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Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time

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ABSTRACT

The compositions of the pyrolysis products of pure low-density polyethylene (LDPE) and polystyrene (PS) and their mixtures have been investigated over a temperature range from 300 to 500 °C. The pyrolysis experiments were carried out in a closed batch reactor under inert nitrogen atmosphere to study the effects of reaction temperature and residence time. LDPE was thermally degraded to oil at 425 °C however, beyond this temperature the proportion of oil product decreased as a result of its conversion to char and hydrocarbon gas. Compositional analysis of the oil products showed that aliphatic hydrocarbons were the major components, but the proportion of aromatic compounds increased at higher temperatures and residence times. On the other hand, PS degraded at around 350 °C, mainly into a viscous dark-coloured oil. The formation of char only increased marginally until 425 °C, but was dramatically enhanced at 450 and 500 °C, reaching up to 30 wt.%. The oil product from PS even at 350 °C consisted almost entirely of aromatic compounds especially toluene, ethylbenzene and styrene. Under increasing temperatures and residence times, the oil product from PS was preferentially converted to char, while gas formation was preferred for the oil from LDPE. For instance at 500 °C, PS produced about twice the amount of char obtained from LDPE indicating the role of aromatic compounds in char formation via condensation of the aromatic ring structure. During the co-pyrolysis of a 7:3 mixture of LDPE and PS, wax product was observed at 350 °C leading to oil at 400 °C, indicating that the presence of PS influenced the conversion of LDPE by lowering its degradation temperature. The mixture produced more oil and less char than the individual plastics at 450 °C.

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1. Introduction

Plastic polymers make up a high proportion of waste and this is expected to continue in the future with the dramatic increase in the volume and range of plastic products in use. The two main types of plastic are: thermoplastics which soften when heated and harden again when cooled and thermosets which harden by curing and cannot be re-moulded. Thermoplastics are by far the most common types of plastic comprising almost 80% of the plastics used in Western Europe. There are six main component plastics in European municipal solid waste which are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). However, the polyethylene plastics, LDPE and HDPE make up over 40% of the total plastic content of municipal solid waste. The consumption of plastics in Western Europe is of the order of 38 million tonnes per year [1] and it is estimated that only about 50% of the plastics produced are available for collection

and recycling, the remainder accumulating in the environment as long term uses of plastics such as building works, including, plastic window frames, pipes, and electrical wiring. Of this collectable waste plastic, about 15%, representing about 3 million tonnes, is recycled in Western Europe. Outlets for recycled plastics include for example, plastic sacks, pipes and garden furniture, sewer pipes, plastic fencing, industrial plastic pallets, traffic cones, playground equipment and garden furniture [1].

The low grade uses for mixed plastic recycled materials has led to research into alternative processing methods to produce higher value products. One example is via feedstock recycling where the plastic waste materials are processed back to produce basic petrochemicals that can be used as feedstock to make virgin plastic [2]. Feedstock recycling can be via hydrogenation at high temperature and pressure or via pyrolysis in an inert atmosphere at atmospheric pressure to thermally degrade the plastics. Pyrolysis of waste plastics is a recycling option that shows great potential and has been investigated by a number of researchers [3–10]. Pyrolysis is the thermal degradation of the plastic in an inert atmosphere and produces gas, oil and solid char products. The yield and composition of the products is influenced by a range of process parameters, including, the type of waste plastic and reactor

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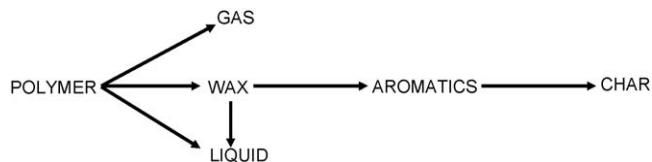
system, but also other factors, such as the gas residence time, temperature and pressure ranges, presence of catalysts, and presence of hydrogen gas or hydrogen donor compounds [6,11–19]. In the work of Marcilla et al. [20], temperature was a major factor in the composition of products during HDPE pyrolysis. They found that in a fluidized bed reactor, polyethylene degraded to mainly n-paraffins and then 1-olefins at 500 °C but at 800 °C, 1-olefins dominated the products followed by n-paraffins. Westerhout et al. [21] reported that at higher pyrolysis temperatures the influence of residence time, product concentration, polymer type, and composition of polymer mixture on product distribution were negligible compared to the influence of temperature.

There have been a number of studies which have been carried out in pressurised closed autoclave-type reactors which have reported very high conversions of the waste plastic to an oil product. For example, Shah et al. [11] investigated liquefaction of post-consumer plastic, at a temperature of 445 °C under an initial hydrogen pressure of 200–800 psig for 60 min. They reportedly obtained more than 80 wt.% yield of hydrocarbon oil product. Pinto et al. [13] undertook pyrolysis experiments with polyethylene, polypropylene and polystyrene in an autoclave reactor at an initial nitrogen pressure of 0.41 MPa and temperature of 430 °C, leading to a mean experimental pressure of 3.5 MPa. They reported conversion of over 90 wt.% of the plastics to oil.

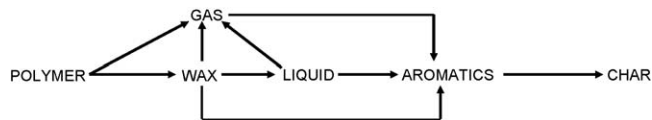
In this study, low-density polyethylene and polystyrene, representing common plastics usually present in high proportion in the plastic waste stream of municipal solid waste, were pyrolysed in a batch, pressurised autoclave reactor. The main objective of this study was to convert the waste plastics to oil products for use as a hydrocarbon fuel oil or raw chemical feedstock. The effects of temperature and residence time have been studied to ascertain the optimum conditions necessary for the production of oil as well as to investigate the effects of these parameters on the compositions of reaction products, with a special emphasis on the oil. Residence time here refers to the length of time (in minutes) for which an experiment was held at a particular (constant) temperature. The choice of this term is intended to avoid the confusion of using the term, reaction time, which would inadvertently include both the reactor heat-up time and actual reaction time or residence time.

Since this batch reactor process was designed for the exploitation of secondary and even tertiary reactions, an attempt was made to explain the formation of products by some kinetic mechanisms for polymer pyrolysis found in the literature. According to the kinetic steps for a fluidized bed reactor developed by Westerhout et al. [21], the product distribution mechanism involved Scheme 1 below.

One important step in Scheme 1 is the possibility of the conversion of low alkanes and alkenes in the gas-phase into aromatics. Recently, Elordi et al. [10] proposed several models involving parallel reactions for the formation of the different lumps



Scheme 2. Kinetic scheme involving secondary reactions by Elordi et al. [10].



Scheme 3. Proposed kinetic scheme for this work.

(products). They went further to choose Scheme 2 which provided the best fit for the experimental data corresponding to all the lumps from polymer pyrolysis at very short residence times in a conical sprouted bed reactor.

The major difference between the two schemes is that, Scheme 1 shows that gas-phase reactions leading to condensation of hydrocarbons, especially olefins, is a possible pathway to aromatic formation, while Scheme 2 does not show that trend. Preliminary experiments in this work showed that the formation of products in a batch reactor could be explained by the modification of the two kinetic mechanisms as shown in Scheme 3.

While these schemes attempt to help in understanding the mechanisms for plastic pyrolysis, it must be noted that the processes occurring in a reactor are much more complex. However, it appears that certain steps in these schemes become predominant as the reaction conditions change.

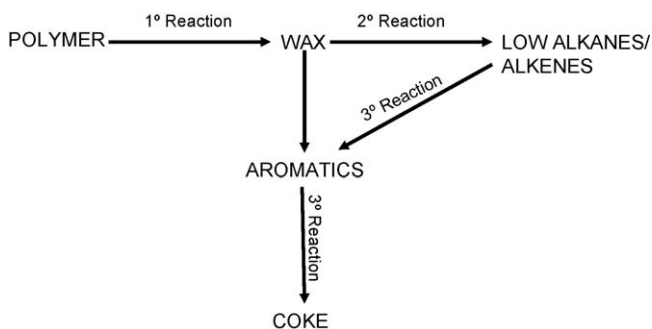
2. Experimental

2.1. Materials

Virgin low-density polyethylene plastic pellets, polystyrene plastic pellets and chemical reagents such as standards and solvents were obtained from Sigma–Aldrich Ltd. The properties of the LDPE plastic samples showed that it had an average molecular weight of 15,000 Da and mean molecular number of 5500 Da determined using gel permeation chromatography (GPC). The particle size was 2 mm, with a density of 0.39 kg L^{−1} at 25 °C. On the other hand, the polystyrene samples had a typical molecular weight of 280,000 Da (GPC) a density of 1.047 kg L^{−1} and a glass transition (T_g) temperature of 100 °C. Both plastics were obtained pure and used as received. Dichloromethane was used as solvent for oil sample preparation prior to analysis.

