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Co-pyrolysis of waste plastics and tires: Influence of interaction on product oil and gas composition

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A R T I C L E I N F O

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A B S T R A C T

The co-pyrolysis of different waste plastics and tires was carried out to investigate the effect of their interaction during co-pyrolysis on the yield and composition of the product oils and gases. Different types of waste plastics, consisting of high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), were co-pyrolysed with the waste tires using a fixed bed batch pyrolysis reactor. The main gases produced from the individual plastics and tires were hydrogen, methane, ethane, ethene, propane, propene, butane, and butene, whereas PET produced mainly carbon dioxide and carbon monoxide. GC/MS analysis of the product oil produced from tire pyrolysis were mostly aromatic compounds produced from the rubber components of the tire. For HDPE, LDPE and PP pyrolysis, the oil produced was of mainly aliphatic composition, PS pyrolysis gave a considerable portion of single ring aromatic and polycyclic aromatic compounds and PET formed mainly oxygenated compounds and aromatic compounds. Co-pyrolysis of the plastics and tires resulted in an increase in gas yield above what would be expected from feedstock addition, suggesting interaction between the feedstocks. Also, oil analysis of the co-pyrolysis oils indicated significant shifts in the oil composition. For the mixed tire with HDPE and LDPE, aliphatic compounds were increased above that expected from addition with lower yields of single ring and polycyclic aromatic hydrocarbons. In contrast, mixing tire with PP produced higher yields of aromatic hydrocarbons and lower yield of aliphatic and alicyclic compounds than expected from additive calculation. Mixing tire with PS produced higher than expected single ring aromatic compounds but lower yields of polycyclic aromatic and alicyclic hydrocarbons. For the tire-PET co-pyrolysis, the production of oxygenated compounds was decreased in comparison to the expected additive data.

1. Introduction

Incorrect disposal of waste plastics is associated with negative impacts on the environment [1,2]. Although recycling of waste plastics via mechanical methods can generate recycled products, they are generally for low grade applications. Also, the other main treatment options of waste landfill and incineration are associated with land and air pollution and represent a waste of resource [3,4]. Many researchers have investigated the use of waste plastics as an essential resource to create new fuels and raw chemical materials through chemical recycling to extract value from the waste plastics [5–7]. Plastic waste can be converted to a secondary raw material such as monomers or pyrolysis oil through the process of pyrolysis [8]. The product pyrolysis oil can be used as a liquid fuel, a source of chemicals or as a feedstock to produce new plastics The chemical composition of the derived pyrolysis oil is dependent on the type of plastic polymer being pyrolyzed. The main plastics found in municipal solid waste are the thermoplastics, low and high density polyethylene, polystyrene, polypropylene and polyethylene terephthalate [9]. Low density polyethylene has a high level of branching and crosslinking in the polymer structure compared to high density polyethylene [7]. However, their product pyrolysis oil composition is very similar as they are both based on polymeric ethylene and consists of mainly n-alkanes, alkenes and alkadienes. Pyrolysis of polypropylene also produces alkenes in the product oil but the oil composition is more complex compared to polyethylene due to the branched structure of the polymer. Since polystyrene has a polymer structure based on aromatic styrene, the oil obtained from pyrolysis of polystyrene is aromatic consisting of mainly styrene, styrene oligomers and single ring aromatic compounds. The polymer structure of polyethylene terephthalate is aromatic and contains oxygenated groups and consequently produces an oil product containing oxygenated compounds including terephthalic acid and benzoic acid [7].

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Another high-volume waste material associated with negative environmental impact and difficulties in effective disposal, are waste tires [10]. In recent years, waste tire management options have included mechanical recycling and shredding of the tire rubber for use in sports fields, and for civil engineering applications and via combustion of the tires. Waste landfill for the disposal of tires is also practised in some countries, but is a waste of the resource. Pyrolysis has also been proposed as an effective management option for waste tires for the production of liquid fuels in high yields [11–13]. The pyrolysis oil from waste tires is mainly aliphatic and aromatic in composition, but also contains sulfur, nitrogen and oxygenated species [11]. Several different types of rubber may be used in the formulation of a tire, including, styrene–butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber and polybutadiene rubber. The pyrolysis of the different types of rubber will influence the product oil composition. For example, pyrolysis of styrene-butadiene-rubber produces an oil containing styrene and other single ring aromatic compounds. Pyrolysis of natural rubber generates an oil containing isoprene, dipentene, single-ring aromatic and polycyclic aromatic hydrocarbons as well as aliphatic alkane and alkene hydrocarbons up to C_{16}.

Several million tonnes of both waste plastics and waste tires are generated each year, representing an acute management problem to ensure environmental sustainability [6,13]. The potential for recovery of high yields of product oil from the pyrolysis of waste plastics and tires has been demonstrated. However, there is interest in the co-pyrolysis of these fossil-fuel derived polymeric wastes as a route to recovering the hydrocarbons rather than loss of the resource through combustion or landfilling. There have been some recent studies on the co-pyrolysis of waste plastics and tires [14]. For example, Hu et al. [14], used coupled thermogravimetric analysis with Fourier transform infra-red spectrometry to study the co-pyrolysis of waste tires with low and high density polyethylene, polystyrene and polypropylene. They reported that the addition of tire to the co-pyrolysis process resulted in a wider thermal decomposition range for the plastics and evidence of interaction of the tire and plastic volatiles was observed influencing the composition of the product oils and gases. Hussain et al. [15], conducted co-pyrolysis experiments involving tire and polyethylene and reported interaction between the waste polymers during co-pyrolysis which influenced the chemical composition of the product oil. Li et al. [16], investigated the co-pyrolysis of waste tires, with polypropylene, polyethylene, polyvinyl chloride and mixed plastic waste using a thermogravimetric analysis - Fourier transform infra-red/mass spectrometry reaction system (FT-ir/MS). They reported synergistic interaction between the tire and the plastic waste, with polyethylene demonstrating the highest interaction with the tire. Dewi et al. [17], investigated the synergistic interaction between tires and plastics with the main aim of determining the effect of the sulfur content of the tire on the product oil composition from the co-pyrolysis process. They reported that the sulfur content of the product oil could be effectively eliminated by mixing polystyrene or low density polyethylene with the tire. In addition, they showed that mixing polypropylene or polyethylene with the tire produced a pyrolysis oil with enhanced concentrations of lighter hydrocarbons. Miranda et al. [18], used an autoclave closed batch reactor system to study the co-pyrolysis of tires and different plastics, polyethylene, polypropylene and polystyrene. They concluded that pyrolysis temperature has a significant effect on the reaction mechanism of the pyrolysis of tire and plastic waste mixtures.

The literature demonstrates that there has been only limited research into the co-pyrolysis of waste tires and plastics. Consequently, there is a need to understand the advantages or disadvantages of co-processing of these abundant waste polymers to produce product oils via the pyrolysis process. In this respect detailed analysis of the product oils and by-product gases is required to understand the interactions of tires and plastics during co-pyrolysis as to how their interaction influences the end-product oil composition. In this work the interaction of waste tires with several different plastics commonly found in municipal solid waste, comprising, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) is reported. The co-pyrolysis was investigated in a fixed bed reactor and detailed compositional analysis of the product oils and gases is presented to determine the extent of interaction and the influence on product gas and oil yield. The aim of the work was to show how the individual plastics found in mixtures of plastics derived from municipal solid waste influence the overall yield and composition of the product oils and gases.

2. Materials and methods

2.1. Materials

The HDPE, LDPE, PP, PS, and PET were supplied from a waste plastics recycling company, Regain Polymers Ltd., Castleford UK, in the form of 2 mm sized pellets. The tire sample was produced from truck tires and was the rubber component only and was shredded to produce a particle size of 6 mm. The waste plastics and tire samples were characterised by proximate analysis using thermogravimetric analysis (TGA) of the individual waste plastics and tire using a Shimadzu TGA-50 analyser. Ultimate analysis of the samples for C, H, N and S was conducted using a Thermos EA-2000 elemental analyser. The results are shown in Table 1.

2.2. Pyrolysis reactor system

The pyrolysis of the tire and plastics and their mixture (co-pyrolysis) was carried out using a fixed bed pyrolysis reactor system, shown as a schematic diagram in Fig. 1. The reactor was constructed of stainless steel with a diameter of 4 cm and a height of 30 cm. The reactor was heated by an external electric ring furnace linked to a heating control system with temperature measurement. The waste sample of plastics, and/or tire (6.0 g total feedstock mass) was placed in a stainless-steel sample boat and placed centrally inside the reactor. For the co-pyrolysis experiments an equal 1:1 mass of 3.0 g of plastic and 3.0 g tire was used to give a total feedstock mass of 6.0 g. Nitrogen was used as a purge carrier gas to ensure flow of the product gases and volatiles through the reactor. The heating regime for pyrolysis consisted of heating from ambient temperature to a final temperature of 650 °C, at a heating rate of 20 °C min^{-1}. At the experimental temperature of 200 °C the product gas collection into the gas sample bag was started. When the pyrolysis temperature reached 650 °C it was held at that temperature for 20 min to ensure complete collection of pyrolysis gases. Three condensers in series, cooled by firstly air and then dry-ice were used to collect the liquid oil products. Uncondensed gases were collected into a

Table 1
Proximate and ultimate analysis of the tire and individual plastic samples.

