow index (g/10 min) TS 1323	Melting point (°C)
Polypropylene		(230 °C, 2.16 kg)	
Virgin	0.1	4.9	152–158
Waste	0.94	6.0	142–146
Polyethylene		(190 °C, 10 kg)	
Waste	0.96	5.4	137–139
Polystyrene			
Waste	1.03	–	150–220

Fig. 1. Schematic illustration of experimental apparatus.

encountered by waste can affect the life cycle of PP. Negative and positive effects of different catalysts and other chemicals on thermal degradation of plastics are given in the reports found in the literature (Audisio et al., 1992).

The thermogravimetric analyses show clearly that degradation is a fast process for the waste compared to virgin PP, followed by higher weight losses at lower temperatures for the former. For example, 50% weight loss temperature is reduced by 24 K in the presence of a impurities (Table 2). The same situation can also be seen for the other characteristic temperatures of PP. Similar behavior was obtained for virgin and waste PE and PS (Kiran et al., 2000). The thermogravimetric onset temperature is found to be slightly lower for virgin than for waste PP, and the calculated E_a values are 167 kJ/mol and 181 kJ/mol for virgin and waste PP, respectively, by using the Freeman–Caroll integral method which is widely used for kinetic analysis of thermogravimetric data (Nishizaki, 1980).

Moreover, the maximum rate of degradation can be effective for production of different types of radicals. The rate at which radicals are formed increases with

stability; therefore the conversion rate is higher if the radicals, which are formed during thermal volatilization, are more stable (Schroder, 1984). When this consideration is applied to the waste PP, the maximum degradation rate with 39% is lower than the value of virgin PP, which is 42.5%. This causes more char forming reactions for waste PP.

Thermal degradation of PP was accomplished by using a modified Gray–King Assay. The Gray–King pyrolysis runs of virgin and waste PP are compiled in Table 3. Overall yields of liquid and residue fractions were determined by the weight difference of experimental apparatus and glasswool and yield of gas fraction by mass balance.

Due to slow pyrolysis conditions, a slower degradation process occurred which resulted in the generation of higher liquid yields for both virgin and waste PP (Koo et al., 1993). On the other hand, both gas and liquid yields were affected by the waste, which also resulted in the chemical composition changes of the yields. For waste and virgin PP, an increase in residue and a decrease in the liquid yield were observed with a weight percentage of 8.08 and 6.73, respectively.

The pyrolysis results show that the liquid product yield is smaller and the gas yield is greater for waste PP compared to virgin PP pyrolysis. Also, the residue amount form the pyrolysis for the virgin and waste PP were; 13, 14% respectively. The waste on PP plastics that are recognized as impurities of whose impurities became a dominant factor usually enhances the char forming reactions to promote the formation of residue at the expense of liquid products (Ekinci et al., 1995).

Table 2
Thermogravimetric analysis of virgin and waste plastics

Stage	Temperature (7 °C)	weight loss (%)	weight loss derivative % (%/min)
Virgin PP			
Onset	423	95.7	4.2
Half life	450	95.7	
Maximum derivative weight	458	37.0	42.5
End	472	00.00	
Waste PP			
Onset	407	98.9	13.9
Half life	426	50.0	
Maximum derivative weight	427	46.7	39
End	458	00.0	

