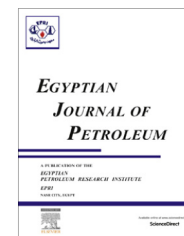




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FULL LENGTH ARTICLE

# Wax co-cracking synergism of high density polyethylene to alternative fuels



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Thermal degradation;  
 HDPE;  
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**Abstract** Attempts have been made to understand the thermal degradation of high density polyethylene (HDPE) and their combined co-cracking using different ratios of HDPE and petroleum wax under nitrogen atmosphere. We have conducted the experiments using HDPE as the raw material and petroleum wax as co-feed by at 400 and 450 °C reaction temperatures. The product distribution was noted along with reaction time of 0.5–3 h for the degradation. Thermal gravimetric analysis (TGA) technique was used to measure the weight change of the feedstock as a function of temperature and time. Differential scanning calorimetry (DSC) was used to determine the degradation temperature. Products were characterized using gas chromatography (GC) and infrared spectroscopy (FTIR), some other standard physical methods were used to determine the main properties of the liquid products. Results show that the mixed plastic-wax samples could be converted into gases, gasoline, and middle distillate depending upon the composition of feed polymer/wax ratio. It was found that the products mostly consisted of paraffin and olefin compounds, with carbon numbers of C<sub>1</sub>–C<sub>4</sub>, C<sub>5</sub>–C<sub>9</sub> and C<sub>10</sub>–C<sub>19</sub> in the case of gases, gasoline and middle distillate respectively.

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## 1. Introduction

Plastics are one of the most widely used materials due to their various advantages and numerous applications in our day to day life. Plastic production has increased by an average of

almost 10% every year on a global basis since 1950. HDPE is the third largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. The increased demand and production of HDPE has led to the accumulation of large amounts in the final waste stream due to its low useful life [1–4]. Various techniques for the treatment of waste polymers have been investigated to complement existing landfill, incinerating and mechanical recycling technologies. Ideally, it would be desirable to convert the waste into a

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value-added product [5–7]. Pyrolysis is one method of reducing plastic wastes [8–9]. It should allow us to recycle back some of the stored energy within the plastic wastes. Pyrolysis uses high-temperatures to break polymer structures into smaller hydrocarbon molecules in an oxygen free atmosphere. The process can handle plastic waste, which cannot be efficiently recycled by other recycling processes and operates without the need of air and generates no pollutants since it is conducted in a closed system. A plant developed by recycling technologies treats mixed plastic waste and provides all the usual advantages of the combined heat and power system [10]. Considerable demand exists for affordable technology that can use environmentally sound methods to extract value from waste that would otherwise be sent to a landfill. The plant is designed to be positioned at the end of a plastic sorting line that already removes material that is not going to be economically recycled, using it instead to provide the electricity and heat needed to recycle the plastics that will be. This avoids the use of virgin fossil fuel in the recycling process, as well as the transport of plastic waste to landfill or as refuse derived fuel to mass-burning facilities. Mixed plastic waste is shredded, the tramp metal removed and the waste is then dried and stored in a bunker. This prepared material is then fed constantly into a pyrolysis reactor where, in the absence of oxygen, the long hydrocarbon chains that form the polymers are thermally cracked into compounds of shorter chain lengths, which exit the chamber as hot gas. The issue with using waste material as a fuel is, of course, that its constituents can vary dramatically, so the quality of the fuel produced also tends to be variable. To combat this problem the system uses a reactor management module to continually adjust the conditions in the reactor to even out such variations. By constantly monitoring the gas being produced the operating parameters can be adjusted to enhance the fuel properties [11–12].

In this work, high-density polyethylene (HDPE) plastic was chosen as used plastic with the objective of optimizing the liquid product yield at a reaction temperature of 400 and 450 °C for a residence time 0.5–3 h under N<sub>2</sub> atmosphere in a batch reactor. The effects of HDPE/wax ratio on the yield of liquid and gaseous products were studied. The physical properties of the pyrolytic oil such as specific gravity and viscosity were studied. The chemical compositions of the pyrolytic oil products were investigated using analysis.

## 2. Experimental

### 2.1. Materials

Waste HDPE was purchased from the Garbage collected place, Manshiat Naser. El – Dewaka, Cairo, Egypt. Light paraffin wax used was obtained from Alexandria Petroleum Company. The characteristics of HDPE raw material and wax feed stock are summarized in (Table 1).

### 2.2. Pyrolysis experiment

The pyrolysis experiments were carried out in nitrogen atmosphere, using a high pressure magnetically stirred batch autoclave (Parr model 4575) with an inner volume of 500 ml and heated by a digital controller, at a temperature of 400 and 450 °C, initial hydrogen pressure of 100 psi. A typical run

**Table 1** Characterization of HDPE raw material and paraffin wax.

Characteristics	Method	HDPE	Paraffin wax
Density, gm/cm <sup>3</sup>	ASTM D4052	0.950	ASTM D1505 0.84
Average molecular weight, g mol <sup>-1</sup>		250,000	440
Melting point, °C		130	62
Refractive index		1.541	1.45
Tensile strength	ASTM D638	3300 psi	–

100 g of the sample was placed into the reactor, which was then sealed. The system was heated at a rate of 20°Cmin<sup>-1</sup> up to 450 °C and maintained there for 0.5–3 h at a speed of 200 rpm. The stirring and heating of the autoclave were shut down then left to cool overnight. Gas and liquid samples were collected and analyzed by gas chromatography.