Proximate analysis				
Feedstock	Moisture Content	Fixed Carbon	Volatile Matter	Ash Content
Tire	0.36	62.30	25.57	13.46
HDPE	0.88	93.15	0.07	8.80
LDPE	0.78	96.04	0.09	5.13
PP	0.48	94.07	0.06	6.37
PS	0.77	95.88	0.09	6.14
PET	0.73	82.33	14.38	5.71
Ultimate analysis				
Feedstock	Carbon	Hydrogen	Nitrogen	Sulfur
Tire	80.01	7.22	0.98	2.42
HDPE	85.01	13.24	0.80	0.00
LDPE	85.69	15.68	0.74	0.00
PP	81.87	15.12	0.65	0.00
PS	90.43	8.95	0.69	0.00
PET	62.03	5.02	0.52	0.00

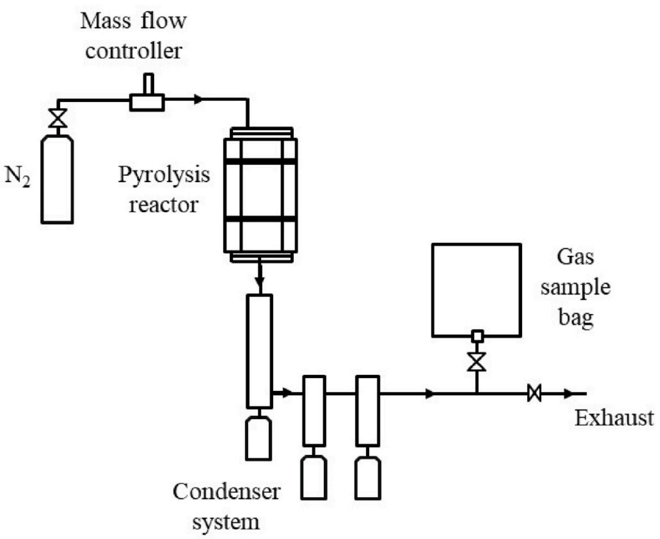

Fig. 1. Schematic diagram of the fixed-bed pyrolysis reactor system.

Tedlar gas sample bag. The solid residue char produced from the pyrolysis remained in the sample boat where it was collected and weighed after each experiment.

2.3. Gas analysis

The pyrolysis process produced a gas which was collected in the gas sample bag and was analysed using packed column gas chromatography (GC) using three separate Varian 3380C gas chromatographs. The first instrument, analysed the permanent gases (H_2, O_2, N_2 and CO) using argon as the carrier gas and a 2 m × 2 mm column packed with a 60–80 mesh molecular sieve and fitted with a thermal conductivity detector (TCD). The second GC measured CO_2 using a Haysep column also using a TCD. The third GC measured C_nH_m hydrocarbon gases (C_1-C_4) with nitrogen as the carrier gas and a 2m × 2 mm stainless steel column packed with Hysesp, 80–100 mesh using a flame ionisation detector (FID). Standards with known concentration were used to calculate the response factors (RF) and enable quantitation for each gas. Each gas sample was injected three times and the average was used to calculate the gas yield.

2.4. Oil analysis

The oil collected in the condenser system was analysed using coupled gas chromatography with mass spectrometry (GC/MS). The GC/MS used was a Varian, CP-3800 GC/Varian with Saturn 2200 MS instrument equipped with a DB-5 capillary column. The GC column with temperature from 40 to 310 °C, heating rate of 5 °C min^{-1}. An auto-sampler was used to inject 2 μL into the GC/MS column. A wide range of standard chemicals were injected to determine response factors and retention times. The GC/MS NIST library was used to aid peak identification of compounds but also the use of calculated relative retention indices. The GC/MS system was able to identify and quantify the major compound peaks present in the pyrolysis and co-pyrolysis oils. These major peaks represented in most cases over 95 % of the total peaks present in the GC/MS chromatograms for the tire, HDPE, LDPE, PP and PS, and also for all the tire/plastic mixtures. The exception was for pyrolysis of PET where only ~83 % of the compounds could be identified. Quantification of the individual compounds was via the use of standards and are presented as wt% in the product oil obtained from the pyrolysis of the tire and the individual plastics and the co-pyrolysis of the tire and plastics mixtures.

2.5. Thermogravimetric analysis of tires and plastics

Initial experiments were carried out to determine the thermal decomposition characteristics of the tire, the individual plastics and the mixtures of tire and plastic. The samples were cryogenically crushed to achieve a fine powder particle size to ensure homogeneity. A Schimadzu TGA-50 thermogravimetric analyser (TGA) was used for the analysis, using 10 mg of sample, with heating rate and temperature programme identical to the fixed bed reactor to replicate the pyrolysis reactor experiments. The thermograms and derivative thermograms which measured the rate of decomposition were analysed to determine, the on-set of pyrolysis, the peak decomposition and end-point temperatures.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 2 shows the thermogravimetric analysis (TGA) and the derivative thermograms (DTG) of the tire and individual plastics. The plastics all showed a single weight loss peak decomposition temperature, whereas the tire decomposition occurred over two weight loss peaks, which may be attributed to a mix of rubbers used in the tire formulation [19]. The thermal decomposition of the tire occurred over a temperature range from 230 to 510 °C with a large DTG peak occurring at 387 °C and a smaller DTG peak at a temperature of 445 °C. Dewi et al. [17], also reported the thermal decomposition of tire to be over a broad range from 240 °C to 500 °C, with two distinct peaks, but a smaller peak at a temperature of 375 °C and a much larger peak at 423 °C. The differences in the thermal degradation profile from their work to that reported here are most probably due to the different types of rubber used in the formulation of the tires.

The thermograms were analysed to determine the temperatures related to the on-set of pyrolysis, the peak decomposition and end-point of pyrolysis. The results are shown in Table 2. The order of thermal degradation in terms of the main peak degradation temperature was PS

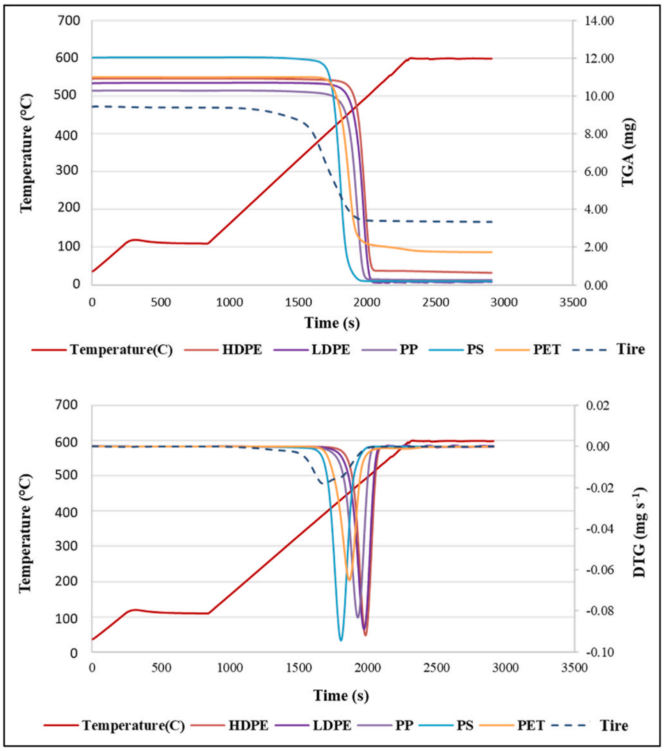

Fig. 2. (a) Thermogravimetric analysis (TGA) and (b) derivative thermograms (DTG) of the tire and individual plastics.

Table 2
Temperatures of thermogravimetric decomposition of the individual plastics and tire.

	HDPE	LDPE	PP	PS	PET	Tire
On-set temperature (°C)	405	430	400	380	380	230
Peak temperature (°C)	495	491	478	434	441	387
End-point temperature (°C)	518	519	511	480	485	510
Mass loss (wt.%)	92.7	98.7	98.0	98.6	81.0	61.0

< PET < PP < LDPE < HDPE with tire decomposition occurring over a range of 230–510 °C.

Fig. 3 shows the thermogravimetric analysis (Fig. 3(a))) and derivative thermograms (Fig. 3(b)) of the tire/plastic mixtures. Fig. 3 shows that when tire was added to the plastic during co-pyrolysis, the onset temperature of the thermal degradation for the plastics was shifted to lower temperatures compared to the thermal decomposition of the individual plastic components (Fig. 2). This phenomenon has also been reported by Hu et al. [14]. The mixtures of tire and the polyalkene plastics (Tire/HDPE, Tire/LDPE and Tire/PP) show thermograms that have two distinct peaks of mass loss, the first attributed to the degradation of the tire and the second due to the degradation of the plastic component of the mixture. Hu et al. [14], undertook co-pyrolysis of tires and different plastics using a thermogravimetric analyser and also reported two DTG peak, a lower peak at ~380 °C due to tire decomposition and second higher peaks due the decomposition of the plastic, 460 °C for Tire/PP and 480 °C for Tire/HDPE and Tire/LDPE. The interaction of the tire with the polystyrene and polyethylene terephthalate (Fig. 3) is influenced by the presence of an aromatic ring in the plastic polymer structure. The thermal decompositions for the mixture of these plastics with tire (Tire/PS, Tire/PET) show clear interaction with the tire, resulting in a single thermal decomposition peak.

