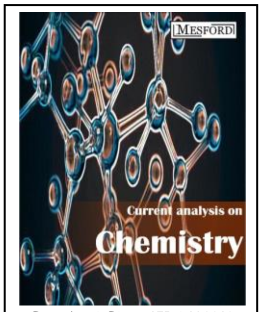

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The Pyrolysis of High Density Polyethylene and Polystyrene Wastes as Environmental Problem Using Used FCC and Ga/Used FCC Catalysts and Different Heating Rates to Produce the Valuable Products

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Abstract:

Thermal degradation of high density polyethylene and polystyrene wastes and their 50:50 mixture have been investigated over used FCC and Ga/used FCC catalysts and different heating rates. The pyrolysis experiments were carried out in a semi batch stirred reactor and TGA instrument. The results show that pyrolysis of polystyrene leads to the production of aromatics, although the role of un-zipping mechanism in the presence of zeolite based catalysts was significantly reduced, but the produced dimer, trimer and tetramers were also decreased and products were often in the gasoline range. In pyrolysis of the 50:50 mixture, aromatics were the main product, which significantly increased with Ga/used FCC. Wax was the main product of thermal degradation of polyethylene, while used FCC and Ga/used FCC catalysts produced liquid in the gasoline range however Ga/used FCC increased the aromatics significantly. Heating power as function of heating rate decreased the cyclic products and the produced coke in the catalytic pyrolysis of polyethylene obviously while heating power had no obvious effect on the polystyrene pyrolysis. By using TGA instrument, the results showed that the DTG curve of polyethylene and polystyrene mixture at low and moderate heating rates was different from the high rate.

Novelty Statement

The results of this paper show that the heating rate has a significant effect on the degradation of polymers. At low heating rates, the type of polymer structure and chemical band is very effective in degradation, while its effect decreases with increasing heating rate. On the other hand, the heating rate and the type of catalyst especially Ga/used FCC, have significant effect on the pyrolysis products that can be helpful in the economization of pyrolysis.

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HDPE; Polystyrene; Polymeric Waste; Used FCC; Ga/used FCC; Heating Rate; Pyrolysis.

1. INTRODUCTION

Many environmental and social problems such as the loss of natural resources, environmental pollution and depletion of landfill space are rooted in waste plastics. Waste plastics are a significant portion of the total municipal solid waste (MSW) and this is expected to continue in the future with the significant increase in the volume and range of plastic products in use [1, 2]. The packaged polymeric films containing commercial polyethylenes and disposable parts (polystyrene) are the main groups of non-recyclable plastics and as significant environmental problem needs to be treated and disposed in landfill. The non-renewable resources of fossil fuels beside the environmental issues stimulate the development of renewable resources. The plastics waste containing polyethylene and polystyrene are the most abundant and inexpensive sustainable source of carbon that can be converted to liquid fuels and chemicals [3-5].

The pyrolysis is a thermal cracking process in which high molecular weights of polymers is converted to low molecular weights in the absence of oxygen [6, 7]. The pyrolysis reaction can be carried out with and without catalyst. Generally, besides structural and process parameters, the type of chemical bonds and side groups in a polymer can determine the final product [8, 9]. Catalysts can affect the type and size of final products due to the fact that at their surface or pore channels, the activation energy is significantly reduced though the catalyst influence decreases with temperature increasing [10-12].

The pyrolysis of polyolefinic wastes using zeolite catalysts is one of the most acceptable and feasible processes to control the degradation mechanism and development of cracking

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processes allowing the products to be upgraded by conversion into the desirable products [13, 14]. The cracking of polymer chains over zeolites occurs on the catalyst surface and/or over the acid sites present in the pore channels. The formed low molecular weight chains in the pyrolysis, can subsequently enter the zeolite pores undergoing different secondary reactions, depending on the varied specification of the zeolites [15-17]. The low cost of spent FCC plus metal promoted used FCC catalysts can be the potential catalysts in the polymer pyrolysis to produce the maximum condensable products in the gasoline range. The presence of low content of different metals in the spent FCC plays important role in the pyrolysis [15, 18].

The pyrolysis products divided into two main groups containing char and volatiles. The volatiles includes condensed liquids as condensables and the high calorific value gases as non-condensables. The type, size and amount of evaporable and non-evaporable components depend on the process parameters such as polymer type, temperature, heating rate, catalyst type and amount, reactor, carrier gas and related degradation mechanisms [19-21].