Table 3
Gray–King pyrolysis of virgin and waste PP at 600 °C

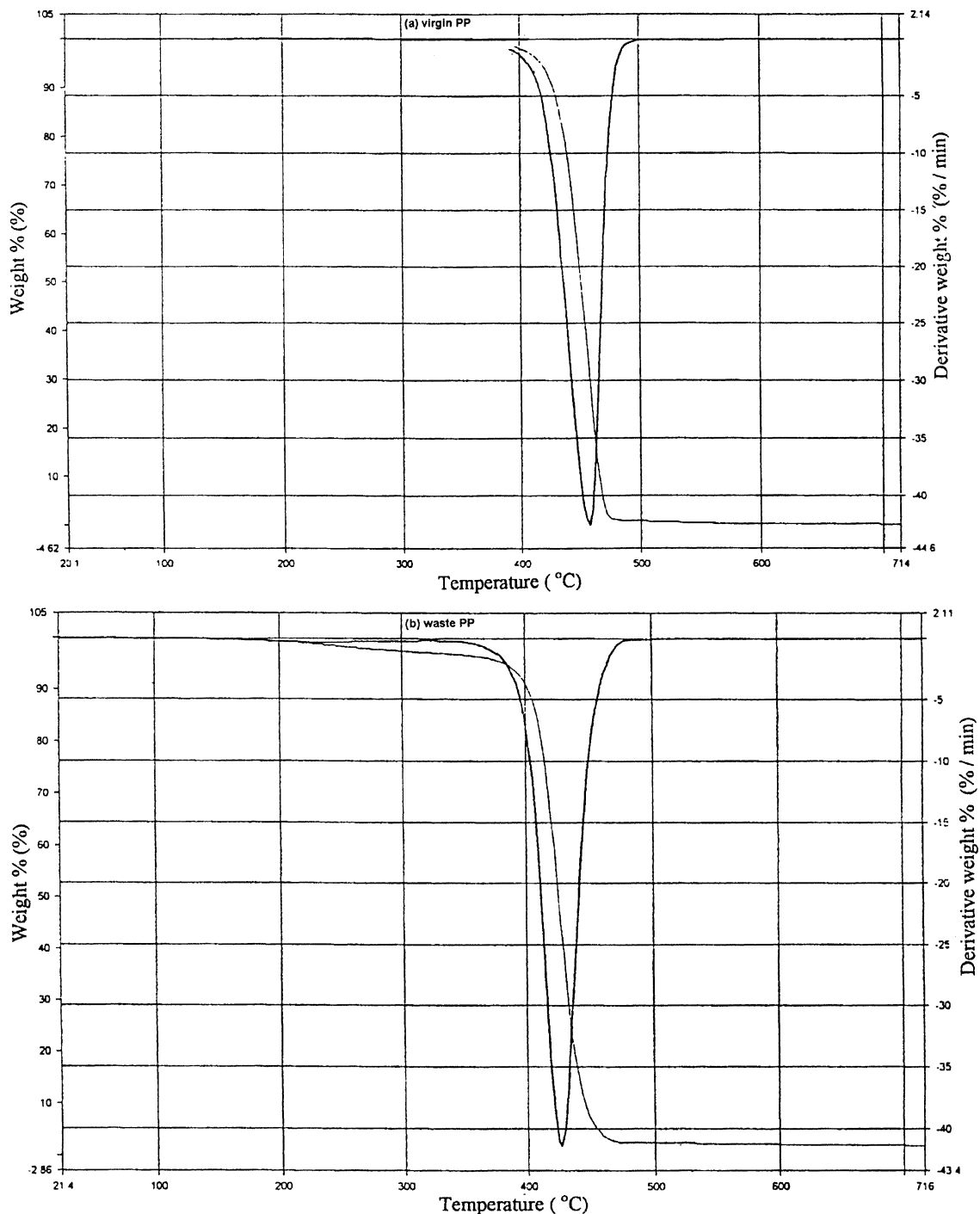| Feedstock	Gas	Liquid	Residue
PP virgin	11	76	13
PP waste	15	71	14

Fig. 2. TGA curves of (a) virgin PP, (b) waste PP in N₂ at a heating program of 10 °C/min.

Comparison of the PP liquid yields of virgin and waste PP with PE and PS show that liquid yields are highest for PS, followed by those for PE and PP (Kaminsky, 1993; and Kaminsky, 1992). The difference between the latter two are insignificant in comparison to the magnitude of yield for PS. The distinctive difference between the pyrolysis product distribution between PS and the other two (PP and PE) is attributed to the chemical structure and associated thermal behavior.

The experimental studies for pyrolysis processes were carried out for the selected mixtures until similar yield distribution was achieved for each type of feedstock. The evaluation of the results showed that the increase of PP content in PE:PP mixtures led to higher values of both residue and gas formation and considerably lower amounts of liquid yield (Fig. 3).