2.2. Reactor system

The reactor utilized in this work was a batch pressurised autoclave reactor, a schematic diagram of which is shown in Fig. 1. The reactor was a 300 mL Parr Mini Bench Top Reactor, Type 4561m stirred pressure reactor made of T 316 stainless steel and was obtained from the Parr Instrument Co., Moline, IL, US. The reaction vessel was stirred using a Parr Instrument Co. magnetic drive. A stirrer shaft with rotor blades at the base was attached to an inner magnetic drive rotor powered through an outer magnetic drive rotor. The reactor was heated using an external mantle type furnace, which contacted the sides and bottom of the reaction vessel. The internal temperature of the heater and the reactor were monitored by J type thermocouples. A heating rate of 10 °C min^{−1} was utilized in this work. The reactor vessel was fitted with a gas



Scheme 1. The kinetic scheme proposed by Westerhout et al. [21].

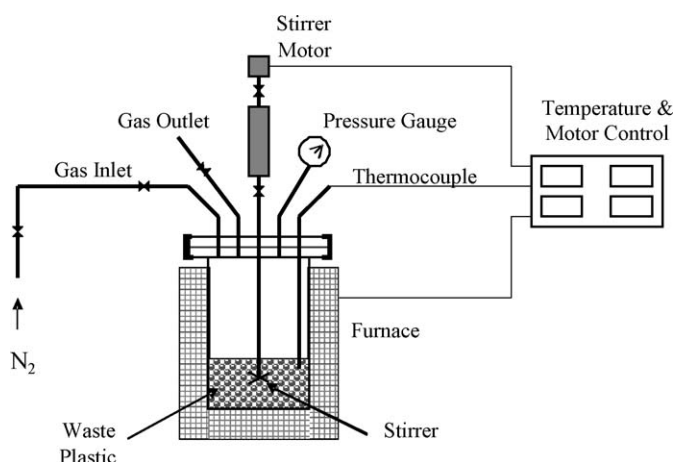


Fig. 1. Schematic diagram of the closed batch reactor.

inlet valve, a gas outlet valve which served for gas sampling, and a third outlet valve for liquid sampling when pressurised. The reactor was equipped with a pressure gauge to measure its internal pressure during experiments. Nitrogen gas was used as reaction atmosphere for all experiments to ensure inert pyrolysis condition. Each experiment was carried out with an initial nitrogen pressure of 0.3 MPa. Since experimental work was carried out in a closed system, the evolution of hot gas reaction products increased the internal pressure of the reactor during experimental runs. Consequently the pyrolysis experiments were subjected to self-generated pressure whose extent depended on reaction temperature and the amount of gas produced. About 10 g of sample was used in each experiment. Residence time was set to zero minutes as soon as the set pyrolysis temperature was reached, and the experiment stopped or held at that temperature for the specific residence times of the experiment. At the end of the reaction, the operating pressure was recorded, the heater switched off and reactor rapidly cooled by air until the temperature inside the vessel reached room temperature. At this point the internal pressure and temperature of the reactor were noted.

For LDPE, a set of experiments was carried out for 1 h each between 350 and 500 °C with experimental pressures of between 0.8 and 4.3 MPa, respectively, to investigate the effect of temperature on the pyrolysis of polyethylene. Longer heat-up times were required to reach higher reaction temperatures by which time pyrolysis of plastics would have begun. However, by using the same heating rate of 10 °C min⁻¹ and residence time of 60 min at each temperature, the challenge of heat-up time was somewhat minimized, so that reaction temperature could be assumed as the predominant parameter. For example, the highest difference in heat-up periods was approximately 15 min (i.e. between 350 and 500 °C), and this was about 1/4th of the residence time used. Another set of experiments was conducted at 450 °C from zero to 120-min residence time to study the effect of reaction time on the pyrolysis products. For PS, the effect of temperature was investigated between 300 and 500 °C giving experimental pressures of 0.31 MPa up to 1.6 MPa. Due to the observed degradation of PS at 350 °C, the effect of residence time was studied at 400 °C from zero to 120 min with corresponding experimental pressures from 0.76 to 1.34 MPa, respectively. Furthermore, a 7:3 mixture of LDPE and PS was used to study the effect of reaction temperature on the co-pyrolysis of the plastics from 350 to 450 °C for 1 h each. After the reactor had cooled, three samples of gas product were carefully taken for gas chromatography analysis. The remaining gas was then discharged, the reactor opened and the vessel weighed to determine the weight of liquid and char products. The char was then separated

from the oil by filtration and weighed. Finally, oil from the reactor vessel was transferred into amber glass bottles and placed in a refrigerator until further analysis. The mass balances were closed using the weight of gas obtained from the Ideal Gas Law at room temperature and the combined weights of oil and char in the reactor, after discharging the gas product. Once the weight of char was determined after filtration, the difference was ascribed to be the weight of oil produced. Each experiment was carried out several times to check for reproducibility.

2.3. Gas analysis

The gaseous product collected at the end of each experiment was analyzed by packed column gas chromatography using two separate gas chromatographs. Hydrocarbons from C₁ to C₄ were determined using a Varian 3380 gas chromatograph with a flame ionisation detector (GC/FID). Nitrogen was used as the carrier gas with a 2 m × 2 mm column packed with 80–100 mesh Hysep packing material. The oven temperature was set at 60 °C for 3 min, then programmed to 100 °C at a heating rate of 5 °C min⁻¹, and held for 3 min, finally heated to 120 °C at 20 °C min⁻¹ and held for 17 min at 120 °C. Permanent gases were analyzed by a second Varian 3380 GC fitted with two thermal conductivity detectors (TCD) and two packed columns. One of the columns was a stainless steel molecular sieve packed column with dimensions 2 m × 1/8 in. × 2 mm, capable of separating permanent gases mixture except carbon dioxide. The other was an 80–100 mesh Haysep 2 m × 1/8 in. × 2 mm stainless steel column for carbon dioxide analysis. Argon was used as the carrier gas. The gas chromatograph oven was held isothermally at 40 °C for the analysis. The detector oven was operated at 120 °C with filament temperature at 160 °C. It is important to note here that nitrogen (purge gas) and hydrogen were the only permanent gases detected in the gas products. The mass of gas produced was determined using the Ideal Gas Law from the concentrations of individual gases obtained from gas chromatography and the value of gas pressure in the reactor at ambient (room) temperature.

2.4. Oil analysis

The oil products derived from the degradation of the plastics were analyzed to determine the main components present in the oil. Each oil product was dissolved in dichloromethane (DCM) and analyzed mainly by capillary column gas chromatography with flame ionisation detection (GC/FID). The GC/FID equipment used was a Carlo Erba HRGC 5300 Mega Series GC equipped with an HP-5 (5% phenyl methyl silicone) capillary column: 30 m in length, 0.53 mm diameter and 5 µm film thickness. The carrier gas was helium. The GC oven temperature programme used for the separation of oil components was as follows; the oven was held at 40 °C for 5 min, then ramped at 5 °C/min to 100 °C, and then ramped at 4 °C/min to 280 °C where it was held for a further 30 min. The FID was held at 300 °C. For oil samples from PS, the hold-time at 280 °C was reduced to just 10 min. Quantification of compounds on the GC/FID was by external standard method and relative retention times once the component has been reliably identified on a gas chromatography/mass spectrometry (GC/MS) instrument. The GC/MS used was a ThermoQuest CE Instrument GC 2000 series fitted with a Restek RTX-5MS column, coupled to a Fisons MD800 single-quad mass detector. The GC oven temperature programme was the same as for the GC/FID listed above. The MS source was held at 200 °C with an emission current of 150 µA. The detector was operated at full scan from 50 to 500 amu. The ion-mass spectra derived were automatically compared to the NIST 98 spectral library and similarity indexes of >70% were used to identify compounds.