Cullis and Hirschler [22] have proposed four mechanism containing unzipping, Random-chain scission, Chain-stripping and Cross-linking for the degradation of polymers. It appears that all of these mechanisms happen in the pyrolysis process with different shares. The share of each mechanism depends strongly on the polymer type though the process parameters such as temperature, heating rate and catalyst can change the degradation mechanism perfectly [11, 18].

The degradation mechanisms can affect the product yield, type and size. For example, unzipping boosts the monomer production and chain scission leads to linear scission while cross-linking mechanism in the complex process tends to produce the non-linear molecules and aromatics and also increases the polyaromatics as non-evaporables [11, 18, 23].

Polyethylene and polystyrene are the vast majority of non-recyclable plastics that are sent to landfills. Also understanding the degradation mechanisms and the effective process and structural parameters can help us to produce the desirable products economically. In this paper, we report the effect of used FCC and Ga/used FCC catalysts and heating rate on the yield of pyrolysis, liquid composition and pyrolysis mechanisms following two main strategies: (i) The effect of used FCC and Ga/used FCC and different heating power on the pyrolysis of HDPE, polystyrene and the (50:50) mixture of them as a practical program using a pyrolysis lab plant (Fig. **1**) and (ii) the mechanism study of the (50:50) mixture of HDPE and polystyrene degradation using TGA method.

2. EXPERIMENTAL

2.1. Material

The polymeric material containing shredded parts using HDPE 52518 and polystyrene 1540 grades from Jam Petrochemical Company (Iran) and Tabriz Petrochemical Company (Iran) respectively. Nitrogen gas (purity 99.99%) was supplied by Roham Co. The Ga(NO3)2 from Merck chemical plus the spent FCC catalyst was obtained from Abadan FCC Refinery.

2.2. Instruments

2.2.1. Catalyst Preparation

The spent catalyst as inactive catalyst was regenerated at 650oC under mild steaming for 4 hours to remove the coke. To produce Ga/used FCC catalyst, 0.78g of Ga(NO3)2 was dissolved in distilled water (100g) under slow stirring at 90oC. In this paper, the wetness incipient method was used to preparation Ga/used FCC catalyst. The Ga solution was added to the regenerated used FCC (30g) at a lab rotary (RV8 model). To reach the dried mixture and without water, the rotary temperature and rotation speed were increased step by step. After wetness incipient, the Ga/used FCC was dried in an oven at 120oC for 16 hours. The calcination of catalyst was done for another 4 hours at 650oC [18].

2.2.2. Analyzing Instruments

To detect the varied metals on the used FCC and Ga/used FCC catalysts, Quantax 200 energy dispersive X-ray spectroscope (EDX) system was used at a WD of 23.00 and 15 KV. Meanwhile EDX was used to calculate Si/Al ratio after Al and Si detecting. To calculate the Surface area of catalysts, BET method using Quantachrome Corp. Nova2200, Version 7.11 was used from adsorption isotherms of nitrogen at 77K.

To investigate the degradation trend of polyethylene and polystyrene mixture, A Netzsch TG 209 thermo-balance was used to carry out the thermo-gravimetric analysis (TGA). The sample mass was 12.0-13.0 mg. The TGA experiments were performed in a nitrogen atmosphere (99.99% minimum purity) with a flow rate of 30 ml min^{-1}.

One of the most important parameters for the degradation of polymers is the activation energy of degradation, which, due to the complexity of polymers, is used by different models to determine its value. For this subject, it is assumed that the rates of conversion are proportional to the concentration of reacted material. The conversion rate and mass loss of polymers are expressed as follows:

$$\frac{\partial x}{\partial t} = \beta\frac{\partial x}{\partial T} = K(T)f(x) \qquad (1)$$

Where "β" is the heating rate and "x" the degree of advance is

$$x = \frac{W0-W}{W0-Wf} \qquad (2)$$

Where W is the weight of the sample at a given time t, W0 and Wf, refer to values at the beginning and the end of the weight loss event of interest respectively. K(T) and f(x) are functions of temperature and conversion, respectively.