Table 3 shows the on-set temperature, peak temperature and end-point temperature for the decomposition of the tire/plastic mixtures and also the overall mass loss, for the experimental results. The calculated results, based on the additive data for the individual TGA analysis for the tire and plastics from Table 2 are also shown in Table 3. The results show that for the polyalkene plastics there is only a small change in the peak temperatures for the first stage tire decomposition and second stage plastic decomposition temperatures. However, the experimental mass loss for the plastics are quite similar to those expected from additive calculation of the individual weight loss data. For the tire/polystyrene and tire/polyethylene terephthalate, Table 3 also shows two peak mass losses for the tire and plastics, at 390 °C and 446 °C for Tire/PS and at 390 °C and 432 °C for Tire/PET respectively. Hu et al. [14], investigated TGA co-pyrolysis of Tire/PS and reported two DTG peaks with peaks at ~380 °C and ~445 °C, representing tire and PS decomposition. However, Li et al. [16], also reported that only one peak of thermal decomposition was observed for co-pyrolysis of tire and PS using a TGA-FTir/MS system.

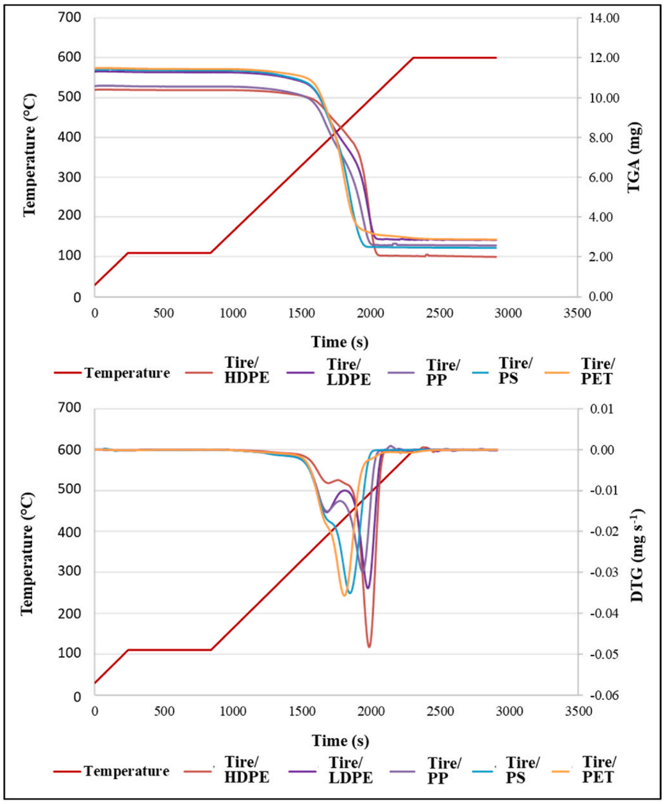

Fig. 3. (a) Thermogravimetric analysis (TGA) and (b) derivative thermograms (DTG) of the tire/plastic mixtures.

Table 3
Temperatures of the thermogravimetric decomposition of the tire/individual plastic mixtures.

	Tire/ HDPE	Tire/ LDPE	Tire/ PP	Tire/ PS	Tire/ PET
Experimental					
On-set temperature (°C)	255	255	255	255	255
Peak Temperature (°C)	(1) 394	(1) 390	(1) 391	(1) 390	(1) 390
	(2) 492	(2) 489	(2) 477	(2) 446	(2) 432
End-point temperature (°C)	520	505	515	500	530
Mass loss (wt.%)	80.6	74.7	75.2	78.1	73.2
Individual additive data					
Peak temperature (°C)	(1) 387	(1) 387	(1) 387	(1) 387	(1) 387
	(2) 495	(2) 491	(2) 478	(2) 434	(2) 441
Mass loss (wt.%)	76.9	79.8	79.5	79.8	71.0

3.2. *Pyrolysis of the tire and individual plastics*

The tire sample and HDPE, LDPE, PP, PS and PET plastics were pyrolyzed individually to determine, the product yield, gas composition and detailed oil analysis. This data can then be used when experiments were conducted using mixed tire/plastic co-pyrolysis to determine any interaction between the waste tire and plastics.

3.2.1. *Pyrolysis product yield and gas composition from the tire and individual plastics*

Table 4 shows the experimental product yield distribution between gas, oil and char from the pyrolysis of the tire sample and the individual waste plastics. The tire and all the plastics produced a hydrocarbon gas and oil/wax, while tire and PET also produced a significant amount of char. The results show a high oil yield compared to gas and char yields. The product yield from the pyrolysis of waste tires showed a high product yield of 54.83 wt% for the oil, 8.69 wt% gas, and 37.33 wt%

Table 4
Product yield from the pyrolysis of individual waste plastics and tire.

	Feedstock sample					
	Tire (wt.%)	HDPE (wt.%)	LDPE (w.%)	PP (wt.%)	PS (wt.%)	PET (wt.%)
Gas yield	8.69	6.45	6.17	4.34	1.68	33.60
Oil yield	54.83	85.50	90.17	89.00	99.20	53.00
Char yield	37.33	5.33	0.00	0.67	1.00	10.17

char. Islam et al. [20], reported similar results for the pyrolysis of waste tire in a fixed-bed reactor and reported a high oil yield of 55 wt% at 475 °C pyrolysis temperature, with char and gas yields of 36 wt% and 9 wt%, respectively. For the plastic pyrolysis experiments polystyrene produced the maximum oil yield at 99.20 wt%, which is comparable to the results reported by others [21]. The pyrolysis of HDPE and LDPE produced largely a wax product at a yield of 85.50 wt% and 90.17 wt% respectively (Table 4). Marcilla et al. [22], conducted pyrolysis of HDPE at 550 °C, and observed an oil yield of 84.7 wt% and gas yield of 16.3 wt %. Pyrolysis of PP produced a high oil yield of 89 wt%, similar to that reported by Fakhrhoseini and Dastanian [23]. The pyrolysis of PET produced a mainly yellow coloured wax/solid powder rather than an oil with a yield of 53.0 wt% in comparison to the other plastic types with a large gas yield of 33.60 wt%, mostly carbon dioxide and carbon monoxide, as well as a high char yield of 10.17 wt%, similar to that reported previously [24].

The main gases produced from tire pyrolysis were hydrogen, methane, ethane, ethene, propane, propene, butane, butene, butadiene, carbon dioxide and carbon monoxide as shown in Fig. 4 and as also reported in several other studies. Fig. 4 also shows the gases produced from the pyrolysis of HDPE, LDPE, PP, PS, and PET. A low gas yield was produced from the pyrolysis of all the types of plastics except PET, which, unlike the other plastics, produced lower hydrocarbons and more CO_2 and CO due to the presence of oxygen in the polymer structure, which was also reported by other researchers [23,25]. The CO_2 and CO are formed through the random scission of the chain, which occurred at the ester linkages, resulting in carboxyl and vinyl ester groups in the decarboxylation process [26]. The thermal degradation of HDPE, LDPE, and PP primarily produced alkane and alkene gases through the random scission process [8,26].

3.2.2. Oil composition from pyrolysis of individual waste tires and plastics

Table 5 shows the yield of compounds in the product oil from the pyrolysis of waste tire, high density polyethylene and low density polyethylene determined by GC/MS. The major compounds presented in Table 5 consisted of over 95 % of the compounds identified in the oil. There were also other minor peaks observed in the GC/MS chromatogram. For the identified compounds yields are expressed as wt.% in the pyrolysis oil.

Tires: The main compounds present in the tire pyrolysis oil were mainly single-ring aromatic compounds and polycyclic aromatic hydrocarbons (PAHs). The concentrations of the PAH, naphthalene, fluorene, and phenanthrene and their homologues were around 14 wt%. According to several studies, tire pyrolysis oil comprises aromatic compounds, but also present are reported to be aliphatic compounds such as alkanes and alkenes [11]. The largest concentration compound was limonene (39.70 wt%), while the other identified compounds were styrene, cyclohexane, cyclobutene, indene, cyclohexene, and benzothiazole.

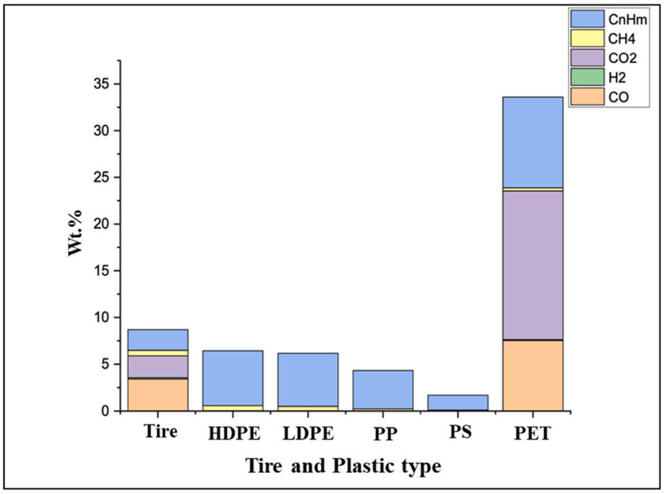

Fig. 4. Gas composition of the pyrolysis of individual tire and plastic (wt.% of the total product yield).

Limonene has also been reported as the major product in the oil from the pyrolysis of waste tires by Pakdel et al. [27]. However, limonene yield in tires is dependent on the type of rubber used in the formulation of the tire and also the pyrolysis process conditions. For example, Kwon and Castaldi [28], attributed the presence of limonene to the presence of decomposition of polyisoprene found in natural rubber [29]. In addition, Zhang et al. [30] demonstrated that limonene concentration is very sensitive to pyrolysis temperature, where they reported that increasing the pyrolysis temperature from 450 to 550 °C, decreased the limonene concentration from 11.97 wt% to 4.72 wt%. The production of high yields of aromatic compounds in the tire pyrolysis oil reported here has also been reported by others [31,32]. For example, Li et al. [32], found that the benzene, toluene, ethylbenzene and xylene (BTEX) concentration in tire pyrolsis oil produced at a temperature of 650 °C was 11.17 wt %. Also, Lopez et al. [31], reported high aromatic content oil for the pyrolysis of truck tires at a pyrolysis temperature of 500 °C, at 33.4 wt% and for pyrolysis of car tires at 43.7 wt%. The aromatic content found in tire pyrolysis oils has also been attributed to the thermal degradation of styrene-butadiene rubber [29]. Aromatic compounds are also reported to be due to secondary reactions in the pyrolysis hot zone [28].