3. Results and discussion

3.1. Plastics pyrolysis in relation to temperature

The influence of reaction temperature on the distribution of reaction products, namely: wax/oil, char and gas during the pyrolysis of low-density polyethylene, polystyrene and their mixtures for a residence time 1 h were studied between a temperature range of 300 and 500 °C under nitrogen atmosphere. The results are presented below.

3.1.1. Effect of temperature on LDPE degradation

At a temperature of 350 °C, the polyethylene pellets only melted into a white, hard, plastic substance with just about 0.7 wt.% of gas formed. As temperature increased to 400 °C, polyethylene decomposed to give 94.7 wt.% viscous, whitish brown waxy material. However, the conversion to oil started at temperatures above 410 °C where the major product was an oily wax. Total conversion of LDPE was accomplished at 425 °C and above. Thermal decomposition produced a high yield of liquid oil with a yield of 89.5 wt.% and 10.0 wt.% gas at a temperature of 425 °C. The oil was a low viscosity dark-brown product with minor waxy components. At higher pyrolysis temperatures, the oil yield decreased due to more cracking and secondary reactions leading to increasing gas yields and the emergence of a char product. Oil yield decreased to 72.4 wt.% at a pyrolysis temperature of 450 °C, while gas and char reached 25 wt.% and 1.75 wt.%, respectively. At 500 °C there was significant formation of char with 15.5 wt.% production, while the oil was cracked to large quantities of gas of 47.0 wt.% with a corresponding decline in oil yield. The significant increase in gas and char production is a result of secondary reactions of the oil vapours [21]. The trend in the product yield was in agreement with the report of Tiikma et al. [22], who examined the effect of temperature on the thermal processing of low-density polyethylene waste and also in the presence of heavy shale oil in an autoclave reactor. They found that the conversion of polyethylene started at 400 °C and the optimum oil yield was at 450 °C. They also reported significant formation of char at 450 °C, which increased with pyrolysis temperature. The detailed compositions of the gaseous and liquid products of LDPE pyrolysis are discussed below.

3.1.1.1. Composition of gas products from LDPE pyrolysis in relation to temperature. During the degradation of LDPE in relation to reaction temperature, the gaseous product was dominated by alkanes followed by alkenes and traces of hydrogen gas. Even though the total hydrogen yield was almost insignificant, it was noticed to increase linearly with increasing the temperature. It rose from <0.01 wt.% at 350 °C to 0.13 wt.% at 500 °C. All the C₁–C₄ hydrocarbon gases increased with reaction temperatures from 350 to 425 °C at which LDPE was converted to oil. Increasing pyrolysis temperature enhanced the yield of alkane hydrocarbon gases, rising from 53.7% at 425 °C to 94.4% of the total gaseous product at 500 °C. On the other hand alkene gases yield dropped and it appeared to do so when conversion to char began. It reduced from 45.8% at 425 °C to 5.26% at 500 °C which corresponded to increased char formation. The increase in hydrogen and alkane contents and subsequent decreases in alkene concentration in the gas products agrees with the work of Westerhout et al. [21,23]. The reduction in alkene concentration was evidence of stripping reactions which could have taken place in the temperature range of 450–500 °C, according to the kinetic mechanism in Scheme 1 [21] and Scheme 3. Hence at higher temperatures, the formation of aromatics and char are the predominant processes occurring.

The detailed composition of the hydrocarbon gas components in relation to pyrolysis temperatures as exhibited in Fig. 2 shows that at 500 °C methane and ethane yields increased 3.2 and 2.1

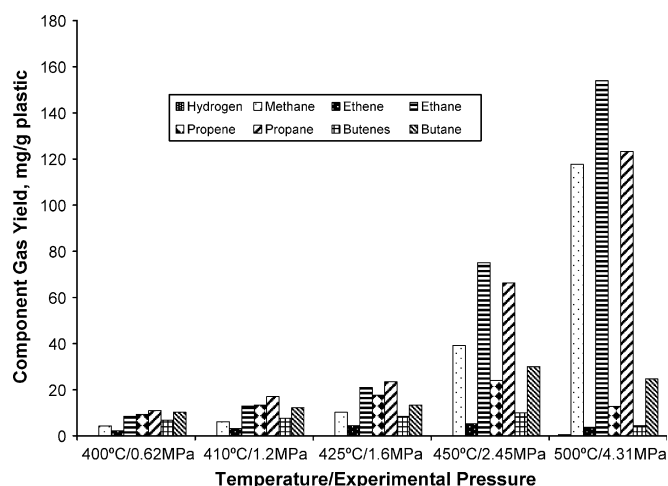


Fig. 2. Composition of LDPE pyrolysis gaseous products in relation to temperature.

times, respectively, compared to their yields at 400 °C. Propane yield was enhanced only by 30% of its yield at low temperature, indicating that it was not highly affected by temperature increase like methane and ethane. Butane yield on the other hand kept decreasing with temperature increase and at 500 °C, and was 25% less than its yield at 400 °C. The compositional contents of the gas products obtained from this work were different from those reported by Marcilla et al. [24], who reported that paraffins dominated the gas products are lower temperatures while 1-olefins were the dominant gas components at higher temperatures in a batch reactor. Throughout the temperature range investigated in this work, alkane gases increased with temperature, while alkenes decreased and this could be due to the residence time (1 h) applied in this work.

Gaseous product obtained from pyrolysis runs at these different temperatures mostly comprised of C₁–C₄ hydrocarbon compounds that have high caloric value. Consequently, the gaseous products could be utilized to supply the energy involved in the pyrolysis process. The calculated calorific value for gas product at these different temperature investigated was between 50.8 and 52.7 MJ/kg which is comparable to that of pure methane gas with a caloric value of 55.7 MJ/kg [25].

3.1.1.2. Composition of liquid products from LDPE pyrolysis in relation to temperature. This discussion is centred on temperatures from 400 °C and above where liquid reaction products were obtained. Upon pyrolysis of LDPE at temperature of 400 °C, the main product was wax which comprised mainly of high carbon number chains possibly due to insufficient energy to completely break down the long aliphatic chains to lighter fragments. Qualitative analysis of the fraction of the wax that was soluble in dichloromethane (DCM) comprised mainly aliphatic compounds that were dominated by high carbon number alkanes followed by alkenes. n-Alkanes, the main components in the DCM soluble wax fragment, were distributed from C₅ to C₄₀. Compounds from C₁₉ to C₂₃ showed the highest concentrations. The presence of long aliphatic chains in wax product from pyrolysis of LDPE at 400 °C was confirmed by some studies. Williams and Williams [26] reported presence of long-chain aliphatics up to C₅₇. Lattimer [27] studied pyrolysis field ionisation mass spectrometry of polyolefins at 400 °C and detected long-chain molecules with up to 114 carbon atoms.

This wide distribution of aliphatic chains in the liquid products showed that the thermal decomposition of LDPE follow the random scission mechanism during the primary cracking process [21]. Alkenes consisted of compounds from C₇ to C₁₈ with

compounds from heptene to dodecene having the largest yields. This range of alkenes called also alpha-olefin compounds are highly required in petrochemical industry where they are used as chemical feedstock for plastic and detergent manufacture. No significant levels of aromatic compounds were found at 400 °C. This wax product could be utilized as paraffin wax or further processed to extract some of beneficial components for industry, and also could be upgraded to produce lighter fuel fractions or gasified to hydrogen to make it more commercially beneficial.

Quantitative analyses of the liquid products were attempted from 425 °C and beyond. Table 1 lists the variety of compounds in the oils in relation to reaction temperature from 425 to 500 °C, where free-flowing oils were obtained. These components were grouped into different organic compound classes i.e. naphthenes (cycloalkanes), n-alkanes, n-alkenes, aromatics and unknowns (unidentified peaks), as shown at the end of the table. It is worthy of note that some of the oils gave over one hundred peaks, however only the identified compounds having more than 0.5 wt.% of the oil have been listed. At 425 °C, the oil product was dominated by uneven lengths of aliphatic chains showing that LDPE thermally cracked randomly into fragments with unequal carbon atom number. At temperature of 425 °C, the LDPE was totally converted to liquid product, dominated by aliphatic hydrocarbons (paraffins was 44 wt.%, and olefins, 11.6 wt.%) and to significant aromatics with yield of around 9.5 wt.%. This depicted the total cracking to small components and furthermore to some aromatics [21], due to some cyclization and aromatization reactions at this temperature. In detergent industries the aliphatic fractions from C₁₂ to C₁₈ as well as alpha-olefins are highly desired feedstocks for the manufacture of raw materials such as alkyl benzene sulphonic acid (ABSA) and sodium lauryl ether sulphate (SLES). This range of compounds was up to 19 wt.% in this oil product, in addition to presence of 12 wt.% of alpha-olefins.