Thermal cracking experiments were carried out using different HDPE-paraffin wax mixtures prepared with relative proportions within the ratio 50/50, 75/25, 82.5/12.5 respectively and also for HDPE alone.

The conversion and yield are defined according to the following:

$$\text{Conversion(wt\%)} = \frac{\text{feed} - \text{residue}}{\text{feed}} \times 100$$

$$\text{Yield(wt\%)} = \frac{P}{\text{feed}} \times 100$$

where *P* represents the oil or gas.

### 2.3. Characterizations

Thermogravimetric analysis TGA of the waste HDPE sample was carried out with a Perkin–Elmer apparatus. TGA was used to study the weight loss vs. temperature, and to determine the reaction temperature range. A known weight of the sample was heated in a silica crucible at a constant heating ratio of 20 °C/min operating in a stream of nitrogen with a flow rate of 20 ml/min from 30 °C to 600 °C. DSC analysis was done in a Perkin–Elmer differential scanning calorimeter under a flow of nitrogen (flow rate 20 ml min<sup>-1</sup>). Samples (5–10 mg) were sealed in aluminum pans and heated at a heating rate of 10 °C min<sup>-1</sup>, and cooled at the same rate. The melting and crystallization temperatures are reported as average values with standard deviations.

Fourier transform Infrared spectroscopy FTIR of the obtained pyrolysis oil was performed with ATI Mattson infinity series apparatus, Model 960 M0009 with resolution of 4 cm<sup>-1</sup>, in the range of 400–4000 cm<sup>-1</sup>.

The components of the gaseous products were analyzed using a Varian CP-3800 GC equipped with two detectors:

1. Thermal Conductivity Detector TCD for analysis of non-organic gases, which were separated in a 7 ft Hysep Q, molecular sieve packed stainless steel column.
2. Flam Ionization Detector FID for C<sub>1</sub>–C<sub>5</sub> hydrocarbon separated in a 60 meter (capillary) DB-1 silicon oil fused silica by using helium as carrier gas at 50 °C and 5 min hold (injector and detector) temperature of 150 and 250 °C,

respectively. The components of the liquid products were analyzed using Agilent 7890A with Flam Ionization Detector FID for C<sub>3</sub>–C<sub>20</sub> hydrocarbons separated in a 30 meter (capillary) Hp-5. The column temperatures were programmed as: 50 °C for 10 min, rise to 300 °C at the rate of 4 °C/min and nitrogen carrier gas flow 1 ml/min.

### 3. Results and discussion

#### 3.1. TGA and DSC analysis of HDPE samples

TGA analysis is a thermal analysis technique that measures the weight change of a material as a function of temperature and time, in a controlled environment. This can be very useful to investigate the thermal stability of a material or to investigate its behavior in different atmospheres (e.g. nitrogen or oxygen). TGA was applied to study the degradation of waste HDPE and paraffin wax in various ranges of temperature. From the TGA curve shown in (Fig. 1), the HDPE degradation started at 390 °C and was completed at 490 °C for a heating rate of 20 °C/min., in accordance to Aboulkas et al. [13]. It is also clear from Fig. 1 that the wax is much less thermally stable than the HDPE. It started decomposition at 200 °C and completely decomposed at 332 °C.

The DSC heating curve presented in Fig. 2 shows two endothermic peaks, the first one at 129 °C represented the melting point of the HDPE. The second dominated peak in the temperature range from 390 to 490 °C, indicating that there is a degradation step where the conversion takes place. It is also shown in (Fig. 2) that the pure wax has a melting temperature peak at 62 °C, and a solid–solid transition peak at 56 °C in accordance to Luyt and Krupa [14]. The final peak at 332 °C was related to volatilization of hydrocarbons which was related to the maximum mass loss.

#### 3.2. FTIR spectra of pyrolytic oil products and HDPE raw materials

FTIR is an important analysis technique that detects the various characteristic functional groups present in the pyrolytic oil and raw materials. Upon interaction of infrared light with the sample, chemical bonds can absorb infrared radiation in specific wavelength ranges regardless of the structure of the rest of the molecules. (Fig. 3) shows the FTIR spectra of

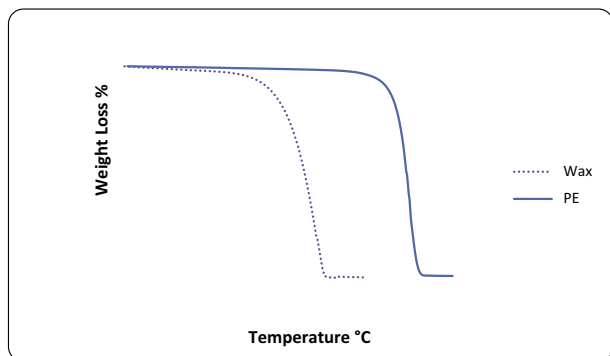


Figure 1 TGA curve of HDPE and raw materials.