Tires may be manufactured using several different types of rubber, however, the most commonly used are, natural rubber, styrene-butadiene-rubber and polybutadiene rubber [11]. The formation of products in the oil will depend on the thermal degradation mechanism of the different rubbers and the process conditions of pyrolysis. For example, natural rubber is a polyisoprene polymer and is thermally degraded through depolymerisation of the bonds of the rubber polymer to produce isoprene which may be followed by intramolecular cyclization or Diels-Alder type reaction to produce dipentene and other isoprene oligomers. Further reaction to produce other aliphatic and aromatic hydrocarbons occurs via chain propagation and intramolecular hydrogen transfer [33]. The thermal degradation of styrene-butadiene rubber involves degradation of the butadiene groups of the rubber polymer at lower temperatures and the styrene groups at higher temperature, leading to the formation of mainly ethylbenzene, styrene and isopropylbenzene [34]. Polybutadiene rubber decomposes in a two-stage process with depolymerisation at lower temperatures producing butadiene and dipentene and a range of hydrocarbons at higher temperature. Importantly, the process conditions of tire pyrolysis, will also influence the product oil and gas composition. For example, secondary reactions of the produced hydrocarbons are greatly influenced by high temperature and/or long residence times. For instance, increased single ring and polycyclic aromatic hydrocarbon concentrations may be produced by Diels-Alder reactions, involving the reactions of alkenes such as butadiene to produce cyclic alkenes which subsequently form aromatic compounds via dehydrogenation [33]. In addition, thermal decomposition of major compounds produced from tire pyrolysis widen the range of possible compounds found in the oil. For example, limonene is known to thermally decompose to give benzene, xylene, toluene, trimethylbenzene, styrene and methylstyrene [11].

High and low density polyethylene: Table 5 shows the concentration of compounds in the oil obtained from the pyrolysis of high density polyethylene and low density polyethylene. The pyrolysis of HDPE and LDPE produced wax instead of oil, with a high abundance of heavier molecular weight compounds. The composition of the wax/oil produced from the pyrolysis of HDPE and LDPE included mostly linear alkanes, with essentially no aromatic compounds generated. The GC/MS total ion chromatograms for HDPE and LDPE, showed the presence of aliphatic long-chain hydrocarbons from carbon number C_8 to C_{28} for HDPE and from C_8 to C_{25} for LDPE, including alkadiene, 1-alkene, and n-alkane, respectively. Triple peaks were detected for each of the carbon numbers,

Table 5
Composition of oil obtained from the pyrolysis of waste tires, high density polyethylene and low density polyethylene.

Tire		High density polyethylene		Low density polyethylene	
Compound	Mass in oil (wt.%)	Compound	Mass in oil (wt.%)	Compound	Mass in oil (wt.%)
benzene	0.14	C8	1.30	C8	0.18
toluene	2.99	C9	3.65	C9	2.68
unknown	3.27	C10	7.52	C10	5.51
1,2-dimethylcyclohexane	3.47	C11	8.80	C11	7.75
ethylbenzene	0.53	C12	9.42	C12	8.90
xylene	4.73	C13	11.47	C13	10.44
styrene	0.18	C14	12.52	C14	12.26
cyclobutane,12-bis(1-methylethenyl)	3.31	C15	10.74	C15	12.79
benzene, 1-ethyl-3-methyl	2.07	C16	9.24	C16	11.53
p-methylstyrene	0.13	C17	3.36	C17	4.43
benzene, 1-methyl-4-(1-methylethenyl)	6.35	C18	2.96	C18	4.04
limonene	39.69	C19	4.92	C19	6.46
cyclohexene,1-methyl	4.18	C20	3.66	C20	4.75
benzen,1-methyl-4-(methylpropyl)	1.45	C21	2.62	C21	3.63
naphthalene	0.04	C22	2.11	C22	2.19
1h-indene,1,3-dihydro-1,6-dimethyl	0.91	C23	1.12	C23	1.40
benzothiazole	3.92	C24	0.70	C24	0.10
2-methylnaphthalene	0.06	C25	0.57	C25	0.18
2-ethylnaphthalene	2.65	C26	0.04		
2,6-dimethynaphthalene	0.22	C27	0.10		
1,4-dimethynaphthalene	0.21	C28	1.01		
4-methylbiphenyl bibenzyl	3.65				
dibenzyl or dibenzofuran	1.31				
unknown	3.14				
c-3 naphthalene	2.89				
2,3,6-trimethylnaphthalene	2.92				
fluorene	0.85				
9-methylfluorene	0.87				
1-methylfluorene	2.05				
phenanthrene	0.02				

with the 1-alkene as the largest peak, and the separation of these peaks occurred clearly in the chromatogram for the low carbon numbers from C_8 C_{22}. At higher molecular weights, the resolution from the GC/MS column decreased, and heavier compounds with a carbon number $> C_{23}$ presented as one peak, (1-alkene). The thermal decomposition of the polyalkene plastics, HDPE and LDPE involves a series of reactions, including free radical initiation, secondary decomposition via random scission and chain-end scission and then recombination of different chains [35]. The C − C bonds which are the weakest bonds in the polyethylene structure and are break to form radicals which are then stabilised via the formation of C = C double-bond alkenes, leading to the formation of alkenes as the main compounds in the product oil [25]. Others have also reported that the oil produced from the pyrolysis of polyethylene was mostly aliphatic and with similar carbon number ranges to that shown in this work [36–38]. Table 6 shows the yield of compounds in the product oil (wt.%) derived from the pyrolysis of polypropylene, polystyrene and polyethylene terephthalate.

Polypropylene: Table 6 shows that the thermal degradation of the polypropylene produced a significant concentration of unsaturated hydrocarbons (alkenes) with a carbon number range from C_6 - C_{25}. Thermal degradation of polypropylene is promoted by random scission of the polymeric chain; as a result, the degradation products are distributed over a wide range of molecular weights. Due to the CH_3 side group in the polypropylene structure, a considerable number of compounds with carbon double bonds (C=C) are formed in polypropylene cracking products [25].

Polystyrene: Table 6 also show the product oil composition from the pyrolysis of polystyrene. The main product in the oil was styrene at 70.08 wt%, and also benzene, xylene, toluene and ethylbenzene at ~4 wt%. The polycyclic aromatic hydrocarbons, naphthalene, biphenyl, fluorene, phenanthrene, and anthracene were also identified in the oil composition. Liu et al. [39], also reported that styrene and mono-aromatic compounds such as, benzene, toluene, ethylbenzene, and methyl styrene, were the most significant compounds present in the oil, accounting for approximately 80 % of the total. The thermal degradation mechanism of the aromatic structured polystyrene polymer has been demonstrated to involve scission, hydrogen abstraction, hydrogen transfer, radical recombination and disproportionation [35]. Thereby, leading to the formation of the monomer styrene and other single ring aromatics and also polycyclic aromatic hydrocarbons in high concentration [37].

Polyethylene terephthalate: Table 6 shows the products (wt.%) identified in the waxy/solid powder produced from the pyrolysis of polyethylene terephthalate. The waxy/solid was dissolved in dichloromethane (DCM), but required sonication and an extended time period to dissolve the sample. Benzoic acid was present in high concentration at 41.10 wt%, while the main aromatic compounds were also observed, such as xylene, styrene, biphenyl, and terphenyl. The chemical structure of PET consists of aromatic, aliphatic and oxygenated groups, leading to the formation of a complex mixture of products during thermal degradation of the polymer. It has been reported that the mechanism for PET thermal degradation include polymer bond scission and retro-hydoalkoxylation to produce benzoic acid and vinyl ($CH_2=CH–$) based compounds. Simultaneously the ester groups of the PET polymer decompose to form carbon monoxide, carbon dioxide and ethene [35]. The pyrolysis of PET produced oxygenated compounds in the product oil, in contrast to the other plastics investigated in this work. Cepeliogullar and Putun [40], also reported that almost 50 wt% of the oil produced during the pyrolysis of PET contained benzoic acid. Other oxygenated compounds present include carboxylic acids, phthalic acid and phenols as well as aromatic compounds.

3.3. *Co-pyrolysis of tire and plastic mixtures*

The tire sample and each of the plastics were mixed in a 1:1 ratio to produce a Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS and Tire/PET mixture which were then co-pyrolyzed in the fixed bed reactor system. The product yield, gas composition and detailed oil analysis were used to determine any interaction between the waste tire and plastics.

Table 6
Composition of oil obtained from the pyrolysis of polypropylene, polystyrene and polyethylene terephthalate.