PP waste by itself and its mixture with PS wastes continuously decreased the amount of liquid yields. This
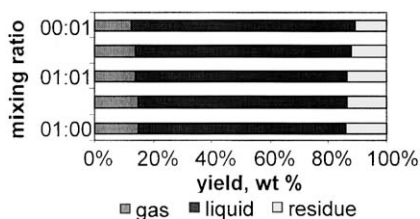
Fig. 3. Variation in yield distribution at different mixing ratios of waste PE:PP plastics at 600 °C.
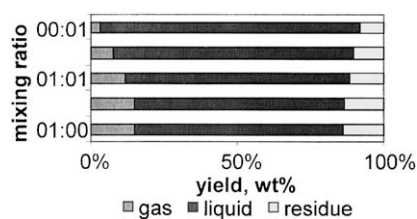

Fig. 4. Variation in yield distribution at different mixing ratios of waste PS:PP plastics at 600 °C.

is consistent with the fixed bed conditions and catalytic effects. Therefore, it can be concluded that the optimum operating condition for maximum oil production is a mixture of low amounts of PP with high amounts of PS (Fig. 4). The gas and residue yields have a synergistic behavior; thus, for all mixtures higher amounts are obtained.

The capacity of PS to produce monomer is much superior compared to PE and PP. For the case of PS, liquid evolution started at much lower temperatures compared to the polyolefins for Gray–King pyrolysis, similar to the thermogravimetric results (Conesa et al., 1997; Bellamy et al., 1974).

Fig. 5 shows the evaluation of the aliphatics that were obtained from GC chromatograms and grouped according to the carbon number (molecular weight). The distribution of the aliphatic compounds show that the intensity is highest at lower carbon numbers, $C_{(7-11)}$, with 56 and 33% values for virgin and waste PP, respectively. The aliphatic compound formation is depressed at medium carbon numbers, $C_{(12-19)}$, and increased at the higher carbon numbers, $C_{(20-24)}$ and $C_{(25+)}$. The PP waste pyrolysis yields considerable amount of $C_{(20-24)}$ and C_{25+} compounds with 55% of total carbons. On the other hand, for the same carbon groups, the virgin PP pyrolysis yields only 25% of total carbons. The reason for this can be attributed to the poor chain fragmentation of the polymer. The large size of the wastes is also an important factor for the generation of carbon compounds with high carbon numbers. On the other hand, the product distribution of aliphatics with respect to C number differs for PE (Kiran et al., 2000; McCaffrey et al., 1996; Westerhout et al., 1997; Siauw et al., 1995).

The results of the NMR spectrum give information regarding mono-aromatics, poly-aromatics and aliphatics (Fig. 6). The increased aliphatic content for PP waste samples resulted in a less pronounced but similar behavior to PS, but unlike PE (Koo et al., 1991; McCaffrey et al., 1996). The mono-aromatic variation content was about 50% (by weight) for virgin PP which decreased to 33% (by weight) for its waste and the poli-aromatic content was about 42% for both virgin and waste PP. Poly-aromatic distribution and the effect of waste samples differed considerably compared to PE and PS (Koo et al., 1991; McCaffrey et al., 1996). The
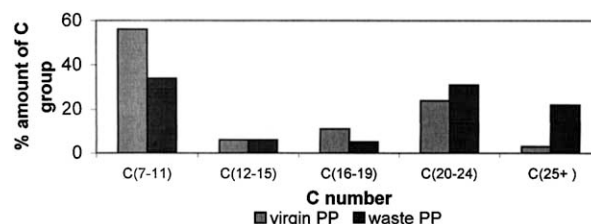

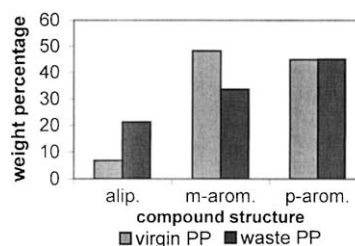Fig. 5. Variation of aliphatic compounds in the liquid yield for virgin and waste PP plastics.

Fig. 6. Variation of aliphatics, mono-aromatics, poly-aromatics in the liquid yield for virgin and waste PP plastics.

fraction of poly-aromatics apparently have highest values for PP waste and virgin plastics. The geometry of the retort contributes to high poly-aromatic formation, a horizontally placed retort, especially under no carrier gas operating conditions, may allow the formation of higher mono-aromatic compounds. The main reason for this is the change in the retention time within the apparatus that affects the primary pyrolysis reaction conditions (Conesa et al., 1994). Another reason for the production of poly-aromatics can also be due to the intra-molecular abstraction of hydrogen. The aliphatic compounds that constitute by weight 7% in the virgin PP products are increased to 22% for the waste product (Fig. 6) (Conesa et al., 1994).