At 450 °C, oil product was still dominated by 31.5 wt.% n-alkanes comprising of much lighter components. This is similar to the result of study by Achilias et al. [3] who investigated LDPE pyrolysis at temperature of 450 °C. However, Marcilla et al. [24], reported the presence of increasing longer chain 1-olefins and n-paraffins up to C₃₉ and C₃₅, respectively, at a between the temperature range 442–468 °C. The oil product was chiefly composed of paraffins and olefins, and it was distributed from C₅ to C₃₀ compounds and dominated by compounds from heptane to pentadecane. Octane and heptane were the main compounds, 3.16 wt.% and 3.78 wt.%, respectively. Alkenes yield was 13.1 wt.% of oil weight, represented by C₅–C₁₅ alkenes in which C₇–C₁₂ compounds were the main olefins. Besides, aromatic compounds were clearly enhanced to nearly 23 wt.%, consisting of a wide range of compounds but dominated by toluene and m/p-xylene. Other aromatic compounds identified included benzene, ethylbenzene, ethyltoluene, naphthalene and alkyl naphthalenes as well as traces of some polycyclic aromatic compounds.

At 500 °C, the quantity and variety of aromatic compounds were highly enhanced to be the main components in oil product, taking up a princely 65–70 wt.% of the oil. Toluene was the main compound in oil product, followed by xylene, benzene, ethylbenzene, propyl benzene, allyl benzene and butyl benzene, naphthalene and alkyl naphthalenes. At temperature of 450 °C, toluene and p/m-xylene were only at concentrations of 3.1 wt.% and 1.79 wt.% of oil product while they increased to 24.3 wt.% and 3.9 wt.% of oil produced at 500 °C, respectively. In addition, paraffins' distribution in this oil was in the light range, they included compounds from C₅ to C₁₉ but their yield was drastically reduced to 17.8 wt.%. Olefins were also highly reduced to only 3.58 wt.% and dominated by C₅ and C₆ since long-chain alkenes are very reactive at high temperatures. This clearly showed that the reduction in olefins and paraffins yield was in favour of aromatic production indicating

Table 1

Main components of the oil products from the pyrolysis of LDPE in relation to temperature (% w/w oil).

	Operating temperature/pressure		
	425 °C; 1.60 MPa	450 °C; 2.45 MPa	500 °C; 4.31 MPa
Compounds			
Pentane	0.53	0.11	0.09
Hexene	1.02	0.26	0.08
Hexane	1.29	0.57	0.72
Cyclohexane	0.43	0.73	0.62
Benzene	0.21	0.64	4.54
Heptene	1.31	1.65	0.53
Heptane	2.26	3.16	0.46
Methylcyclohexane	0.61	1.36	0.83
Toluene	0.35	3.05	24.3
Octene	1.35	1.83	0.01
Octane	2.45	3.78	0.19
Cycloheptane	0.20	0.41	0.04
Dimethylcyclohexane	0.50	0.76	0.01
Ethylbenzene	0.25	0.89	3.06
p/m-Xylene	0.62	1.79	3.90
Styrene	0.82	0.54	0.07
o-Xylene	nd	0.61	3.24
Nonene	1.28	1.81	0.10
Nonane	2.32	2.89	0.82
Allylbenzene	0.21	1.02	4.84
Propylbenzene	0.20	0.86	1.12
Decene	1.39	1.16	0.06
Decane	2.20	2.67	0.06
Trimethylbenzene	0.20	0.75	3.23
Indane	0.10	0.72	0.36
Indene	0.17	0.13	0.68
1,3-Diethylbenzene	0.23	0.82	1.95
Undecene	1.48	1.04	0.05
Undecane	2.62	2.50	0.29
Dodecene	1.21	1.13	0.30
Dodecane	2.56	2.02	0.05
Naphthalene	0.50	0.57	2.97
Tridecene	0.99	1.33	0.19
Tridecane	2.61	1.74	0.05
Methylnaphthalene	0.90	0.36	4.22
Tetradecene	0.92	0.86	0.98
Tetradecane	2.51	1.56	0.67
Ethylmethylbenzene	0.22	0.55	1.90
Diphenylmethane	0.54	0.89	2.98
Pentadecene	0.69	0.50	0.10
Pentadecane	2.51	1.35	0.51
Hexadecene	0.53	0.46	0.10
Hexadecane	2.29	1.18	0.65
Heptadecane	2.59	0.83	0.26
Octadecane	2.48	0.79	0.32
Nonadecane	2.33	0.67	0.49
Eicosane	2.01	0.48	0.10
C ₂₁ –C ₃₀ alkanes	9.98	1.85	1.20
Compound classes			
Naphthenes	2.69	5.56	1.50
Alkanes	46.2	31.7	17.8
Alkenes	12.4	13.1	3.58
Aromatic	12.0	22.9	68.0
Unknowns	19.1	17.9	nd

that cyclization and aromatization took place around 500 °C. The evolution of compounds in the liquid products was in line with the mechanistic trends proposed by Westerhout et al. [21] and Elordi et al. [10], so that the predominant processes at higher temperatures would involve the conversion of liquid products directly to aromatics and some gases, and the stripping of gases to form aromatics and finally char.

3.1.2. Effect of temperature on polystyrene pyrolysis

The study of the degradation of polystyrene (PS) in the batch reactor was carried out from 300 °C, but no visible reaction was observed at this temperature. However at 350 °C, the entire PS

sample was completely degraded into highly viscous dark-coloured oil. Char formation was observed at 350 °C, representing about 1 wt.% of the plastic, while a little amount of hydrocarbon gas was also formed. As the temperature increased to 400 °C and even up to 425 °C, there were slight increases in the proportion of char and gas formed, but the oil became less viscous. The amount of char produced increased significantly as the reaction temperature was increased to 450 °C and then to 500 °C. At 450 °C, the amount of char was 19.6 wt.% of the plastic feed, and this increased further to 30.4 wt.% at 500 °C. The gaseous product did not show any dramatic increase with temperature, and the maximum amount produced was 2.50 wt.% at 500 °C. The increased formation of char led to a decrease in the amount of liquid product. For instance at 425 °C, the oil product was about 97 wt.% of the plastic feed, but this reduced to just under 80 wt.% at 450 °C, and dipped further at 500 °C by more than 12 wt.% to about 67 wt.%. There was therefore a strong relationship between the amounts of char and oil products formed from PS in relation to reaction temperature. This result may be explained by the presence of mainly aromatic compounds in the liquid degradation product of PS. There was therefore a link between aromatic content of the oil and the formation of char via the condensation of the aromatic ring structure [10,28]. Carniti et al. [29] undertook pyrolysis of polystyrene in a closed vessel at up to 420 °C and reported that the product yield and composition was directly related to the conditions of the closed system which prevented the volatile products and intermediates from leaving the reaction vessel. As there was no significant gas formation, it suffices to note that methane was the main hydrocarbon gas produced, reaching up to 62% of the total gas at 500 °C. Unlike polyethylene, the gaseous products from PS were too low to serve as a source of fuel gas for the pyrolysis process.

3.1.2.1. Composition of oil products from PS pyrolysis in relation to temperature. The oil products obtained from the thermal degradation of polystyrene in relation to reaction temperature were dissolved in dichloromethane and analyzed for their chemical compositions. Table 2 shows the list of the major compounds identified in the oils obtained in relation to temperature. The oils consisted, albeit entirely of aromatic compound or the concentrations of any aliphatic compounds were too low to be detected in the presence of their predominant aromatic counterparts. The major compounds included benzene, toluene, ethylbenzene, styrene, cumene, alpha-methyl styrene, diphenylpropane and triphenylbenzene. It appeared that generally, the lighter aromatics namely benzene, toluene and ethylbenzene dominated the oil products within the entire temperature range. However, their concentrations increased significantly with increasing reaction temperatures. For instance at 350 °C, toluene and ethylbenzene,

which were the two components with the highest concentrations in the oil, were about 8.7 wt.% and 9.5 wt.%, respectively. These two compounds increased to 21.7 wt.% and 32.6 wt.% at 400 °C, and then increased less gradually to reach 28.4 wt.% and 36.6 wt.%, respectively, at 500 °C. Conversely, the large molecular weight compound such as triphenylbenzene showed a decreasing trend as reaction temperature was raised. Cumene showed a steady trend throughout the temperature range studied whereas, styrene monomer which gave nearly 8 wt.% in the oil at 350 °C, reduced to a mere 1.09 wt.% at 400 °C, from where it continued a downward trend with increasing temperature. The low values obtained for styrene even at 350 °C was due to the fact that the reaction was held for 1 h at each temperature. The decrease in styrene concentration and the increase in ethylbenzene levels in the oil may indicate that the latter was formed from the hydrogenation of the former. Styrene radical which could easily form from the degradation of PS is known to be very reactive and this may explain the low levels styrene molecule in the oils.