Polypropylene		Polystyrene		Polyethylene terephthalate	
Compound	Mass in oil (wt. %)	Compound	Mass in oil (wt. %)	Compound	Mass in oil (wt. %)
cyclohexane, 1,3,5-trimethyl	1.01	benzene	0.50	xylene	0.06
2,4-diethyl-1-methyl-cyclohexane	27.33	toluene	0.47	styrene	0.07
decane, 4-methyl	1.37	ethylbenzene	0.08	benzoylformic acid	1.13
Unknown	0.26	xylene	3.22	ethanone, 2,2-dihydroxy-1-phenyl-	2.96
2,3,3- trimethyl-1-hexene	2.34	styrene	70.08	ethanone, 2-(formyloxy)-1-phenyl-	21.90
cyclopentane,1-butyl-2-2propyl	1.24	naphthalene	0.04	methanol, oxo-, benzoate	2.74
1-undecene, 7-methyl-	4.39	benzene, 3-cyclohexen-1-yl-	1.70	acetophenone	1.83
1,7-nonadiene,4,8-dimethyl-	2.86	Biphenyl	0.25	naphthalene	0.15
2-undecene, 4,5-dimethyl-	0.96	2,7-Dimethylnaphthalene	0.02	benzoic acid	41.10
1-tetradecene	1.47	C-3 naphthalene	1.16	trimethylphenol	1.36
dodecane, 2,6,10-trimethyl-	1.07	1-methylacenaphthalene	0.84	benzoic acid, 4-methyl	1.68
1,1′-bicyclohexyl, 2-(1-methylethyl)-, trans-	11.89	9-methylfluorene	0.15	benzoic acid, 4-ethyl	1.97
cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-	4.29	2-methylfluorene or unknown	1.61	biphenyl	1.75
1,2-dicyclohexylbutane	9.43	methyl fluorene	12.12	4-ethylbenzoic acid, 3,4-dichlorophenyl	0.42
cyclohexane, 1-(cyclohexylmethyl)-4-ethyl-, trans-	1.77	1,3-diphenyl-3-methylcyclopropene	1.70	diphenylmethane	0.16
cyclohexane, 1,1’-(1,2-dimethyl-1,2-ethanediyl)bis-	2.71	phenanthrene	0.26	1,1′-biphenyl, 4-methyl-	0.16
dodecane, 5-cyclohexyl-	5.33	1-methylphenanthrene	0.48	ethanone, 1,1’-(1,3-phenylene)bis-	0.27
cyclodecane, octyl-	1.95	phenylnapthalene	0.15	benzene, 1,4 dimethyl-2,5bis(1-methylethyl)	2.93
1-nonadecene	0.97	1,5-diphenyl-1,5-hexadiene	0.18	phthalic acid, di-(1-hexen-5-yl) ester	0.76
2-methyl-7-octadecene	3.12	benzo[a]fluorene	0.08	phthalic acid, ethyl 4-isopropylphenyl e	0.55
unknown	1.33	m-terphenyl	0.17	(1,1 biphenyl)-2,2-dicarboxaldehyde	0.17
1,19-eicosadiene	4.06	p-terphenyl	0.04	m terphenyl	0.04
3-eicosene	2.14	dibenz[a,c]anthracene	3.86	p-terphenyl	0.28
9-eicosene	2.53	1,3,5 triphenylbenzene	0.05		
heneicosane	0.65				
1-docosene	2.20				
cyclopentane, 1,1’-[3-(2 cyclopentylethyl)-1,5-	0.05				
1-tetracosene	0.84				
cyclodopentane,(4-octyldodecyl-)	1.64				
2-tetracosene	0.76				

3.3.1. *Product yield and gas composition from the co-pyrolysis of tire and plastics*

Table 7 shows the product yield distribution of gas, oil and char produced from the co-pyrolysis of the tire and plastic mixtures. Also shown are the addive yields, calculated based on the predicted yields calculated from the individual tire and plastic pyrolysis data. The results demonstrate a certain interaction between the plastics and tires, resulting in a significantly higher gas yields than predicted for all the mixtures. The tire/polystyrene co-pyrolysis produced the lowest gas yield (7.61 wt%), but higher than predicted, while the oil yield was consequently slightly lower (69.67 wt%) than expected. Co-pyrolysis of the tire/polypropylene mixture produced the highest oil yield (73.50 wt %) of all the other tire/plastic mixtures. The char yields were slightly lower than predicted for all the mixtures, suggesting that there was interaction between the tire and plastics during the co-pyrolysis process. This could be via gas-solid (char) interacion or interaction of the evolved volatiles. It has been reported that the release of radicals during pyrolysis promotes depolymerisation of plastics [41]. Also, the char itself can react with the decomposition products from the pyrolysis of plastics [42].

Table 7
Product yield from the mixtures of the tire and waste plastics, experimental and additive data (results calculated based on the additivity data of the individual samples).

	Experimental				
	Tire/HDPE	Tire/LDPE	Tire/PP	Tire/PS	Tire/PET
Gas yield	13.94	12.13	12.77	7.61	24.58
Oil yield	70.50	71.67	73.50	69.67	56.33
Char yield	16.50	15.83	18.33	20.17	21.67
	Additive data				
	Tire/HDPE	Tire/LDPE	Tire/PP	Tire/PS	Tire/PET
Gas yield	7.57	7.43	6.52	5.19	21.15
Oil yield	70.17	72.50	71.92	77.01	53.92
Char yield	21.33	18.67	19.00	19.17	23.75

Fig. 5 shows the gas composition obtained from the pyrolysis of the tire and plastic mixtures. Mixing the tire with each plastic produced the main gases of methane, C_2-C_4 hydrocarbons, carbon monoxide and carbon dioxide, which all have a higher gas yield than the calculated additive prediction. The gas analyses of Tire/HDPE, Tire/LDPE, and Tire/PP revealed higher concentrations of CO, CO_2, and hydrocarbon gases. Whereas, the Tire/PS mixture showed lower concentrations of these gases. The Tire/PET mixture gave high gas yields of mainly CO, CO_2, which reflected the high oxygen content of PET.

3.3.2. *Composition of oil obtained from the co-pyrolysis of the tire/plastic mixtures*

Table 8 shows the composition of the product oil obtained from the co-pyrolysis of Tire/PP, Tire/HDPE and Tire/LDPE. The results represent the yield of compounds present in the oil obtained from the pyrolysis of tire/plastic (wt.%).

Tire/HDPE and Tire/LDPE: Table 8 shows the composition of the oil obtained from the co-pyrolysis of tire/high density polyethylene and tire/low density polyethylene. The main influence of mixing tire with HDPE in relation to the product oil composition was a decrease in the

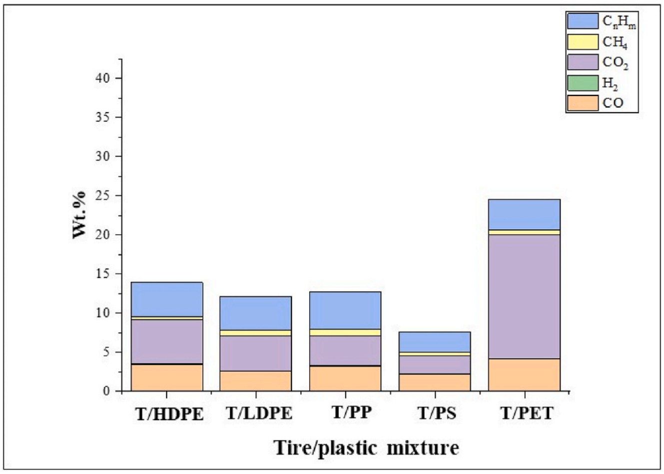

Fig. 5. Gas composition derived from the pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET).

concentration of the aliphatic compounds, represented as triple alkane, alkene and alkadiene peaks from carbon number $C_{19} – C_{33}$, as shown in Table 8. For each carbon number hydrocarbon group, not all three of the alkane, alkene and alkadiene hydrocarbons were present in the oil. While the lighter aromatic compounds present in the product oil were essentially produced from the tire pyrolysis contribution, such as toluene, xylene, and limonene. Additionally, PAHs that included naphthalene, fluorene, and phenanthrene and their derivatives were also found in the oil, as was expected based on the tire pyrolysis oil composition (Table 5). In relation to the co-pyrolysis of Tire/LDPE, Table 8 also shows that the major effect of mixing tires with LDPE was to also produce a pyrolysis oil with a decreased concentration of aliphatic compounds in the carbon number range $C_{20} – C_{33}$, compared with LDPE pyrolysis alone (Table 5). As was the case for HDPE, the co-pyrolysis of tire and LDPE also showed that not all of the alkane, alkene and alkadiene hydrocarbons for each carbon number were identified in the oil. The presence of toluene, xylene, and methyl styrene, and PAHs, illustrate the contribution from pyrolysis of the tire.

Tire/polypropylene: Table 8 shows the oil composition and yield obtained from the pyrolysis of the tire/polypropylene mixture. The addition of the tire to the plastic had a significant effect on the product oil, producing more aromatic compounds in high concentrations. It also revealed a low abundance of compounds with a higher molecular

Table 8
Composition of oil obtained from the pyrolysis of tire/high density polyethylene, tire/low density polyethylene and tire/polypropylene.