For mono-aromatic distribution, the order of magnitude and trends were similar to PE. Even though the trend was similar, the magnitude of mono-aromatic compounds was higher for PS (Kiran et al., 2000). Investigation of the distribution of liquid products in regard to solubility classes provides a general chemical class comparison.

The main mono-aromatic compounds that were determined in the GS–MS chromatograms of virgin and waste PP are reported in Fig. 7. Toluene, xylene,
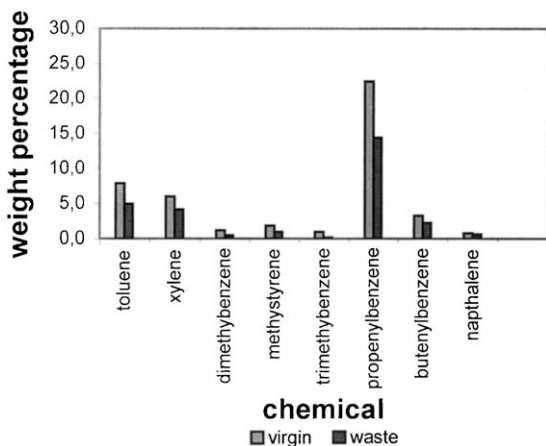
Fig. 7. Weight percentage of chemicals; toluene, xylene, dimethybenzene, methylstyrene, trimethylstyrene, propenylbenzene and napthalene for the liquid pyrolysis yield of virgin and waste PP plastics.

Fig. 8. Variation of aliphatic compounds in the yield at different mixing ratios for waste PE:PP plastics.

dimethylbenzene, and methylstyrene were the main products that have a single aromatic ring (Klemchuk, 1997; Kaminsky, 1992). The weight percentage of toluene and xylene is approximately the same for waste PP, with a value of 4%. The production of propenylbenzene, with 22.41% for virgin and 14.38% for waste PP, has the highest mono-aromatic yields among the liquid products. It is followed by toluene and xylene. However, considerable amounts of trimethylbenzene were also observed. Naphthalene was determined to be 0.74% and 0.6% of the liquid products of virgin and waste plastics, respectively. The identification of total mono-aromatics from GC–MS chromatograms is between 28 and 44% by weight for waste and virgin PP. This also proves that there is a certain decrease in mono-aromatic and in naphthalene production for the pyrolysis process of virgin and waste PP. Similar behavior was observed for PE and PS samples previously studied (Kiran et al., 2000). Even though PP gave the least liquid yield as compared to PE and PS, the product distribution was more complex in composition to the other two plastics.

For the mixtures of PE:PP pyrolysis, the identified products are between 35 and 40% by weight. From Fig. 8, it can be deduced that PE:PP mixture degradation enhanced the formation of high amounts of C_{7-11} aliphatics. The C_{7-11} carbon group formation is relatively constant for all mixture ratios of PE:PP, with 40% of the total carbon groups. The same conclusion is valid for the $C_{(12-15)}$ and $C_{(16-19)}$ numbers with generation of 4% and 7%, respectively. However, $C_{(20-24)}$ formation is the lowest for PE waste without any addition of PP waste. On the contrary, the C_{25+} generation is very high for PE waste, with 40%. The values for $C_{(20-24)}$ and C_{25+} in Fig. 8 are the same as in Fig. 5. The addition of PE to the mixture does not change the C number occurrence very much: the variation is between 30 and 22%. The aliphatic compound
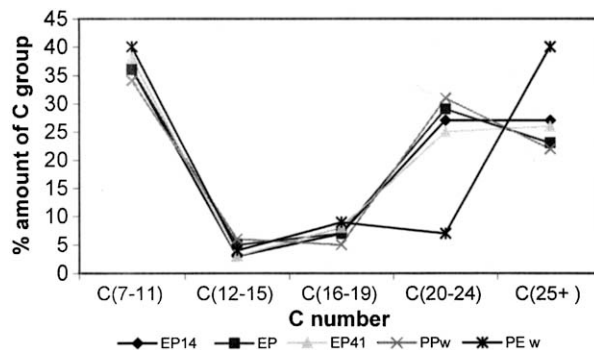
formation is highest at a 50:50 ratio PE:PP, for a yield value of 36% by weight (Fig. 9). For poly-aromatics, the highest yield, of 45%, is observed for PE:PP mixtures in which the addition of PE is omitted from the feedstock. The mixture ratio does not lead to a considerable variation, which is between 31 and 34% for mono-aromatic compound formation.