3.1.3. Effect of temperature on Co-pyrolysis of LDPE and PS

The effect of reaction temperature on the products from the co-pyrolysis of mixed plastics was investigated using a mixture of plastic pellets consisting of 70% polyethylene and 30% polystyrene, from 350 to 450 °C. Interestingly, even though, LDPE did not decompose at 350 °C when reacted alone, the major product from the mixed plastics was wax. When the temperature was increased to 400 °C, the major product was a dark-coloured oil. From these two observations, it could be inferred that PS had a catalytic effect on the degradation of LDPE. To check this, only 7 g (rather than 10 g) of LDPE was loaded into the reactor, the result was still melted LDPE. At 350 °C, the mixture produced more gas than each of the individual plastics alone. As the temperature increased to 400 °C, the gas product increased to 4 wt.% and no char formation was observed. The remainder was oil product. At 425 °C, the gas increased to 8.6 wt.%, and the slight presence of char was observed with 1.2 wt.%. The amount of gas obtained at 425 °C was higher than PS but lower than LDPE at this temperature. From the previous sections, it was shown that PS produced some char but not any significant amount of gas at this temperature. Conversely, LDPE produced more gas and no char at this temperature. Hence, it becomes obvious that the gas product from the mixture would be largely due to the LDPE, while the char would be attributed more to PS. At 450 °C, the gas and char products from the mixture increased to 12.8 wt.% and 3.5 wt.%, respectively. Fig. 3 shows the distribution of the components of the gaseous products, invariably dominated by the alkanes. Again, the LDPE seemed to controlled gas formation but also possibly prevented a large proportion of the plastics been converted to char. For example, only 1.75 wt.% of char was obtained from 10 g of LDPE at 450 °C, but with 10 g of the mixed plastic sample, char product was 19.2 wt.%. It would have been expected that 3 g of PS would have given about to 5.7 wt.% of char but in the presence of LDPE, only 3.5 wt.% char was found. In addition, oil product from the plastic mixture at 450 °C was significantly higher than each of the individual plastics. A synergy may thus exist, in which PS and LDPE reacted to produce more oil than LDPE and PS alone, less char than PS and less gas than LDPE, respectively.

3.1.3.1. Composition of oil product from PE and PS co-pyrolysis. In general, the oils obtained from the plastic mixture were a concoction of compounds found from the individual plastics. Table 3 shows the list of compounds in the oil products from the co-pyrolysis of LDPE and PS. They consisted on naphthenes (cycloalkanes), n-alkanes, n-alkenes and aromatic compounds. Obviously, the naphthenes, paraffins and olefins can be said to be direct products of LDPE degradation, while the majority of the

Table 2

Major compounds in the pyrolysis oil products from polystyrene in relation to temperature (%w/w oil).

Compounds	Operating temperature/pressure			
	400 °C; 1.14 MPa	425 °C; 1.26 MPa	450 °C; 1.47 MPa	500 °C; 1.60 MPa
Benzene	0.38	0.73	1.27	1.63
Toluene	21.7	23.1	27.0	28.4
Ethylbenzene	32.6	39.3	39.0	36.6
Styrene	1.09	0.80	0.39	0.61
Cumene	10.2	9.10	9.36	9.60
Propylbenzene	0.6	0.77	0.90	1.29
Methylstyrene	1.37	0.39	0.33	0.55
Diphenylmethane	0.91	0.83	1.00	1.61
1,2-Diphenylethane	1.44	1.16	0.60	0.37
Phenylanthracene	0.98	1.02	1.01	1.25
1,2-Diphenylbenzene	1.27	1.26	1.87	1.89
Triphenylbenzene	6.30	5.13	3.83	3.18

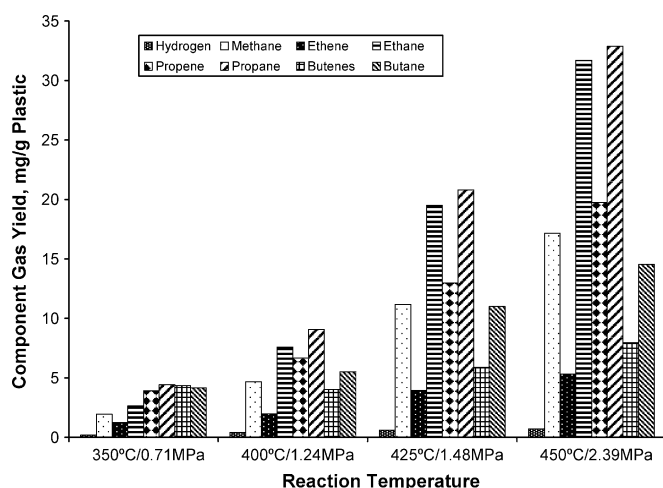


Fig. 3. Composition of gaseous products from the pyrolysis of LDPE and PS in relation to temperature.

aromatics would have come from PS especially at 400 and 425 °C. Roughly, the oil product at 400 °C consisted of about 32 wt.% n-alkanes, 8.4 wt.% olefins and 38 wt.% aromatics. The composition of the oil at 425 °C was not significantly different from the oil at 400 °C. However, at 450 °C, the proportion of n-alkanes fell to under 25 wt.%, while aromatics increased to 48 wt.%; olefins remained fairly stable. Hence, the increase in the proportion of aromatics has a direct link with the reduction in the proportion of n-alkanes. It has been shown in Section 3.1.2 that the oil products from PS degradation comprised essentially of aromatic compounds, hence increasing temperature did not alter the proportion of aromatics from PS degradation; rather it altered the components making up the aromatic products. At the same time, increasing temperature has been shown in Section 3.1.1 to decrease the proportion of alkanes during LDPE degradation in favour of aromatic compounds formation [10,21].

3.2. Plastics degradation in relation to residence time

Extended exposure of the primarily produced gases and hydrocarbon vapours in the hot zone of the closed reactor could promote product formation and reformation due to secondary cracking reactions of the primary product components. For LDPE, the effect of residence time was studied at 450 °C, while polystyrene was studied at 400 °C, based on the nature of the products obtained from the degradation in relation to temperature for 1 h. The time range studied here comprised of zero time (the time at which pyrolysis reaction temperature reached 400 °C for PS and 450 °C for LDPE) up to 120 min.

3.2.1. Effect of residence time of LDPE pyrolysis

Low-density polyethylene was totally converted to 91.1 wt.% oil and 8.70 wt.% gas at zero residence time at 450 °C. Oil product was at the highest yield while gas yield was lowest compared to longer residence times. Thereafter, as residence time increased, oil yield reduced to reach 83.5 wt.% and 16.3 wt.% for oil and gas products, respectively. The oil decreased to 72.4 wt.% at residence time of 60 min whereas gas yield increased to 26 wt.%, with the emergence of char at 1.75 wt.%. Oil product was 69.4 wt.% after 90 min of reaction, while the proportions of gas and char products increased to 27.8 wt.% and 2.60 wt.%, respectively. Oil yield reduced further to nearly 61 wt.%, while gas product went up to 28.5 wt.% when reaction time increased to 120 min. At this time, the amount of char produced was 10.1 wt.%. Note that no char formation was observed at zero and 30-min runs, but it emerged when

Table 3

Components of the oil products from the co-pyrolysis of LDPE and PS (% w/w oil).