Tire/High density polyethylene		Tire/Low density polyethylene		Tire/Polypropylene	
Compound	Mass in oil (wt.%)	Compound	Mass in oil (wt.%)	Compound	Mass in oil (wt.%)
toluene	0.08	toluene	0.35	benzene	0.48
p-xylene	0.18	xylene	0.38	toluene	20.16
o-xylene	0.21	cyclohexene,1-methyl-4-(methyl ethenyl	0.68	cyclopentane, 1,1,3,4-tetramethyl	2.89
limonene	1.41	methyl styrene	0.81	2,4-dimethy-1-heptene	1.71
unknown	0.90	benzene,1-methyl-2-(1-methylethenyl	1.18	ethylbenzene	2.19
naphthalene	0.51	d-limonene	6.15	o-xylene	5.88
unknown	0.31	unknown	1.08	p-xylene	4.33
1-methylnaphthalene	0.57	naphthalene	0.63	m-xylene	2.76
1,3 or 1,6 dimethyl naphthalene	0.78	1-methylnapthalene	0.68	cyclohexene,1-methyl-5-(1-methylethenyl	5.09
dibenzofuran	0.97	1,3 or 1,6 dimethyl naphthalene	0.94	benzene,1,2,3-trimethyl-	4.84
9-methylfluorene	1.11	dibenzofuran	1.05	benzene, 1-ethyl-3-methyl-	1.73
2-methylfluorene	0.28	9-methylfluorene	1.17	benzene, 1,2,4-trimethyl-	13.90
unknown	1.36	unknown	0.39	decane, 4-methyl-	1.78
phenanthrene	0.02	1-methylfluorene	1.42	cis-.beta.-methyl styrene	0.92
C19	2.00	anthracene	1.78	cyclohexene, 4-methyl-1-(1-methylethyl)-	3.28
C20	2.37	2-phenylnaphthalene	0.32	benzene, 2-ethyl-1,4-dimethyl-	3.42
C21	2.65	C20	0.43	cyclohexene, 1-butyl-	1.50
C22	0.43	C21	0.50	benzene, 1,2,4,5-tetramethyl-	3.98
C23	0.51	C22	0.57	2,4-dimethylstyrene	1.34
C24	8.01	C23	0.08	benzene, 1-ethyl-2,4-dimethyl-	2.66
C25	0.68	C24	2.81	naphthalene	0.52
C26	9.22	C25	2.43	benzene, 1-methyl-4-(1-methyl-2-propenyl	0.70
C27	0.26	C26	1.39	benzene, pentamethyl-	0.49
C28	4.37	C27	8.34	7-tetradecene	0.50
C29	4.40	C28	3.90	cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-	2.48
C30	13.35	C29	1.42	1,2,3-trimethylindene	0.48
C31	15.12	C30	14.28	naphthalene, 1,4-dimethyl-	2.78
C32	16.19	C31	15.150	naphthalene, 1,7-dimethyl-	1.68
C33	15.34	C32	14.99	undecane, 4,6-dimethyl-	0.49
		C33	13.90	naphthalene, 2-(1-methylethyl)-	0.46
				7-heptadecene	0.55
				naphthalene, 2,3,6-trimethyl-	2.00
				naphthalene, 1,6,7-trimethyl-	0.77
				azulene, 4,6,8-trimethyl-	0.47
				naphthalene, 1-methyl-7-(1-methylethyl)-	0.46
				naphthalene, 1,2,3,4-tetramethyl-	0.88
				9-eicosene	0.81
				1-docosene	0.39
				1-tetracosene	0.43

weight, particularly the aliphatic compounds (alkenes) as well as the alicyclic hydrocarbon compounds, which were mostly formed from the polypropylene. Benzene, toluene, ethylbenzene and xylene (BTEX) compounds were found in high concentrations with toluene found in very higher concentration compared to other compounds. There was also a significant production of benzene, naphthalene, and their derivatives. Wong and Broadbelt [43], also reported that interaction occurs when polyalkene polymers are co-pyrolyzed with aromatic polymers.

Table 9
Composition of oil obtained from the pyrolysis of tire/polystyrene and tire/polyethylene terephthalate.

Tire/Polystyrene		Tire/Polyethylene terephthalate	
Compound	Mass in oil (wt.%)	Compound	Mass in oil (wt.%)
benzene	0.21	benzene	1.76
toluene	2.47	toluene	7.18
5,5-dimethyl-1,3-hexadiene	0.72	6-methyl-6-hepten-4-yn-3-ol	1.57
2,4-dimethyl-1-heptene	6.08	ethylbenzene	2.59
ethylbenzene	2.86	xylene	6.35
p-xylene	1.92	styrene	0.44
o-xylene	2.43	2-cyclohexen-1-ol, 4-ethyl-1,4-dimethyl-	1.21
styrene	11.44	benzene, 1-ethyl-3-methyl-	5.47
benzene, 1-ethyl-4-methyl-	4.09	benzene, 1,3,5-trimethyl-	2.18
benzene, propyl-	3.82	1-(2-methylphenyl)	1.41
cis-beta-methyl styrene	6.25	benzene, 1,2,3-trimethyl-	1.37
benzene, 1-methyl-2-(1-methylethyl)-	4.42	benzene, 1-methyl-4-(1-methylethyl)-	7.92
limonene	4.72	limonene	4.25
benzene, (2-methyl-1-propenyl)-	2.62	2h-indeno [1,2-b] oxirene, octa hydro-, (1a	1.40
7-tetradecene	2.00	unknown	3.21
naphthalene	0.12	cyclohexene, 1-methyl-4-(1-methylethylid	3.26
benzothiazole	1.40	unknown	3.91
(1-methylpenta-1,3-dienyl) benzene	0.68	benzene, 1-methyl-4-(1-methylpropyl)-	1.04
benzene, 3-cyclohexen-1-yl-	3.79	benzene, 1,2,4,5-tetramethyl-	0.58
1,2,3-trimethylindene	1.32	unknown	6.57
Diphenylmethane	0.96	2,4-dimethylstyrene	0.549
1,2-diphenylethylene	0.60	benzoic acid, ethyl ester	3.98
benzene, 1,1'-(1,2-dimethyl-1,2-ethanedi	2.54	unknown	1.35
benzene, 1,1-(1,3-propanediyl) bis	5.90	naphthalene	0.15
benzene, 1,1-(1,2-propanediyl) bis	1.85	benzoic acid	17.34
benzene, 1,1'-(3-methyl-1-propene-1,3-di	3.67		
benzene, 1,1'-(1-methyl-2-cyclopropene-1,2-diyl) bis	0.86	benzothiazole	1.73
benzene, 1,1'-(1-butene-1,4-diyl) bis-, (	1.94	(1-methylbuta-1,3-dienyl) benzene	0.62
naphthalene, 1-phenyl-	0.62	2-methylnaphthalene	0.09
1-pentene, 1,5-diphenyl-	2.83	biphenyl	1.97
2,6-diphenyl-1,7-heptadiene	0.56	2,6-dimethylnaphthalene	0.03
1,5-diphenyl-1,5-hexadiene	1.07	naphthalene, 1,7-dimethyl-	0.18
Unknown	1.56	diphenylmethane	0.63
m-terphenyl	0.19	1,1′-biphenyl, 4-methyl-	0.40
p-terphenyl	0.06	fluorene	1.05
unknown	1.30	benzophenone	0.52
1-propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	2.47	octadecane, 6-methyl-	0.47
dibenzo[a,c]anthracene	4.32	phenanthrene	0.05
unknown	2.78	o-terphenyl	0.02
1,3,5 triphenyl benzene	0.82	m-terphenyl	0.07
		p-terphenyl	0.05

Table 9 shows the composition of the oil determined by GC/MS derived from the co-pyrolysis of tire/polystyrene and tire/polyethylene terephthalate. The results represent the yield of compounds (wt.%) present in the product oil.

Tire/polystyrene: Table 9 shows the composition of the oil obtained from the co-pyrolysis of the tire/polystyrene mixture. The major compounds listed in Table 9 show that styrene was detected in the highest concentration (11.44 wt%) compared to the other compounds. However, the pyrolysis of polystyrene alone, produce an oil with 70.08 wt% of styrene (Table 6), indicating that interaction between the tire and PS promoted degradation reactions of the styrene to produce other aromatic compounds. Moreover, BTEX compounds were identified in high concentration. PAHs were also found in the oil derived from the pyrolysis of the Tire/PS mixture, which included naphthalene, diphenyl, terphenyl, and anthracene. The highly aromatic product oil from Tire/PS pyrolysis is also linked to their individual pyrolysis oil composition which was mainly aromatic. Because of the structure of polystyrene and the presence of a phenyl group in the structure, aromatic compounds account for more than 90 % of the pyrolysis products from polystyrene [44,45]. Pyrolysis products from tires are also dominated by aromatic compounds [11] and mixing PS with tires increased the percentage of these compounds, which produced a highly aromatic oil. Miranda et al. [46], investigated the co-pyrolysis of tires with plastic (30 % rubber tires and 70 % plastics (20 % PE, 30 % PP, and 20 % PS)). They found that the product oil had a complex composition consisting of 47 % alkanes, 14 % alkenes, and 39 % aromatics. The aromatic compounds were obtained in high concentration at the expense of the alkane fraction.

Tire/polyethylene terephthalate: Table 9 shows the composition of the oil produced from the pyrolysis of the tire/polyethylene terephthalate mixture. The main compounds produced from PET pyrolysis was benzoic acid, while tire pyrolysis produced mainly limonene. On the other hand, PAHs compounds, such as naphthalene, fluorene, and phenanthrene were indicated in this mixture. Furthermore, oxygenated compounds were identified in the product oil as a part of the PET pyrolysis oil. In addition, more BTEX and aromatic contents were produced compared to the individual PET pyrolysis oil.