GC–MS chromatograms of PE:PP mixtures are evaluated in detail in Fig. 10. The similarity in thermal degradation mechanisms of polyolefins is apparent in cases of toluene, xylene and methystyrene. The formation of these compounds with an approximate value of 4% for toluene and xylene, and of 0.8% for methylstyrene were not affected by the different mixing ratios of PE:PP. Propenylbenzene is the highest mono-aromatic produced from the pyrolysis of different mixtures of PE:PP, with a value around 16%. Although in most of the mono-aromatics the product amount decreases as the PP ratio increases in the mixture, the opposite is valid for the production of the only poly-aromatic: naphthalene. Its production increased from 0.06 to 0.6% as the PP amount was increased in the mixture ratio.

The amount of gaseous products obtained for pyrolysis of waste plastics is more than virgin ones (Fig. 11). This phenomenon probably indicates that the process of primary cracking of tars and waxes is produced at a temperature different from the temperature of the virgin plastics (Day et al., 1995; Cozzani et al., 1995; Audisio et al., 1992). The loss of C_5 fraction in the gas products is due to the long chained hydrocarbons in the liquid yield. The recycling of monomers in the case of PE waste is higher than that of PP waste. The gas products that were determined from the pyrolysis of virgin and waste PP did not exceed 41 and 51% gas, respectively. The products were known to be methane, ethane, propene and butane. The propene yield of waste PP (12.97%) is much lower than virgin one (16.00%) in comparison with the other products. The proportion of volatile products of virgin and waste PP pyrolysis in their composition is more distributed when compared to the virgin and waste PE.
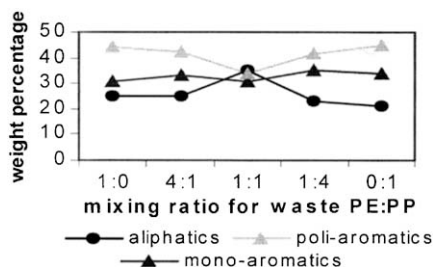
Fig. 9. Variation of aliphatics, mono-aromatics and poly-aromatics in the liquid yield at different mixing ratios of waste PE:PP plastics.
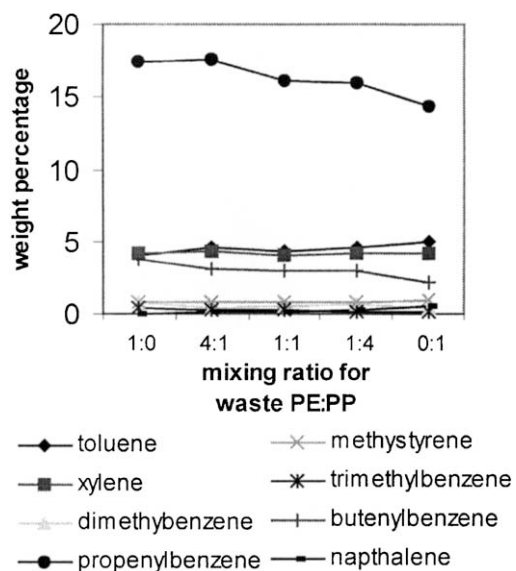

Fig. 10. Weight percentages of chemicals; toluene, xylene, dimethybenzene, methylstyrene, trimethylstyrene, propenylbenzene and napthalene for liquid pyrolysis yield of mixtures of PE:PP wastes at different ratios.
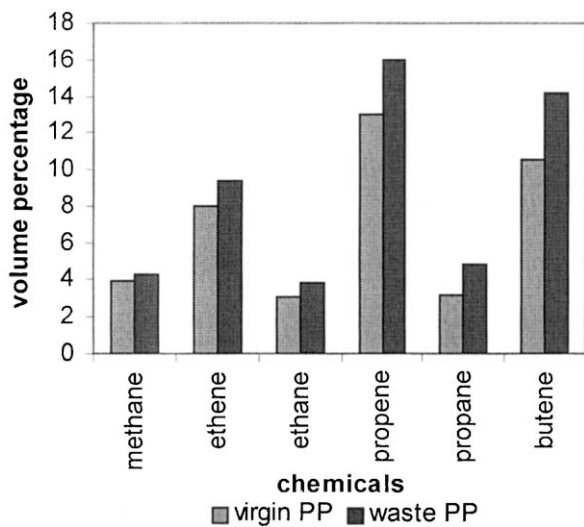

Fig. 11. Variations of methane, ethane, ethane, propene, propane and butane for virgin and waste PP plastics.