Serial no./compounds	Operating temperature/pressure		
	400 °C; 1.24 MPa	425 °C; 1.48 MPa	450 °C; 2.39 MPa
1. Pentene	0.15	0.18	0.33
2. Pentane	0.24	0.41	0.72
3. Hexene	0.54	0.70	1.06
4. Hexane	0.65	1.08	1.50
5. Cyclohexane	0.17	0.47	0.67
6. Benzene	0.25	0.44	0.78
7. Heptene	0.63	0.84	1.23
8. Heptane	1.32	1.93	2.52
9. Methylcyclohexane	0.22	0.38	0.82
10. Toluene	14.3	17.5	18.6
11. Octene	0.77	0.87	1.09
12. Octane	1.25	1.85	2.13
13. Dimethylcyclohexane	0.15	0.17	0.50
14. Ethylbenzene	8.85	9.17	11.8
15. m/p-Xylene	0.42	0.55	0.98
16. Nonene	0.70	0.80	0.97
17. Nonane	1.40	1.99	2.17
18. Cumene	2.05	2.50	1.99
19. Propylbenzene	0.77	0.95	1.35
20. Decene	0.76	0.89	1.04
21. Decane	1.15	1.75	1.66
22. Diethylbenzene	0.67	0.54	1.20
23. Undecene	0.71	0.76	0.86
24. Undecane	1.50	1.89	1.63
25. Tetrahydronaphthalene	0.61	0.56	1.12
26. Dodecene	0.52	0.52	0.46
27. Dodecane	1.45	1.74	1.37
28. Naphthalene	0.59	0.60	0.95
29. Tridecene	0.57	0.54	0.55
30. Tridecane	1.73	1.91	1.54
31. Methylnaphthalene	0.67	0.49	0.86
32. Tetradecane	1.67	1.79	1.23
33. Pentadecane	2.07	2.10	1.45
34. p-Cymene	0.68	0.52	0.50
35. Dimethylnaphthalene	1.06	0.98	2.08
36. Diphenylethane	0.15	0.66	0.37
37. Hexadecane	2.40	1.68	1.06
38. Heptadecane	3.15	2.61	1.27
39. Octadecane	2.21	1.86	1.18
40. Nonadecane	2.03	1.82	1.04
41. Phenylmethylbenzene	0.58	0.51	0.28
42. C ₂₀ –C ₃₀ alkanes	8.73	6.61	2.07
43. Triphenyl benzene	0.67	0.99	1.01
Compound classes			
Naphthenes	1.00	1.80	2.73
n-Alkanes	32.3	32.8	24.6
n-Alkenes	8.40	7.23	8.76
Aromatics	38.0	39.3	48.0
Unknowns	10.2	9.82	9.08

experimental time was extended to 60 min and longer. Moreover, its yield was enhanced 6 times when experiment time doubled to 120 min from 60 min.

This agrees with the previous results of Williams and Slaney [6] and Tiikma et al. [22] who separately reported char formation at long residence time during LDPE pyrolysis. The above results suggest that the polymer was totally cracked during increasing reaction temperature to 450 °C, such that even at zero time, the LDPE was totally converted to oil and gas products. Longer residence time provided opportunity for secondary reactions (isomerisation, aromatization and hydrogenation/dehydrogenation reactions) to occur; hence it was observed that some oil was consumed towards gas and char production. Oil yield consequently decreased with extended residence times of primary products in the reactor. Again, the emergence of char indicates some stripping reactions taking place at some carbon chains resulting in the revolution of lighter compounds and hydrogen. Similar results

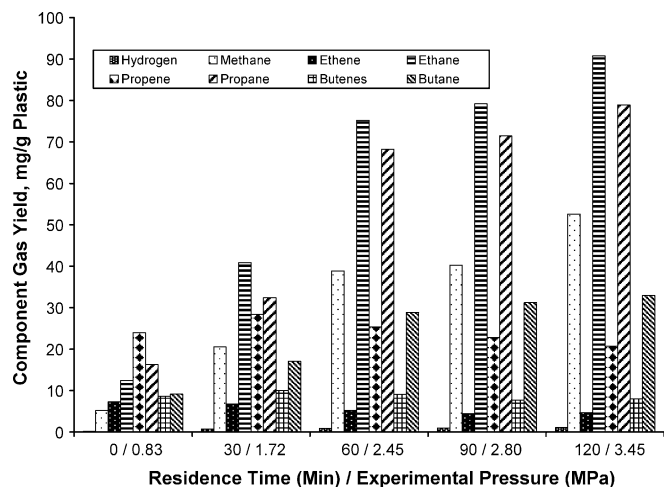


Fig. 4. Composition of LDPE pyrolysis gaseous product in relation to residence time.

were reported by Tiikma et al. [22], where the reaction time influenced the products at the same temperature, as some of oil product was converted to gas and char after 90 min. The effect of residence time on the composition of the gaseous and liquid (oil) products is discussed further below.

3.2.1.1. Composition of LDPE gaseous product in relation to residence. Generally, hydrogen yield was the lowest among the components of the gaseous production during the degradation of LDPE in relation to residence time. However, its yield improved more when residence time was stretched to 60 min and became nearly stabilized at longer residence times of 90 and 120 min.

Alkane components of the gas product increased with increasing the residence time. They were doubled with each 30 min increase in residence time up to 60 min. Thereafter, the rate of increase of alkanes dropped slightly; the increase was only 10% when residence time increased to 90 min and by a similar margin at 120 min. In contrast, alkenes yield was optimum after 30 min at 4.7 wt.%, having increased from 3.6 wt.% at zero time. With further increase in residence time, it decreased in the region of about 10–12% with each 30-min increase until 120-min. Alkene gases yield decreased at residence time of 60 min at which char appeared in the product. There was an apparent reciprocal relation between olefin yield and both paraffin yield and char formation with increasing of pyrolysis time. This suggested that the loss in alkenes favoured the production of lighter compounds, and could have been accompanied by stripping reactions for char formation. These observations are in line with the kinetic mechanisms proposed in this work and with those of Westerhout et al. [21] and Elordi et al. [10].

Fig. 4 clearly shows how alkane gases namely, methane, ethane and propane evolved with longer residence time but butane was not significantly affected. At zero time, alkenes represent nearly 50 wt.% of gas product, where propene was the main product followed by propane and ethane gases. At long residence time of 120 min, propene was among the compounds with low yield while propane, ethane and methane showed the highest yield among the others. Generally, alkene gases reduced with longer residence time. For instance, at residence time of 120 min, ethene declined to around 18% of its yield at zero time similarly propene and butene yield reduced to about 25% of their yield at zero time.

3.2.1.2. Composition of LDPE oil products in relation to residence time. Table 4 lists the major compounds and their concentrations in weight percents of oil products obtained. At the end of the table, the components of the oil products are divided into cycloalkanes

(naphthenes), alkanes, alkenes, aromatics and unknowns (unidentified peaks). At low residence time the oil consisted mainly of aliphatic compounds with varied carbon atom number, an indication of the random scission mechanism. At zero residence time, paraffins were the main compounds at 39.4 wt.% of the oil product, and including compounds from C_5 to C_{36} and dominated by compounds with 5–25 carbon atoms. The most prominent n-alkanes were C_{20} , C_8 , C_{21} followed by C_{11} , C_7 , C_{22} and C_9 . Higher alkanes with carbon number more than 30–36 carbon atoms existed in concentration less than 0.5 wt.% each. Alkenes were distributed from C_5 to C_{19} . Uniquely, the yield of alkenes with C_{10} , C_8 and C_7 was the highest among the aliphatic compounds, with 2.5 wt.%. The alkenes were mostly in the form of alpha-olefins. Low concentration of some dienes such as 1, 9-tetradecadiene and 1, 12-tridecadiene were found also. At zero time, the total yield of alkenes was highest at 26 wt.% compared to other residence times, suggesting a promising way to produce high yield of alpha-olefins. Aromatic yield was only 6.81 wt.%, which was the lowest yield obtained compared to longer residence times. The aromatic compounds were dominated by toluene, xylenes, benzene and alkyl benzenes.

Even though the oil composition at 30 min was similar to that of oil at zero time it improved towards smaller hydrocarbon chains. It contained lighter compounds and in addition, the aromatic yield was doubled. Alkanes were not highly affected when pyrolysis time elongated 30 min, representing about 35.2 wt.% of the oil product. The major alkanes were from C_5 to C_{32} but dominated by C_7 and C_8 in the region of 3.4 wt.% each, then C_9 , C_{10} and C_{11} at 2.3 wt.% each. In contrast, the yield of alkenes was reduced significantly to 19.7 wt.% and the high individual yield of some alkenes e.g. C_7 – C_{10} , that was obvious at zero time, became lower than their corresponding saturated hydrocarbons.