3.4. *Tire-plastic co-pyrolysis interaction effects*

The impact of mixing waste tire with different plastics in relation to the yield and composition of the product oils and gases may be seen by comparing the co-pyrolysis product yields to the value predicted using the additivity rule from the yields of the separate feedstock components. Any interaction between tire and plastic may be identified when the experimental value exceeds (positive) or is less than (negative) the calculated additive value [14]. The calculated interaction data for the product yields are shown in Fig. 6, which includes gas, oil, and char yields for the tire/plastic mixtures investigated in this study. Gas yields for all the mixtures of Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET revealed positive values at 6.37, 4.70, 6.26, 2.43, and 3.44 wt %, respectively. This demonstrated that the volatile materials increased with temperature which led to an increase in gas yield at the expense of oil yield. The char yields observed a positive value for Tire/PS at 1.0 wt % compared to the other mixtures that showed negative values at −4.83, −2.84, −0.67, and −2.08 wt% for Tire/HDPE, Tire/LDPE, Tire/PP, and Tire/PET, respectively.

The oil yields of Tire/HDPE, Tire/PP, and Tire/PET showed higher values than calculated by feedstock addition at 0.36, 1.59, and 2.42 wt %, which was considered as a very slight difference between the co-pyrolysis experimental and calculated additive oil yields. That may be explained by the minimum interaction that can be seen between HDPE and tire during the co-pyrolysis process. Whereas the co-pyrolysis of Tire/PP and Tire/PET obtained a significant and higher interaction effect. Tire/LDPE and Tire/PS obtained lower, negative values at −0.83 and −7.35 wt%, respectively, as the experimental results were less than the calculated additive results. This is due to the high gaseous products

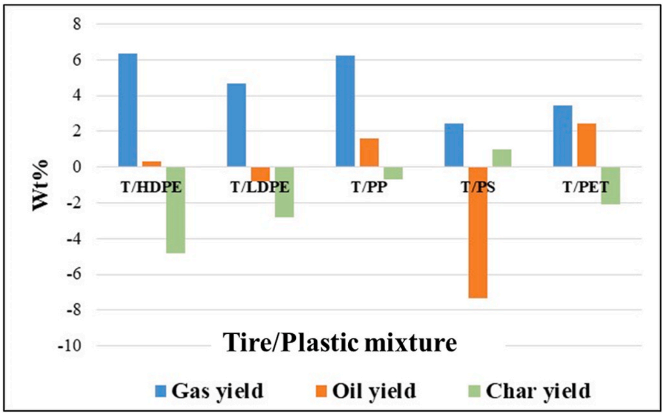

Fig. 6. Interaction effect of mixing tire/plastic on product yield from the pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET).

evolved from the co-pyrolysis at the expense of oil formation. Furthermore, changes in the branched chain of the plastic polymer may result in distinct pyrolysis breakdown behaviour when interacted with natural and synthetic rubber components in tires, which may explain the variation in interaction effects during the co-pyrolysis process [14]. Hu et al. [14], investigated the co-pyrolysis of Tire/HDPE, Tire/LDPE, Tire/PP and Tire/PS using a coupled thermogravimetric analyser with Fourier transform infra-red spectrometry and reported synergistic interaction between the tire and plastic which influenced the composition of product oils and gases.

The main investigated gases in the co-pyrolysis of tires and plastics were, hydrogen, methane, C_nH_m hydrocarbons (C_2-C_4), carbon monoxide and carbon dioxide. Fig. 7 shows the interaction results, which showed higher values of CO_2 were produced experimentally than would be expected from additive calculation based on the pyrolysis of the individual feedstocks for all the mixtures. For example, Tire/PET was associated with high yields of gas species generated from the individual tire and PET. While the CO yield revealed a lower than expected value for the Tire/PET mixture compared to the other mixtures. Moreover, the hydrocarbon gases (CnHm), showed a negative interaction effect for Tire/PET representing a lower yield of hydrocarbons that were generated by the pyrolysis of the individual tire feedstock. Hydrogen and methane showed low calculated interaction values which make it difficult to assess their interaction effects. Hu et al. [14], reported that the co-pyrolysis of Tire/HDPE, Tire/LDPE, Tire/PP and Tire/PS resulted in a reduction in the yield of methane in the product gas than would be expected from that predicted by addition.

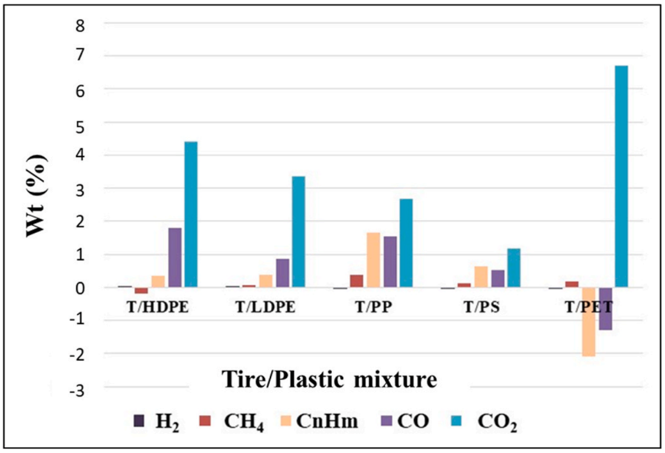

Fig. 7. Interaction effect of mixing tire/plastic on gas composition from pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET).

Dewi et al. [17], investigated tire and plastics interaction using a pyroprobe-gas chromatograph, thermogravimetric analysis and a fixed bed reactor system for their experiments. They investigated co-pyrolysis of Tire/LDPE, Tire/PP and Tire/PS. They reported synergistic interaction between tire and plastic which was dependent on the plastic type. For example, mixing tire with LDPE produced a higher yield of oil with enhanced concentration of light hydrocarbons. The co-pyrolysis of Tire/PP and Tire/PS produced negligible change in the total oil yield but a marked change in oil composition.

The mixtures of Tire/HDPE, Tire/LDPE, and Tire/PP were classified according to the main oil components, and the results are shown in Fig. 8. BTEX, refers to benzene, toluene, ethylbenzene and xylenes; Aromatic refers to benzene derivatives, biphenyls, limonene, terphenyl, and indene; PAHs refers to for example, naphthalene, anthracene, phenanthrene, pyrene and fluorene and their derivatives; Aliphatic refers to carbon numbers above C_8; Alicyclic compounds refers for example to cyclopentane and cyclohexane etc.,

Aliphatic compounds were increased above that expected from the results obtained from the tire and plastic feedstock pyrolysis data for the co-pyrolysis of Tire/HDPE and Tire/LDPE with lower than expected values for the BTEX, PAHs, alicyclic, and aromatic compounds. Miranda et al. [18], have also reported a strong inter-relationship between aliphatic and aromatic compounds due to interaction between tires and plastics during co-pyrolysis. Dewi et al. [17], have proposed a reaction mechanism for the interaction of tires and plastics during co-pyrolysis which is dependent on the type of plastic in the co-pyrolysis mixture. HDPE, LDPE have a higher H/C ratio than that of the tire which promotes the large formation of hydrogen radicals during the pyrolysis process, and these promote the breaking of the polymer chains of the tire rubber and the consequent formation of hydrocarbon radicals. These hydrocarbon radicals then bond with the radicals produced from the thermal decomposition of the polyalkene plastics to form alkanes and alkenes and a reduction in the formation of aromatic compounds. This mechanism is supported by the data for Tire/HDPE and Tire/LDPE shown in Fig. 8, but less so for the Tire/PP where there is a more positive interaction to produce less aliphatic compounds and more aromatic compounds. Fig. 8 shows that the composition of the oil for the co-pyrolysis of Tire/PP revealed positive values for BTEX, PAHs, and aromatic compounds. For Tire/PP co-pyrolysis the reaction mechanism may be related to the presence of natural rubber in the tire which promotes the pyrolytic decomposition of PP. This increases secondary

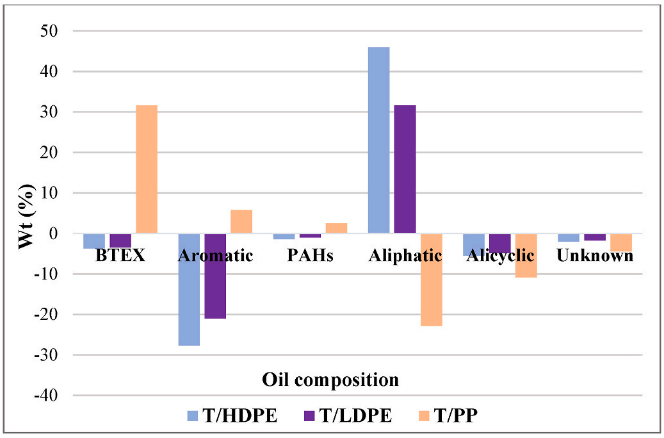

Fig. 8. Interaction effect of mixing tire/plastic on oil composition from pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE) and tire/polypropylene (T/PP).

reactions and recombination to produce light compounds, such as BTEX. Hu et al. [14], undertook co-pyrolysis of tires and different plastics using a thermogravimetric analyser and reported a positive interaction between the Tire/HDPE and Tire/LDPE, at higher temperatures of ~450 °C. For the Tire/PP co-pyrolysis they reported positive interaction at lower temperatures (<445 °C) which they attributed to the decomposition of natural rubber in the tire interacting to decompose the PP. However, at temperatures above 445 °C, once the natural rubber had fully decomposed, there was negative interaction between tire and PP. They have suggested that the synthetic rubber component of tire (e.g. styrene-butadiene-rubber) may also have an influence on plastic polymer thermal degradation at higher temperatures of pyrolysis. Dewi et al. [17], also proposed that the tire char acts as a catalyst for the cracking of polyalkene plastics since the tire char contains Lewis and Brønsted acid sites which promote the polymer degradation.