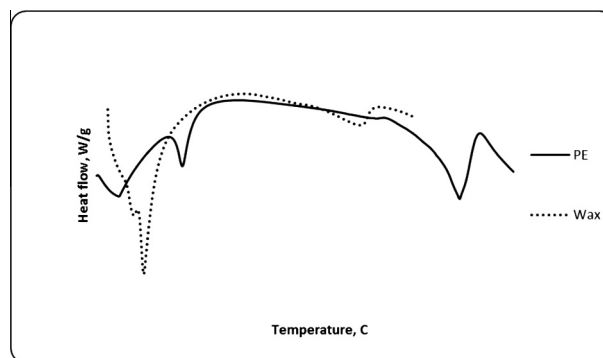


Figure 2 DSC of raw materials.

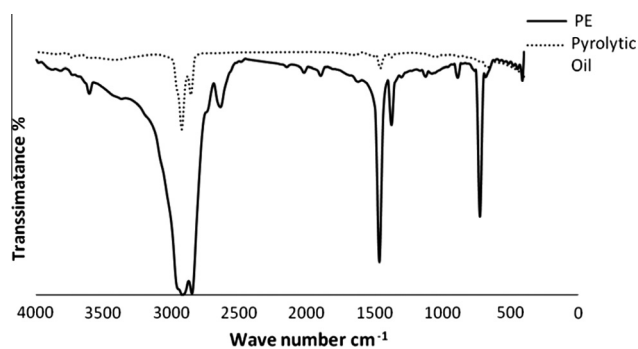


Figure 3 The FTIR spectra of a pyrolytic oil product and HDPE raw materials.

Table 2 FT-IR assignment of HDPE and pyrolytic oil.

Assigned (cm <sup>-1</sup> )	Vibrational mode	Functional group
3473	C–H stretching	–CH=CH <sub>2</sub> or >C=CH <sub>2</sub> alkene
2955	C–H asymmetrical stretching	C–H <sub>3</sub> alkane
2924	C–H asymmetrical stretching	–C–H <sub>2</sub>
2855	C–H symmetrical stretching	–C–H <sub>2</sub>
1673	C=C stretching	–CH=CH <sub>2</sub> or >C=CH <sub>2</sub> or CH=CH–
1456	C–H scissoring	–CH <sub>2</sub> –
1456	C–H symmetrical bending	–CH <sub>3</sub>
1376	C–H symmetrical bending	–CH <sub>3</sub>
875	C–H bending	–CH=CH <sub>2</sub>
744	C–H bending	–CH=C<

HDPE raw material and one of the produced pyrolytic oil (all the produced pyrolytic oils have the same spectra with different intensities).

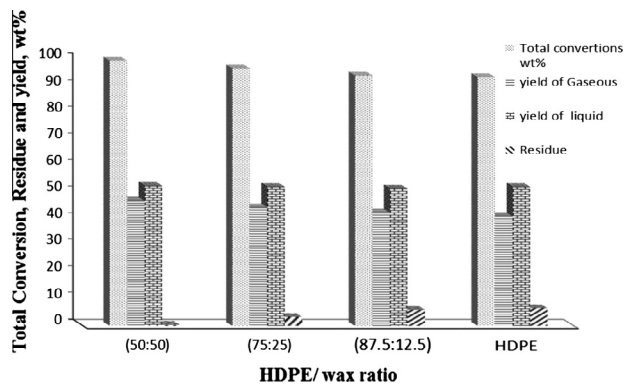
The different assignments of the FTIR spectra are summarized in (Table 2) which shows the presence of mostly alkanes and alkenes. The results were consistent with the GC results.

### 3.3. Effect of paraffin wax content on HDPE pyrolysis

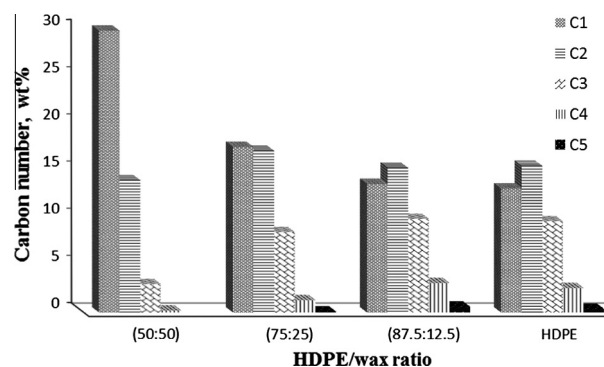
Thermal cracking experiments were carried out using different HDPE-paraffin wax mixture prepared with relative proportion of HDPE/paraffin wax ratios in the ranges of 50:50, 75:25, 87.5:12.5 and also for HDPE alone conversion over 93 wt% was attained according to HDPE proportion in the mixture. In addition, it can be appreciated that a significant enhancement in the product output takes place with increasing proportions of the paraffin wax in the mixtures. Thus, the overall product output increased from 93.4 to 99.6 as shown in (Fig. 4). However, the yield of gaseous compounds tends to increase with increasing paraffin wax content in the mixture. The opposite is observed for the higher HDPE content (Fig. 4). This result is due to the lower thermal stability of the paraffin wax than the HDPE polymer as indicated by TGA analysis (Fig. 1). It can be deduced that the primary pyrolysis takes place through a free radical transfer that can lead to low yield of gaseous compounds. Nevertheless, the more gases obtained from secondary pyrolysis of the wax product can be interpreted as a consequence of the pyrolysis reaction [15,16]. Also the growing yield of gas for the higher paraffin wax sample could be caused by the differences in the stability of polymer chains and paraffin wax. Therefore at higher paraffin wax content, the C–C bonds cracked more rapidly than at HDPE raw material. The yield of condensable oil and the non-condensable gas/volatile fractions of the reaction constitute the major products as compared to the solid residue fractions (Fig. 4), while the residue decreases as paraffin wax content increases in the blend. Introducing more of the wax induces a gradual decrease in the temperatures at which the degradation starts [17–19].