The yield of monomers; ethene and propene produced in the PE:PP mixtures with the ratio of 1:0 and 0:1 were 18.5% and 27.5% respectively (Fig. 12a). This low monomer production may be due to the formation of various other hydrocarbons. It can be deduced that the concentration of aliphatics was directly influenced by no application of carrier gas to cause losses in sampling.

In the pyrolysis of PS–PP waste mixture, the propene content increases continuously with the increasing amounts of PP, up to a value of 28% PP from the ratio of 1:0 to 0:1. (Fig. 12b).

The alkene/alkane ratio dependence can be seen more easily by selecting a specific number of carbons at which the products are concentrated and comparing the alkene/alkane ratio at this carbon number for virgin and waste plastics and also various mixtures of wastes (Figs. 13 and 14).

Fig. 13 shows the graph of alkene/alkane ratios for compounds of C_2 and C_3 plotted against virgin and waste PP. The chromatogram results of the C_3 alkene/alkane ratios for virgin and waste PP show that the effect of waste on the ratio is negligible. On the other hand, C_2 alkene/alkane ratios of virgin and waste PE are roughly the same (Piiroja, 1989). In the literature regarding C_{1-4} hydrocarbons, the alkene/alkane ratios are always in higher amounts due to unsaturated C_2, C_3 and C_4(Piiroja, 1989).

Also, the relative amounts of saturated and unsaturated products at each carbon number change as the ratio of waste PE and PP mixtures differ (Fig. 14). Specifically, for the mixtures with an increasing concentration of PP, the alkene/alkane ratio for C_3 increases up to 5.27. The reason for this is the formation of propene monomer in addition to the propene production from waste PE. Moreover, the C_2 alkene/alkane ratio shows a decrease with the addition of waste PP to the mixture. The lowest value belongs to the PE:PP mixture of 1:4 ratio, with 2.56.

In the case of PS:PP mixtures, due to the gas yield distribution of waste PS (Fig. 14), the alkene/alkane ratios show many fluctuations. Also, no ratio could be achieved because of the absence of ethane, ethane and propane in waste PS. However, only the gas fraction analysis of PS–PP mixtures with a ratio of 20:80 showed that the ratio of alkene/alkane was approximately 2.35.

4. Conclusions

The impurities which consist of dirt and food residues resulted in differences for the weight loss and maximum derivative weight loss curves of virgin and waste PP. The results consider decrease in the onset, half-life and end temperatures and increase in the weight loss (%) for maximum derivative weight loss during the interval. Moreover, the pyrolysis results for the Gray–King
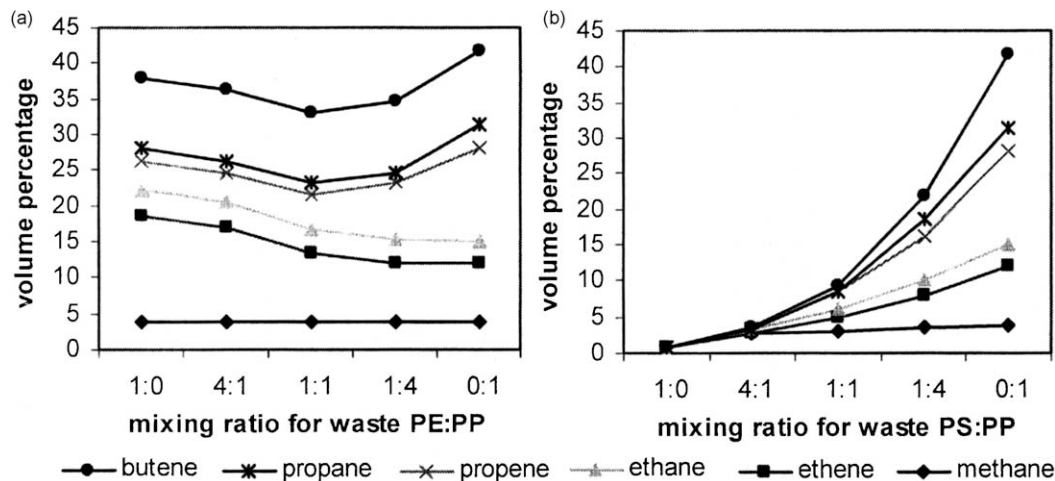
Fig. 12. Variations of methane, ethane, ethane, propene, propane and butane for (a) PE:PP (waste) and (b) PS:PP (waste) mixtures.
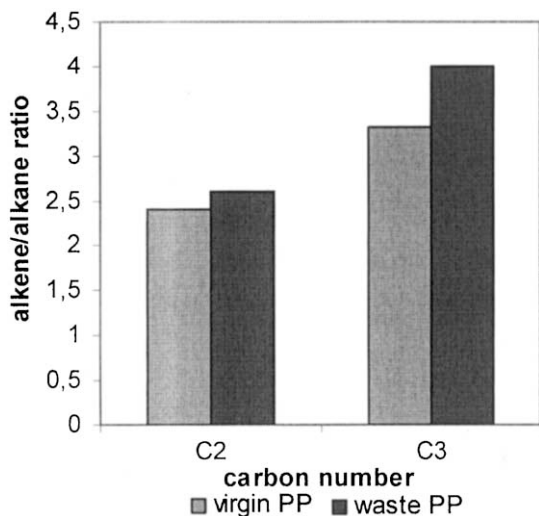