Fig. 9(a) shows the Tire/PS interaction for the product oil produced from co-pyrolysis, and positive interaction values of 3.57 and 4.60 wt% for BTEX and aromatic compounds, respectively. However, negative values for PAHs at −12.37 wt%, and alicyclic hydrocarbons at −5.48 wt % are shown. It has been suggested [17], that the thermal decomposition of the tire produces alkyl radicals which react with the phenyl and benzyl radicals produced from the pyrolysis of the PS to form benzene derivatives and subsequently single ring aromatic compounds. The pyrolysis of tire would also produce more hydrogen radicals than PS so as to promote the hydrogenation reaction of benzene derivative radicals to promote the formation of BTEX. Li et al. [16], have reported that the pyrolysis products of PS can promote the decomposition of natural rubber and butadiene rubber. The co-pyrolysis of Tire/PET produced interaction resulting in changes in oil composition (Fig. 9(b)) which showed high value for BTEX, while lower values for the oxygenated compounds. The co-pyrolysis of Tire/PET produced more volatile chemicals, which include light hydrocarbons, carbon dioxide, and carbon monoxide.

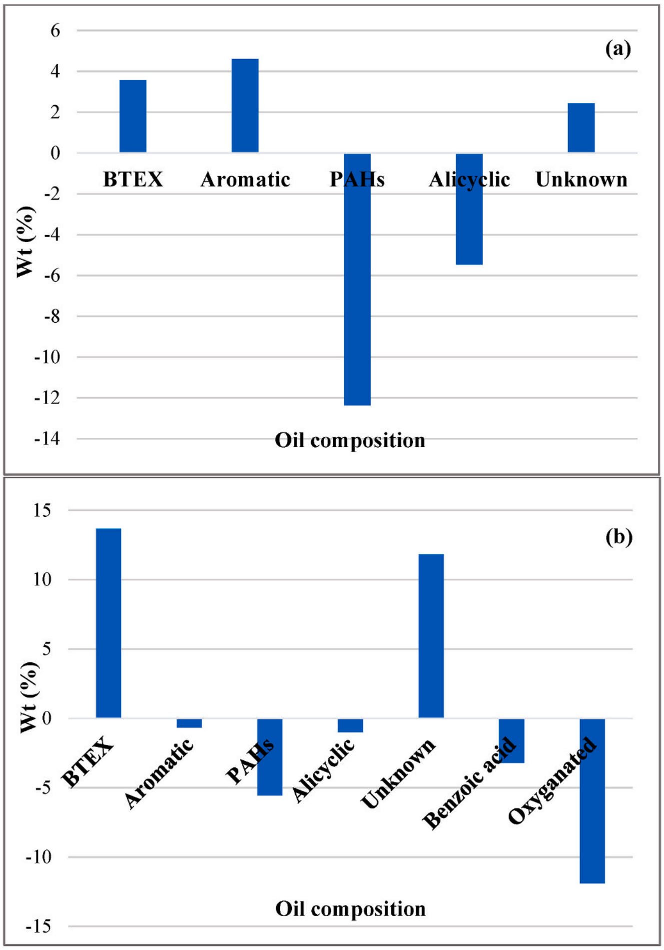

Fig. 9. Interaction effect of mixing (a) tire/polystyrene and (b) tire/polyethylene terephthalate on pyrolysis oil composition.

A further factor that can influence interaction between the tire and plastics during co-pyrolysis is the different formulations of natural and synthetic rubbers used to manufacture the tire. Also, different tire manufacturers may use different fillers and additives in the manufacturing process which will influence the thermal degradation of the tire. For example, it has been reported that the thermal decomposition of natural rubber using TGA at a heating rate of 20 °C min^{-1}, occurs over the temperature range, 330–420 °C, whereas styrene-butadiene rubber decomposes over a temperature range between 370 and 515 °C [19]. On the other hand, the TGA decomposition of polybutadiene rubber occurs in two steps between 370 – 405 °C and 425–525 °C. The release of pyrolysis volatiles at these different temperature ranges will influence their availability for interaction with the evolved volatiles from plastics pyrolysis which occur at different temperature (Fig. 2). Also, Kyari et al. [47], have investigated the pyrolysis of several different brands of tire and showed that distinct differences in gas composition, for carbon dioxide, carbon monoxide, hydrogen, methane, and other hydrocarbon gases. Similarly, the product oil from the different tire brands showed significant differences in composition for several hydrocarbons, for example, limonene, ethylbenzene and ethyltoluene and for PAH, such as, naphthalene, phenanthrene, and pyrene.

Overall, the results have shown that co-pyrolysis of tires and waste plastics can generate high yields of pyrolysis oil at ~70 wt% for Tire/HDPE, Tire/LDPE, Tire/PP and Tire/PS, but only 56 wt% for the Tire/PET mixture. A key advantage of the co-pyrolysis of tire with HDPE and LDPE, was that the product oil was a liquid oil rather than a waxy product produced by pyrolysis of the HDPE and LDPE alone. Collection and processing of waste plastics and waste tires through co-pyrolysis has been demonstrated as a viable process to produce a liquid oil suitable as a medium grade liquid fuel. Both waste plastics and tires are generated in high tonnages each year and require waste management. Co-pyrolysis as a process for the management of waste plastics and tires has advantages in that in addition to the high yield of oil, gas yields are improved which enable the gas to be considered as a fuel for the heating of the pyrolysis process. In addition, the oil composition can be changed by design, through the selective mixing of different plastics with the tire to manipulate the end product oil composition in terms of the concentrations of aromatic and aliphatic components.

This work has presented results on the yield and composition of the product oils and gases produced from mixing waste tire rubber with waste plastics. In particular, the interaction of tire with the individual plastics, high density and low density polyethylene, polypropylene, polystyrene and polyethylene terephthalate has been investigated and detailed oil and gas yields and compositions presented. However, in practice in an industrial context, the plastics would not be separated and then processed individually with the tires as that would not be commercially viable. Realistically, the process would involve mixed waste plastics and tires co-pyrolyzed together. The main aim of this work was to show how the individual plastics interact with the tire to alter the product oil and yield and composition. Thereby, the influence of the different plastics in the mixed plastic feedstock on the final oil and gas product yield and composition can be predicted.

4. Conclusions

In this research, pyrolysis of waste plastic, waste tire, and 1:1 mixtures of the tire and plastics has been conducted using a fixed-bed reactor. Pyrolysis of the HDPE and LDPE plastics produced a wax/oil product in high yield, at 85.50 wt% for HDPE and 90.17 wt% for LDPE. However, a liquid oil was produced for pyrolysis of PP (89 wt%), and PS

(99.20 wt%). PET produced only 53.0 wt% and a high gas yield consisting of mainly CO and CO_2, derived from the oxygenated content of the PET. Pyrolysis of tire produced an oil yield of 54.83 wt% and a high char content of 37.33 wt%. The results showed the liquid oil produced from the pyrolysis of tires and PS was mostly composed of aromatic compounds, such as the BTEX, and PAH. The liquid oil formed from the pyrolysis of HDPE and LDPE, on the other hand, was mostly waxes of high molecular weight consisting of aliphatic compound ranging from C_8 - C_{28}, composed of a series of alkanes, alkenes, and alkadienes. Whereas PP produced more alicyclic compounds, such as methylcyclohexane. PET pyrolysis oil consisted of compounds, such as xylene, styrene, but was mainly composed of oxygenated compounds, for example, benzoic acid.

Co-pyrolysis of 1:1 mixtures of the tires and individual plastics involved interaction, resulting in significantly higher yields of gas than expected for all the plastic mixtures. The co-pyrolysis of tire with HDPE and LDPE produced a liquid oil product rather than the waxy product produced for pyrolysis of the plastics alone. Gas composition was also influenced by interaction between the tire and plastic, with much higher yields of methane, C_2 – C_4 (C_nH_m) hydrocarbons, carbon monoxide and carbon dioxide, for HDPE, LDPE, PP and PS plastics, but, Tire/PET co-pyrolysis gave higher than expected carbon dioxide, but lower C_2 – C_4 hydrocarbons (C_nH_m) and carbon monoxide yields were found. The oil produced from the co-pyrolysis of the tire with the polyalkene plastics, Tire/HDPE and Tire/LDPE, showed interaction between the polymer pyrolysis products resulting in higher yields of aliphatic compounds and lower yields for the BTEX, PAHs, alicyclic, and aromatic compounds. It was suggested that the increased production of hydrogen radicals from co-pyrolysis promoted alkane and alkene production coupled with de-aromatisation reactions. However, the co-pyrolysis of the tire with the PP polyalkene Tire/PP showed negative interaction for aliphatic compounds resulting in lower yield, but higher yields for aromatic compounds, BTEX and PAHs. The mechanism for Tire/PP interaction was linked to the decomposition of natural rubber in the tire which promotes plastic polymer degradation and secondary reactions to form single ring aromatic hydrocarbons. Co-pyrolysis of Tire/PS produced positive interaction for aromatic compounds, since both tire and PS produce aromatic oils, however, the Tire/PS interaction induced reduction in the yield of PAH. Co-pyrolysis of Tire/PET showed positive interaction for BTEX and reduction in the content of oxygenated compounds, which released the oxygen from the PET in the form of increased yields of carbon dioxide.

CRediT authorship contribution statement

Noof Alzahrani: Writing – original draft, Investigation. **Mohamad A. Nahil:** Methodology. **Paul T. Williams:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of interests

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Paul Williams is Editor in Chief of Journal of the Energy Institute. The editorial process for this paper was handled by Prof Haiping Yang, who is Associate Editor of the journal.

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