Hydrocarbon distribution in gas products are shown in Fig. 5. All the gaseous products were in the carbon number range of C<sub>1</sub>–C<sub>5</sub>. The carbon number distributions show two maximums at C<sub>1</sub> and C<sub>2</sub> owing to hydrogenolysis process at higher temperature. Less C<sub>4</sub> hydrocarbons were observed in the pyrolysis gases. These hydrocarbons have high calorific value. Consequently, the gaseous products could be utilized to supply the energy involved in the pyrolysis process [20].

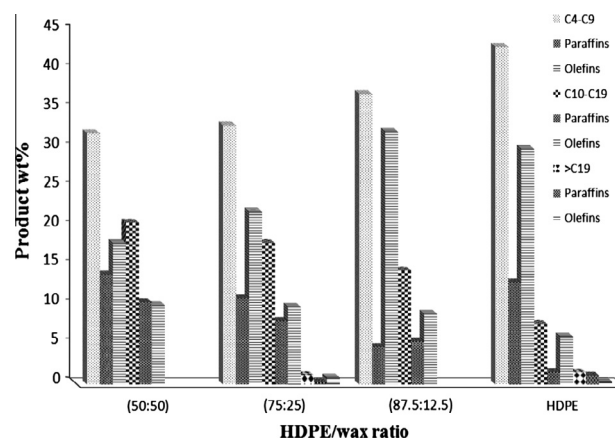
Three different liquid fraction products were obtained in the pyrolysis; Gasoline (C<sub>5</sub>–C<sub>9</sub>), middle distillate (C<sub>10</sub>–C<sub>19</sub>) and oil (C<sub>19</sub><sup>+</sup>) as shown in Fig. 6. All fractions contain n-paraffins and n-olefins, and did not contain aromatics. The



**Figure 4** Total conversion of and product yields as a function of HDPE/wax ratio.



**Figure 5** Hydrocarbon distribution in gaseous product of as a function of HDPE/wax ratio.



**Figure 6** Hydrocarbons distribution in pyrolytic oil liquid product as a function of HDPE/wax ratio.

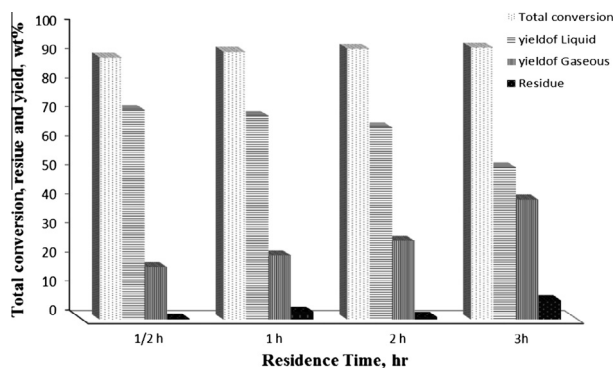
fraction of the gasoline range components (C<sub>5</sub>–C<sub>9</sub>) in oil product was 82.4 wt% for pure HDPE. However, with the increase of the paraffin wax content in the feed, the fraction of the gasoline range components was decreased to 60.8 wt% for higher wax content, whereas, the kerosene/diesel range components (C<sub>10</sub>–C<sub>19</sub>) were increased. It is supposed to be due to different degradation characteristics of wax and HDPE.

### 3.4. Effect of residence time on product yield

The extended residence times of hydrocarbon gases and components in the vapor phase at high temperatures could create an enabling environment for secondary reactions to occur in the reactor. The effect of residence time on the pyrolysis products of HDPE raw material was studied at 450 °C from 0.5–3 h. Oil yield reduced with longer reaction time to reach 52.2 wt% at a residence time of 3 h. In contrast, the gas product increased to reach 41.2 wt% at this reaction time. At 0.5 h reaction time, oil yield increased to reach 72 wt%, while the gas yield decreased more than three times to reach 12 wt% when the experimental time was reduced from 3 to 0.5 h (Fig. 7).

Therefore, longer residence time provided the opportunity for secondary reactions, which increased cracking so that some oil was consumed during those reactions toward gas production [21].





**Figure 7** Total conversion of HDPE pyrolysis and product yields as a function of residence time.

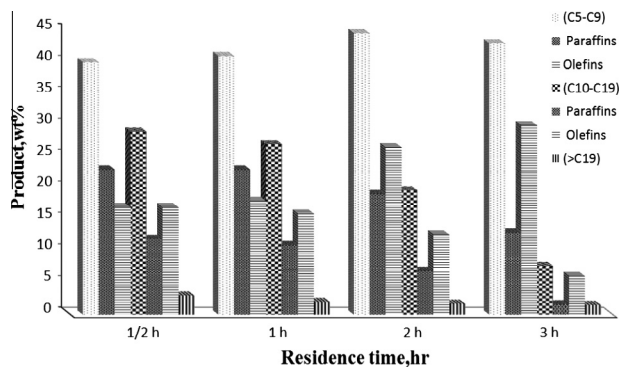
### 3.5. Effect of residence time on product composition