The oil obtained at after 60 min of reaction has been described in Section 3.1.1.2. Liquid product at 90 min consisted of more aromatics with smaller paraffin and olefin yields. Alkane and alkene yields reduced in the favour of aromatic formation. The concentration of paraffin compounds was 28.4 wt.%, distributed mainly from C_5 to C_{28} mainly and dominated by light alkanes such as heptane and octane with concentration of more than 4 wt.%, followed by nonane and decane, each around 2.5 wt.%. Total olefins was 11.5 wt.%, distributed mainly from C_7 to C_{14} but dominated by compounds from C_7 to C_{10} , with the presence of other distributed alkenes until C_{17} at much smaller levels. Heptene had the highest concentration of 2 wt.%. The yield of aromatics improved considerably at longer time where their yield increased to nearly 26 wt.% at 90-min residence time, dominated by toluene, m/p-xylene, benzene, ethylbenzene, with other low concentrated monocyclic aromatics such as alkyl benzenes and alkyl toluene compounds. The yield of polycyclic aromatics was also enhanced and included naphthalene, methylnaphthalene and ethylnaphthalene, with concentration around 0.5 wt.% each.

After 120 min, aromatic yield was further enhanced to 33 wt.%, showing a 5-fold increase compared to zero minutes. The aliphatic components were dominated by short-chain compounds. Among these, alkanes yield was 27.4 wt.%, translating to a decrease of slightly less than 6% compared with its yield at residence time of 90 min and 27% compared with its yield at zero time. The alkanes were dominated by compounds from C_5 to C_{18} with traces of longer-chain compounds up to C_{24} . The main alkanes were heptane and octane with yield about 4.74 wt.% and 4.54 wt.%, respectively. Olefins further reduced by 6% compared to their yield at 90-min time. They were distributed within the light range compounds from C_7 to C_{14} , and the predominant members were in the range of C_7 – C_{10} . The highest concentrations were obtained for C_7 and C_9 olefins both with 2.1% (w/w), respectively. Several authors [21,26,27] have reported that long residence times influence the

Table 4

Components of the oil products from the pyrolysis of LDPE in relation to residence time (% w/w oil).

Serial no./compounds	Residence time/operating pressure				
	0 min; 0.83 MPa	30 min; 1.72 MPa	60 min; 2.45 MPa	90 min; 2.80 MPa	120 min; 3.45 MPa
1. Pentene	0.79	0.72	0.65	1.10	0.12
2. Pentane	1.28	1.70	1.29	2.14	0.03
3. Hexene	1.61	1.48	1.14	1.02	0.83
4. Hexane	0.16	0.43	1.29	1.54	1.23
5. Cyclohexane	0.80	1.42	1.27	1.09	1.08
6. Benzene	0.24	0.30	0.67	1.48	1.82
7. Heptene	2.40	2.86	1.87	2.07	2.93
8. Heptane	1.85	3.79	4.30	4.17	4.74
9. Methylcyclohexane	0.88	1.61	1.93	2.42	2.60
10. Toluene	0.47	0.58	4.70	4.56	6.21
11. Octene	2.44	2.57	1.90	1.75	1.76
12. Octane	2.20	4.00	4.59	4.18	4.54
13. Cycloheptane	nd	0.46	0.59	0.44	0.44
14. Dimethylcyclohexane	0.25	0.42	0.95	0.99	1.11
15. Ethylmethylcyclopentane	0.47	0.59	nd	nd	nd
16. Ethylbenzene	0.08	0.33	1.22	1.27	1.78
17. m/p-Xylene	0.78	1.34	3.47	2.67	4.77
18. Styrene	0.12	0.52	0.54	0.34	2.36
19. o-Xylene	0.26	0.41	0.61	1.93	2.88
20. Nonene	2.03	2.01	2.27	2.07	1.12
21. Nonane	1.82	2.89	3.32	3.65	3.61
22. Allylbenzene	0.17	0.55	1.02	1.52	2.16
23. Decene	2.46	1.93	1.88	1.45	1.67
24. Decane	1.67	2.34	3.09	2.30	2.35
25. Indane	0.16	0.45	0.72	0.85	0.88
26. Undecane	2.04	1.44	1.04	0.55	0.39
27. Undecene	1.83	2.28	2.50	2.07	2.00
28. Naphthalene	0.06	0.15	0.47	0.56	0.78
29. Dodecene	1.78	1.33	1.13	0.54	0.45
30. Dodecane	1.67	1.94	2.02	1.82	1.77
31. Tridecene	1.66	1.45	1.33	1.21	0.30
32. Tridecane	1.57	1.72	1.74	1.29	1.33
33. Tetradecene	1.67	1.07	0.86	0.60	0.58
34. Tetradecane	1.53	1.73	1.56	1.25	1.14
35. Pentadecene	1.45	0.77	0.50	0.23	0.15
36. Pentadecane	1.55	1.62	1.35	1.11	0.98
37. Hexadecene	1.30	0.73	0.46	nd	nd
38. Hexadecane	1.64	1.49	1.18	1.30	1.12
39. Heptadecene	1.34	0.55	nd	nd	nd
40. Heptadecane	1.56	1.33	0.99	0.70	0.86
41. Octadecene	1.23	nd	nd	nd	nd
42. Octadecane	1.45	1.19	0.79	0.57	0.52
43. Nonadecane	1.35	1.07	0.67	0.43	0.42
44. Eicosane	2.25	1.10	0.48	0.26	0.22
45. C ₂₁ –C ₃₂ alkanes	13.2	4.18	1.96	0.60	0.49
Compound classes					
Naphthenes	3.42	6.39	5.56	6.87	7.26
Alkanes	39.4	35.2	31.7	28.4	27.4
Alkenes	26.0	19.7	13.1	11.5	10.8
Aromatics	6.81	13.9	22.9	25.9	32.5
Unknowns	15.3	16.8	17.9	16.5	17.2

formation of aromatics and char during polymer pyrolysis using different types of reactors.

3.2.2. Effect of residence time of polystyrene pyrolysis

In relation to residence time at 400 °C, polystyrene was completely degraded mainly into liquid products with some char and gas even at zero minutes. Char production remained fairly stable at about 1 wt.% up to 90 min and increased to 3.4 wt.% after 120 min of reaction. In a similar manner, gas production hovered from 0.6 wt.% to just above 1 wt.% after 120 min. The gaseous product was dominated by methane, ethane, ethene and propane. The gaseous product obtained after 120 min contained about 42% by weight of methane. The oil product remained consistently dark-coloured throughout but with less viscosity as the residence time increased. In all cases, the quantity of oil produced was more than

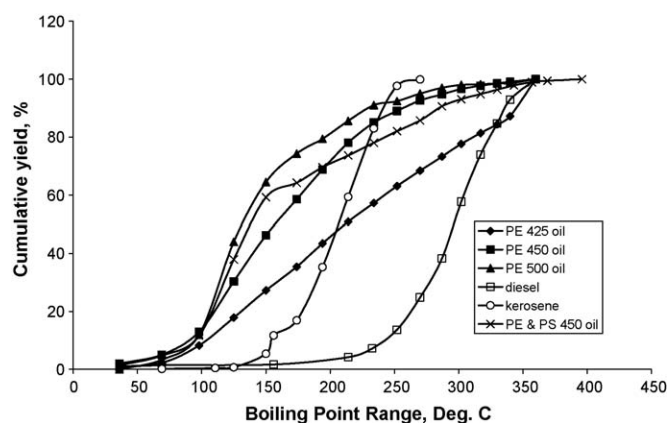
95 wt.% of the plastic feed. Being the only major product obtained under this pyrolysis conditions, its composition is discussed below.

3.2.2.1. Composition of PS pyrolysis oil products in relation to residence time. As shown in Table 5, at zero minutes, styrene was the predominant component of the oil product with about 68.8 wt.%. It is interesting to note that the concentrations of toluene, ethyltoluene, cumene and triphenylbenzene were all individually higher than that of ethylbenzene at this residence time. As the reaction time increased to 30 min, the proportion of styrene fell dramatically to a mere 2.87 wt.% and continued the downward trend with increasing residence time. The amount of styrene monomer obtained from this work at zero minutes compared favourably to the work of Scott et al. [30], who carried out fast pyrolysis of polystyrene in fluidized bed reactors.