Fig. 13. Variations at the alkene/alkane ratios for C_2 and C_3 of virgin and waste PP.

Fig. 14. Variations at the alkene/alkane ratios for C_2 and C_3 of (a) PE:PP (waste) and (b) PS:PP (waste) mixtures.

Assay has also proved that the impurities in the PP waste plastic led to higher amounts of gas yields indicating that possibilities of cracking to gaseous molecules is more favored.

The liquid yield from the co-pyrolysis of PE:PP and PS:PP mixtures is suppressed as the PP waste ratio, on the basis of weight, increases. PP in comparison with PE pyrolysis yields considerably higher amounts of its monomer. The effects of impurity characteristics are reflected on GC chromatography with the hydrocarbon compound formation of higher C numbers. The poly-aromatic content of PP is not affected with con-taminant, apparently the highest values for virgin and waste PP may be due to the retort design. Among the mono-aromatic compounds, propenylbenzene, followed by toluene, has the highest yield for both virgin and waste PP. Naphthalene as a poly-aromatic compound has been detected in PP samples. C_{7-11} formation has
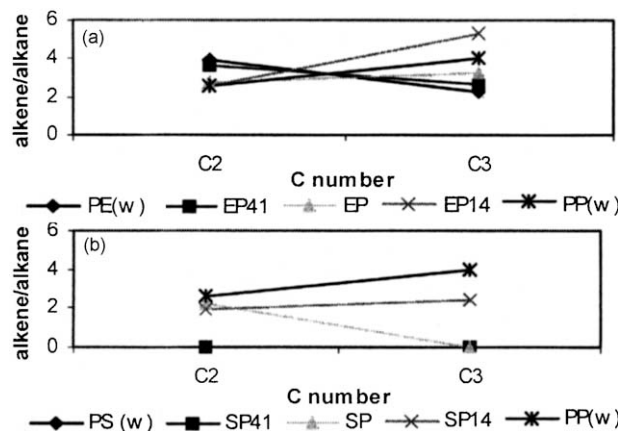
been kept approximately constant and the highest quantities for different mixing ratios of PE:PP wastes. On the other hand, the PE waste value for C_{25+} appar-ently has the same value as C_{7-11} Also, the C_{20-24} for waste PP and its mixtures with PE are similar. The poly-aromatic formation of PE:PP mixture is suppressed at a 1:1 mixing ratio. On the contrary, the aliphatic forma-tion is encouraged at the same mixing ratio. For the formation of different mono-aromatic compounds it can be deduced that propenylbenzene is the highest for PE:PP mixtures but shows a decrease with the addition of PP to the mixture. The other most produced mono-aromatics, xylene and toluene show slight changes with the addition of PP to the mixture.

In general, gas yields, including the monomer pro-pene, showed a decrease in the volume percentage due to the impurities. For the mixtures of PE:PP, the $C_3–C_4$ formation increased totally with the increase of PP in the mixture. The addition of PP waste plastic to the waste mixtures caused an increase in the alkene/alkane ratio for both C_2 and C_3.

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