Fig. 8 presents, the effect of residence time on the composition of the oil products obtained at 450 °C. The oil consisted mainly of aliphatic compounds. At 30 and 60 min, the oil consisted of 23 wt% paraffins within the range C<sub>5</sub>–C<sub>9</sub> as the main compounds. Higher alkanes with carbon numbers more than C<sub>9</sub> existed but in concentrations less than 23 wt%. C<sub>5</sub>–C<sub>9</sub> alkenes gave a total concentration of around 30 wt%. Oil composition at 0.5 h residence time was similar to oil at 1 h residence time mainly and dominated by light alkanes. Olefins around 30 wt% were distributed mainly from C<sub>5</sub> to C<sub>9</sub>. The liquid product at higher residence time (2 and 3 h) gave more alkene and less alkane yields. The concentrations of paraffinic compounds were 19 and 13 wt% at 2 and 3 h respectively, distributed from C<sub>5</sub> to C<sub>9</sub>. The effect of residence time was much more pronounced on the alkenes compared to alkanes.

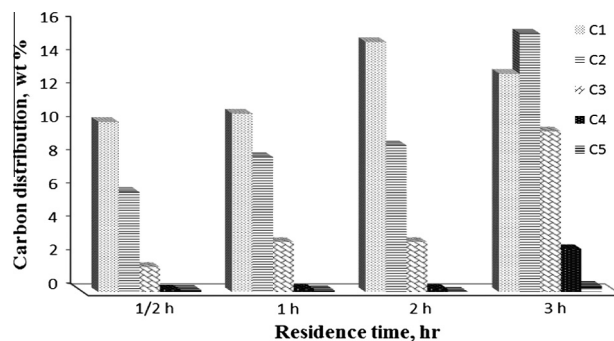
Hydrocarbon distribution in gas phase is shown in Fig. 9. The maximum percentage of C<sub>1</sub> and C<sub>2</sub> hydrocarbons were found at higher residence time owing to hydrogenolysis and secondary cracking processes.

### 3.6. Effect of temperature on products yield

The effect of reaction temperature on the distribution of reaction products during the pyrolysis of pure polyethylene was studied under inert nitrogen atmosphere and temperatures of



**Figure 8** Hydrocarbon distribution in pyrolytic oil of HDPE pyrolysis at 450 °C as a function of residence time.



**Figure 9** Hydrocarbons distribution in gaseous product of HDPE pyrolysis as function of residence time at 450 °C.

400 °C and 450 °C for 0.5 h each. Table 3 shows that at 400 °C the liquid oil formed 89 wt% of the pyrolysis product together with hydrocarbon gas. At higher temperature of 450 °C, the oil yield decreased due to the secondary reactions and more cracking of hydrocarbons, leading to increasing gas yield. Oil yield decreased significantly at higher temperature to 72 wt%, while gas yield rose considerably to 18 wt%. In this work, the optimum oil yield was at 400 °C with an oil mainly rich in both short-chain and long-chain aliphatic hydrocarbons. However, the oils at 400 and 450 °C contained compounds comparable to those found in gasoline and middle distillate (kerosene and diesel) [21].

### 3.7. Effect of temperature on composition of the oil products

Table 3 shows the distribution of the components of the oil into different classes of alkane and alkene compounds. At 400 °C, n-alkanes were the highest components reaching 43.3 wt% of the oil product. The alkanes were arranged

**Table 3** Total conversion and product yield of HDPE pyrolysis as a function of reaction temperature (0.5 h residence time).

Temperature, °C	400 °C	450 °C
Total conversion, wt%	89	90
Residue	11	10
<i>Product yield, wt%</i>		
Gas	12	18
Liquid	77	72
<i>Hydrocarbon distribution in liquid product, wt%:</i>		
C <sub>5</sub> –C <sub>9</sub>	38	40
Olefins	15.5	17
Paraffins	22.5	23
C <sub>10</sub> –C <sub>19</sub>	35.2	29
Olefins	14.4	17
Paraffins	20.8	12
>C <sub>19</sub>	3.8	3
<i>Hydrocarbon distribution in Gaseous product, wt%:</i>		
C <sub>1</sub>	5	3.7
C <sub>2</sub>	4.6	5.3
C <sub>3</sub>	2.2	3.7
C <sub>4</sub>	0.1	0.2
C <sub>5</sub>	0.01	0.1

from C<sub>5</sub>–C<sub>19</sub>. This distribution of aliphatic chain proves that thermal decomposition of the polyethylene follows a random scission mechanism during the primary cracking phase. Compounds >C<sub>19</sub> showed 3.8 wt% of the total components in the oil portion. Alkenes represented 29.9 wt% of the product from C<sub>5</sub> and up to C<sub>19</sub>, which are known as the alpha-olefin compounds and which are highly attractive to the petrochemical industry as chemical feedstock. With increasing reaction temperature to 450 °C, the oil product was still dominated by alkanes at 35 wt% in the range of light components [22].

The chromatographic separation of oils on the gas chromatography was used to determine the simulated distillation to analyze the boiling point distribution of the oil products. This helped to predict the potential use of the oil products. The results in Table 3, show the gasoline and kerosene/diesel fractions in the liquid products at 400 and 450 °C. The potential use of the oil depends on the boiling point therefore, if the C<sub>5</sub>–C<sub>9</sub> oil fraction is considered as gasoline substitute and C<sub>10</sub>–C<sub>19</sub> fraction considered as kerosene/diesel range substitute, then the oil produced at 400 °C contained more of the kerosene/diesel fraction, while there was more naphtha range components in the oil produced at 450 °C.