Table 5

Major compounds in the pyrolysis oil products from polystyrene in relation to residence time (% w/w oil).

Serial no./compounds	Residence time/operating pressure				
	0 min; 0.76 MPa	30 min; 1.07 MPa	60 min; 1.14 MPa	90 min; 1.23 MPa	120 min; 1.34 MPa
1. Benzene	0.05	0.33	0.38	0.39	0.30
2. Toluene	3.32	18.8	21.7	19.4	20.3
3. Ethylbenzene	0.60	35.8	32.6	33.5	33.4
4. Styrene	68.8	2.87	1.09	0.43	0.55
5. Cumene	1.50	6.07	8.58	10.2	9.96
6. Propylbenzene	nd	0.45	0.60	0.51	0.48
7. 2-Ethyltoluene	2.93	2.78	1.38	0.57	0.44
8. Naphthalene	nd	0.16	0.13	0.06	0.06
9. Diphenylmethane	0.10	0.65	0.91	0.72	0.72
10. Anthracene	nd	2.88	0.45	3.04	3.03
11. 1,2-Diphenylethane	0.28	1.26	1.44	1.25	1.36
12. 2,2-Diphenylpropane	nd	0.34	0.42	0.39	0.28
13. 1,3-Diphenylpropane	nd	0.98	0.33	0.07	0.01
14. Phenylanthracene	0.34	1.09	0.98	1.06	1.11
15. Diphenylbenzene	1.14	3.47	3.44	3.24	3.74
16. Triphenylbenzene	0.96	3.67	4.29	4.77	5.67

**Fig. 5.** Modified simulated distillation plot for some pyrolysis oils compared to diesel and kerosene.

However, at longer residence times, as seen in this work, styrene concentration dropped dramatically, indicating the high reactivity of styrene under the pyrolysis in a batch reactor and longer residence times. On the other hand, the concentrations of both toluene and ethylbenzene increased to around 35.6 wt.% and 21.7 wt.%, respectively. It is obvious that the degradation of PS to its monomeric unit, styrene was the first major pyrolytic reaction of polystyrene [30]. The dramatic increase in the concentrations of toluene and ethylbenzene somewhat corresponded to the decrease of styrene, indicating that these compounds may have been formed from the reaction of styrene itself, rather than from the direct degradation of polystyrene. For instance, the hydrogenation of styrene would yield ethylbenzene. Ethylbenzene itself could be transformed by the cleavage of the $-C-C-$ bond of the ethyl substituent followed by hydrogenation to produce both toluene and methane. The concentration of cumene increased about 6 times from zero to 30 min and then only gradually increased with increasing residence time. The other compound with significant concentrations included diphenylpropane, diphenylbenzene, triphenylbenzene, whose concentrations increased slightly with residence time.

3.3. Fuel properties of the plastic pyrolysis oils

Some fuel properties of the oils derived from the pyrolysis of plastics have been determined to show how they compare with some common fossil fuel fractions. A modified ASTM D 2887-8

standard simulated distillation of the oils derived from LDPE and LDPE/PS plastics within the temperature range 400–500 °C was carried out. Fig. 5 shows the plot of the percentage cumulative yields of the components of the oil against their boiling point ranges. Due to the limited amounts of oils obtained, the Carlo Erba GC/FID was used with a linear temperature programme to elute the oil components in the order of their boiling points. The peak areas leading to each n-alkane interval was summed up and divided by the total peak area to obtain the cumulative yield. The plot obtained was compared to the plots for diesel and kerosene fuels. It is clear that the LDPE oil obtained at 450 °C after 60 min, gave the closest match yet to kerosene. It is suggested that blending the oils obtained at two or more reaction conditions or with specific crude oil fractions might yield a product with improved fuel properties.

The calorific values of some of the oils were calculated from the calorific values of their individual constituents and their respective proportions. However, to confirm these values, the CVs of some oils were determined using a calorimeter bomb obtained from Parr Instrument Co. USA. The equipment was a Parr 6200 Isooperibol Bomb Calorimeter. The experimental CV being referred to here was determined in the mode of higher heating value (HHV). The results from the calculated CV and the experimental values were

Table 6

The calculated and experimental calorific values of some of the pyrolysis oils.

Oil sample source	Temperature/pressure	Calculated CV	Experimental ^a CV
PE/60 min	425	38.2	37.7
PE/60 min	450	40.5	–
PE/60 min	500	40.2	–
PS/60 min	425	37.1	–
PS/60 min	450	37.2	36.6
PS/60 min	500	37.4	–
70% PE:30% PS (60 min)	400	39.7	39.5
70% PE:30% PS (60 min)	425	39.7	–
70% PE:30% PS (60 min)	450	39.7	–
Oil sample source	Residence time (min)	Calculated CV	Experimental CV
PE @ 450	0	38.0	–
PE @ 450	30	39.3	37.8
PE @ 450	90	42.7	42.3
PE @ 450	120	41.6	–
PS @ 400	0	36.4	–
PS @ 400	30	37.1	–
PS @ 400	90	37.0	–
PS @ 400	120	37.0	36.1

^a Selected sample.

consistently close as shown in Table 6. Oils derived from pyrolysis of LDPE possessed low viscosity with calculated calorific values 40.4 and 40.2 MJ/kg for oil produced at 450 and 500 °C, respectively. These values indicate high combustion energy of the LDPE pyrolysis oils compared to medium fuel oil with a CV of 43 MJ/kg and rubber tyre pyrolysis oil with CV of 41–44 MJ/kg [31]. They are also close to that for gasoline and diesel which have CV of 47 and 45 MJ/kg, respectively. At lower temperatures, the CVs for LDPE pyrolysis oils were lower possibly as a result of the presence of long-chain compounds and dissolved carbon in the oil matrix. As seen earlier, the oils from polystyrene were made up of aromatic hydrocarbons. The CV for PS pyrolysis oils were generally lower than LDPE oils, probably due to the fact that the individual aromatic compounds, generally have less combustion energies than aliphatic hydrocarbons with the same number of carbon atoms in LDPE oils. For example, both hexane and benzene each contains six carbon atoms but the CV of hexane is 44.75 MJ/kg while that of benzene is 41.8 MJ/kg.

4. Conclusions

There are obvious strong influences of reaction temperature and residence time on the yield of pyrolysis products and the distribution of their components for both plastic samples. Thermal cracking of LDPE in a batch reactor resulted in production of a broad range of hydrocarbon compounds where the yield of aromatics and aliphatics (olefins and paraffins) deeply depended on the pyrolysis temperature and residence time. LDPE plastic began to decompose at 400 °C possibly by random scission method and the highest yield of oil was at temperatures of 425 and 450 °C. At temperatures of 450 °C the oil composition becomes lighter than lower temperatures and the first appearance of char was noticed. At a high temperature of 500 °C the oil yield was low but its composition tended heavily towards light compounds with over 60 wt.% of the oil aromatic. In addition, production of high yield of hydrocarbon gases and char was observed due to secondary reactions, additional cracking reactions, isomerisation and aromatization. In this work, the optimum oil yield from LDPE was at 425 °C with an oil mainly rich in both short-chain and long-chain aliphatic hydrocarbons. However, the oils at 450 and 500 °C contained high ratios of compounds comparable to those found in diesel and gasoline fuels, along with higher amounts of hydrocarbon gases and char. Even at zero residence time at 450 °C, LDPE plastic sample was totally degraded to high yield of aliphatic-rich oil. Longer pyrolysis time altered the oil composition, where aromatic and other light fractions were produced in higher concentrations. In general, LDPE pyrolysis oil has comparable high calorific value of up to 42.7 MJ/kg.

Polystyrene started to degrade at 350 °C, and when mixed with LDPE, led to the formation of liquid oil even at 400 °C. PS degraded initially into a viscous oil and as the residence time and temperature increased, the obvious changes were in the formation of less viscous oil and char. The formation of up to 30 wt.% of char at

500 °C was an indication of the condensation of the ring structure of the aromatic compounds at higher temperatures. It can therefore be concluded that this closed batch system can be used to effectively degrade LDPE and polystyrene to produce high grade fuel-like oils for energy production, new industrial raw materials or chemical feedstock for the petroleum refinery. For instance ethylbenzene and toluene are major raw materials in paints manufacture. Thus this pressurised plastic pyrolysis process may be a convenient way of obtaining high quality fuel fractions simply by varying some parameters like reaction temperatures and residence times or by blending products from different reaction conditions.

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