### 3.8. Physical properties of pyrolytic oils

The oil obtained after thermal pyrolysis appears dark brown in color. The pyrolytic oils were characterized in term of fuel properties. The obtained fuel properties were compared with gasoline, kerosene and diesel and these properties are summarized in Tables 4 and 5. The results illustrate that the densities and specific gravities of the oil were about the same as that of gasoline. This is attributed to the presence of higher compounds in all the obtained oils. The kinematic viscosities were lower than unity due to the presence of higher percentage of lighter compounds of the gasoline fraction. Low viscosity shows the positive quality in the handling and transporting of the oil [23,24]. The quality of the obtained fractions in the

process is also better in terms of quality in a test like pour point.

### 3.9. Reaction mechanism

It is well known that plastic and paraffin wax in general decompose into oil and gas when isolated from air (oxygen) and heated to higher temperature through pyrolysis process. The pyrolysis is basically degradation of large hydrocarbons into smaller ones with lower molecular weights. Thermal degradation is accompanied by with a free radical chain reaction. When free radicals react with hydrocarbons, new hydrocarbons and new free radicals are produced. Also, free radicals can decompose into olefins and new free radicals.

#### 3.9.1. Reaction mechanism of HDPE pyrolysis

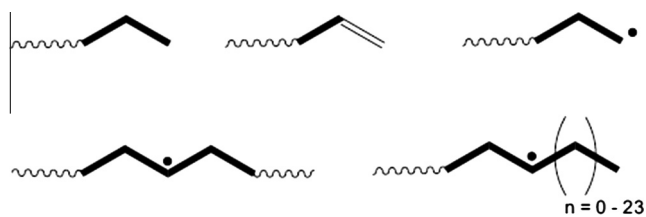
Polymer pyrolysis usually involves three general reaction pathways to product formation. Unzipping (UZ), or successive endchain β-scission reactions, yields monomer from the polymer chain. UZ can be seen as the reverse of ideal free-radical polymerization. Backbiting (BB) involves specific intramolecular hydrogen transfer reactions followed by mid-chain β-scission to yield a series of specific low molecular weight products (LMWPs). The products obtained from BB pathways are often referred to as non-statistical products because the formation of some products is favored over the formation of others based on the ease of different intramolecular hydrogen transfer reactions [25]. Random scission (RS) involves intermolecular hydrogen transfer followed by mid-chain β-scission to yield a diverse array of low molecular weight products (LMWP). RS products are often referred to as statistical products because every product has an equal probability to be formed, since each abstractable hydrogen of a given type (e.g., benzylic, secondary, tertiary) on a polymer backbone is equally available as a target for intermolecular hydrogen transfer. Polyethylene is especially susceptible to both BB and RS pathways because every mid-chain hydrogen yields an equally stable secondary carbon radical.

**Table 4** Physical properties from pyrolytic oil of HDPE pyrolysis products at different residence times at (a) 400 °C, (b) 450 °C.

Properties	Time, h					
	Method	0.5 <sup>a</sup>	0.5 <sup>b</sup>	1	2	3
Density at 20 °C (g/cm <sup>3</sup> )	ASTM D4052	0.8400	0.8311	0.8219	0.8101	0.8042
Specific gravity at 20 °C		0.8415	0.8326	0.8234	0.8116	0.8056
AP <sup>o</sup> I gravity at 20 °C	ASTM D 4052	36.70	38.45	40.35	42.85	44.51
Kinematic Viscosity at 40 °C (cSt)	ASTM D 445	1.68	1.50	1.2	0.99	0.98

**Table 5** Physical properties of pyrolytic oil product as a function of HDPE/wax ratio and HDPn3E alone (at 450 °C, 3 h).

Properties	Method	HDPE/wax ratio			
		50/50	75/25	82.5/12.5	HDPE
Density at 20 °C (g/cm <sup>3</sup> )	ASTM D4052	0.7926	0.7938	0.8012	0.8042
Specific gravity at 20 °C		0.7940	0.79522	0.8026	0.8056
AP <sup>o</sup> I gravity at 20 °C	ASTM D 4052	46.71	46.44	44.80	44.51
Kinematic viscosity at 40 °C (cSt)	ASTM D 445	0.913	0.926	0.98	0.98
Pour point °C		< -33	< -33	< -33	< -33



**Figure 10** Structural details used to distinguish polymeric species track.

The structural characteristics track in the HDPE are shown in Fig. 10 and include saturated and unsaturated end groups, end-chain radicals, general mid-chain radicals, and specific mid-chain radicals from the 2nd to the 25th position. Low molecular weight products (LMWPs) and low molecular weight radicals (LMWRs) are tracked explicitly. LMWP tracked included all alkanes from methane (C1) up to n-tricosane (C23) and alkenes from ethylene (C2=) up to 1-hexacosene (C26=).

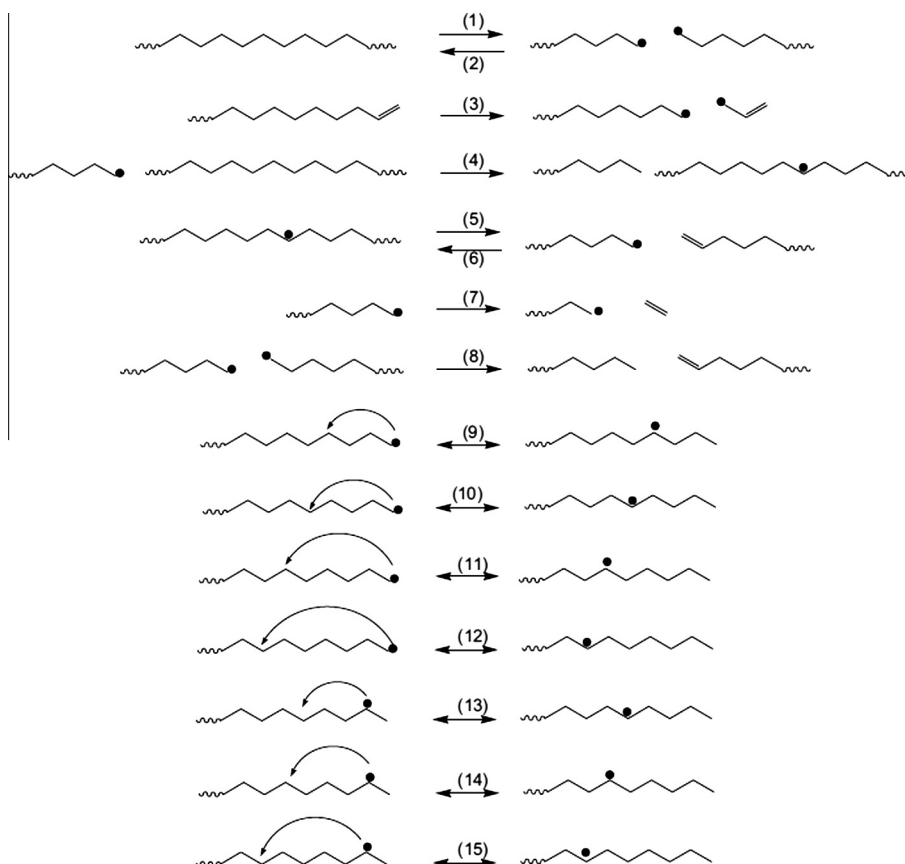
The mechanistic chemistry is described by allowing all the species in the system to react according to a set of elementary reaction families before the method of moments is applied. For HDPE pyrolysis the following elementary reaction families

were included in the model: (1) bond fission, (2) radical recombination, (3) allyl bond fission, (4) hydrogen abstraction, (5) mid-chain  $\beta$ -scission, (6) radical addition, (7) end-chain  $\beta$ -scission, (8) disproportionation, (9) 1,4-hydrogen shift, (10) 1,5-hydrogen shift, (11) 1,6-hydrogen shift, (12) 1,7-hydrogen shift, (13)  $\chi, \chi + 3$ -hydrogen shift, (14)  $\chi, \chi + 4$ -hydrogen shift, and (15)  $\chi, \chi + 5$ -hydrogen shift. These reactions are depicted in Fig. 11.

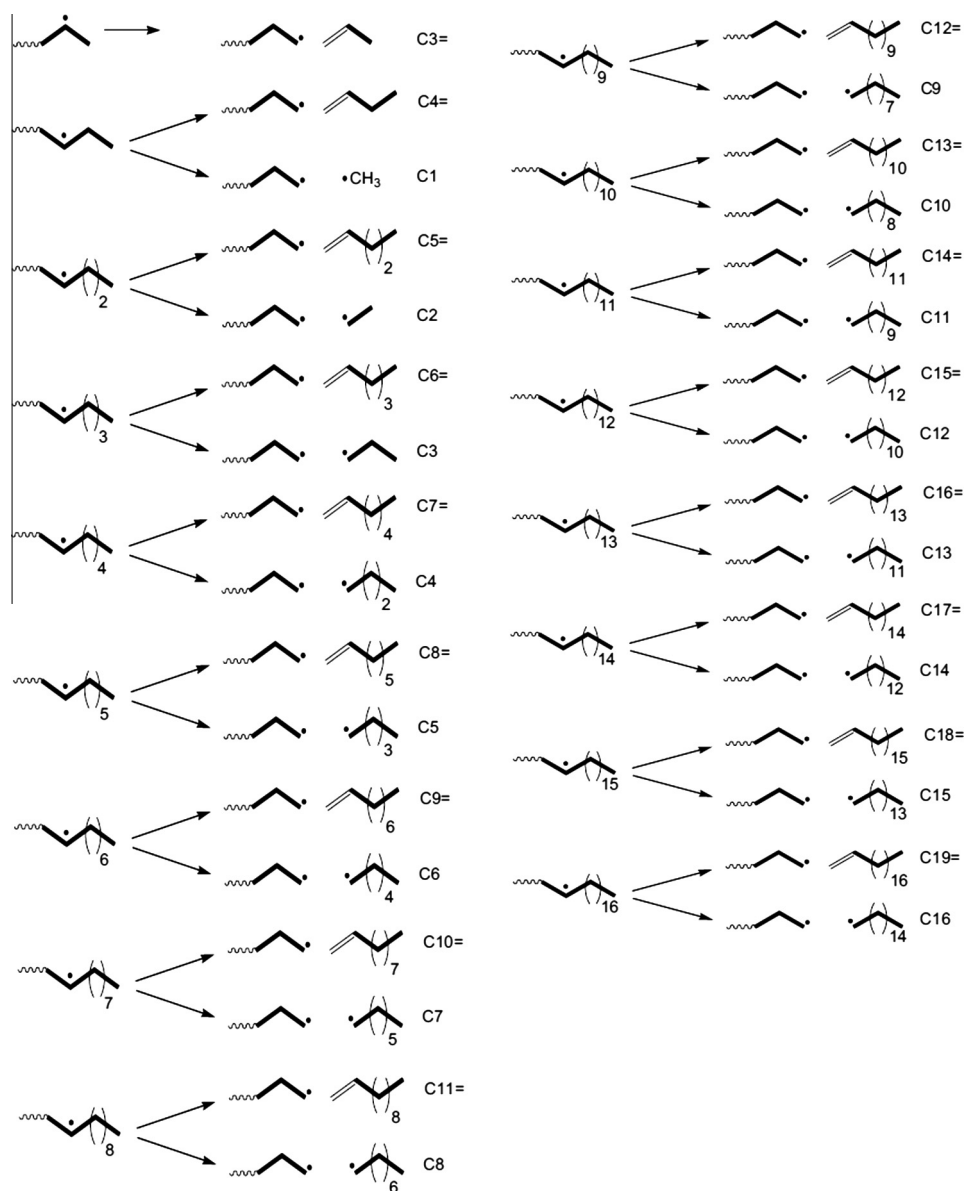
Combining the above reaction families and the method of moments, a detailed representation of the mechanistic chemistry was created.  $\beta$ -Scission reactions are the primary routes to LMWP formation. The UZ pathway forms ethylene (C2=) through end-chain  $\beta$ -scission. The other LMWPs are formed via mid-chain  $\beta$ -scission of the specific mid-chain radicals. The mid-chain  $\beta$ -scission products of each specific radical are depicted in Fig. 12. The n-1 alkene product is formed directly from the  $\beta$ -scission of the nth position mid-chain radical. The n-2 alkyl radical is also formed by  $\beta$ -scission of the nth position mid-chain radical, which can then form the n-2 alkane by abstracting hydrogen from another polymer chain.

### 3.9.2. Reaction mechanism for paraffin wax pyrolysis

Many of the steps in the chemical mechanisms for paraffin cracking are understood in a general sense, but some of the



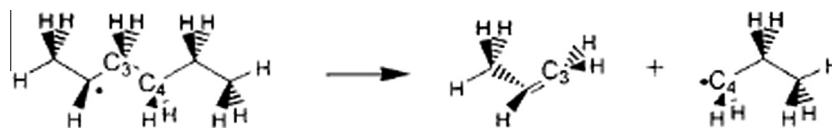
**Figure 11** Reaction pathways included in the mechanism for HDPE. (1) Bond fission, (2) radical recombination, (3) allyl bond fission, (4) hydrogen abstraction, (5) mid-chain  $\beta$ -scission, (6) radical addition, (7) end-chain  $\beta$ -scission, (8) disproportionation, (9) 1,4-hydrogen shift, (10) 1,5-hydrogen shift, (11) 1,6-hydrogen shift, (12) 1,7-hydrogen shift, (13)  $\chi, \chi + 3$ -hydrogen shift, (14)  $\chi, \chi + 4$ -hydrogen shift, and (15)  $\chi, \chi + 5$ -hydrogen shift.



**Figure 12**  $\beta$ -Scission products of specific mid-chain radicals during HPDE pyrolysis. Alkanes are formed by hydrogen abstraction by alkyl radicals, which is one possible reaction channel available to these alkyl radicals.

details are still unknown. For instance, in thermal cracking and acid-catalyzed cracking, a monomolecular  $\beta$ -scission rule is well-known and generally accounts for most of the C–C bond cracking 1, 2.

The initiation step seems fairly well understood to be C–C bond fission to form two radicals, with the preferred C–C ruptures occurring between the most highly substituted carbons [26].





#### 4. Conclusion

Thermal degradation process for depolymerization of HPDE to useful hydrocarbon fuels has been studied at 400 and 450 °C for residence time 0.5–3 h in a batch reactor. Paraffin wax was used as co-feed. Characterization studies by GC and FT-IR indicate that the depolymerization products are essentially all straight chain hydrocarbons. GC studies show that both gaseous and liquid fuel products of the thermal cracking process include hydrocarbon compounds ranging from C<sub>1</sub>–C<sub>5</sub> and C<sub>5</sub>–C<sub>26</sub>, respectively. It has been shown that the yield and composition of hydrocarbon fuel products varies with HDPE/wax ratio, residence time and reaction temperature. The product yield varied with both, increasing pyrolysis temperature and residence time. The gaseous effluent comprised mainly of C<sub>1</sub>–C<sub>4</sub> hydrocarbons dominated by methane and ethane at a high wax content, high temperature and long reaction time. However propane and butane were increased with higher HDPE content. Also, the different variables affected the chain length of the paraffinic and olefinic compounds of the pyrolytic oil. The combination of the different classes of compounds in the pyrolytic oil compared very well with the composition of gasoline and diesel fuels light gas can be used as heat source. By converting waste plastic to fuel, we solve two issues: (1) the transport of plastic waste to landfill or as a refuse derived fuel to mass burning facilities. (2) and the other of the fuel shortage. These dual benefits, will exist only as long as the waste plastics last, but will surely provide a strong platform for us to build on a sustainable clean and green future.

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