The kinetic parameters, activation energy (Ea) and pre-exponential factor (A) of the 50/50 mixture of HDPE and polystyrene degradation under each heating rate, were determined by the integral method [24, 25]. To consideration of degradation, many investigators assumed that solid fuel pyrolysis is a first order reaction [26, 27].

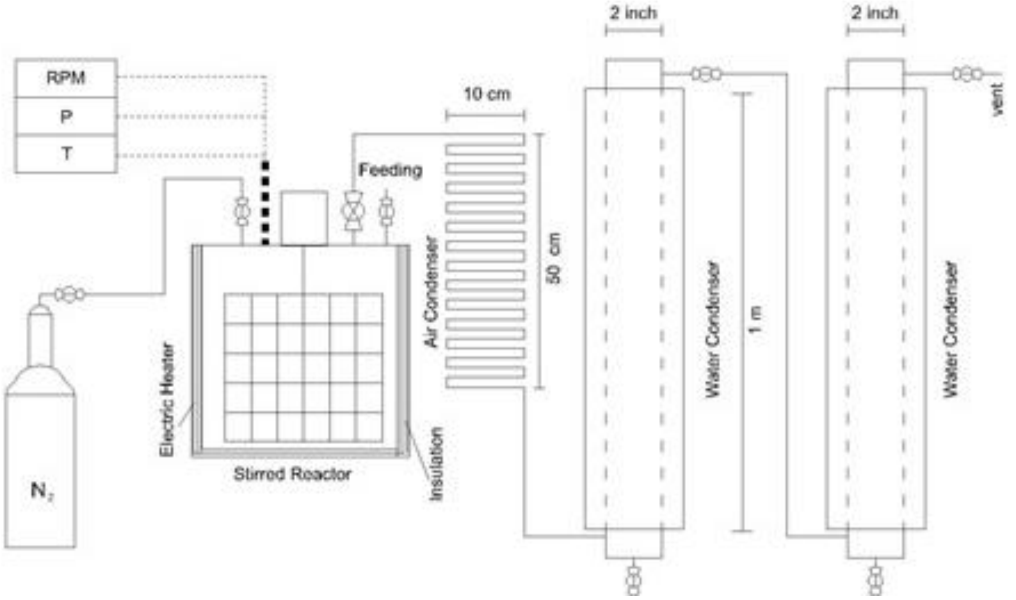

Fig. (1). Flow scheme of the laboratory stirred reactor.

To identify and consideration the varied components and carbon number in the condensed products, a gas chromatograph mass spectrometry of model GC–MS-QP5000 was used. A capillary column (60 m*0.32 mm) coated with a 1 µm film of DB-1 was used to carry out the identify analyses. The oven temperature was programmed, 40 oC hold for 10 min to 300 oC at 5 oC min-1 hold for 10 min. The components were identified using the NIST12 and NIST62 library of mass spectra and subsets HP G1033A.

2.2.3. Pyrolysis Process

The pyrolysis experiments were carried out using a 1 L semi-batch stirred reactor made of 316 stainless steel under atmospheric pressure. Fig. (**1**) shows the schematic diagram of pyrolysis set up. The experiments conditions were HDPE, polystyrene and their 50:50 mixture as row materials, used FCC and Ga/used FCC as catalysts, heating power (1000-4000 W), nitrogen stream (300 ml min-1), agitator speed (50 RPM) and the final temperature of 450 oC. At ambient temperature, the mixture of catalyst and polymer was added to the reactor and then after purge of the reactor using nitrogen gas, reactor heater under specific heating power was turned on. Under nitrogen atmosphere as carrier, the evaporative products are came out from the reactor and after passing through the three condensers containing an air condenser and two water condensers.

A portion of gaseous product that condensed in the water condensers and stored in the sampling bottles as the condensed product and the non-condensable product vented from the last condenser. Without any analysis, the non-condensable products were vented and the condensed hydrocarbons products (residue in the condensers contained C4 to C10+) were identified using GC–MS. To determine the non-condensable yield, the coke yield was determined gravimetrically after completion of the reaction and by subtracting the weight of condensed hydrocarbons and solid products from the sample weight, the gas yield was calculated.

3. RESULTS AND DISCUSSION

Table **1** shows the characteristics of used FCC and Ga/used FCC zeolites including BET surface area and elemental structure also different metals however their Si/Al atomic ratio were little different from each other and the Ga/used FCC had lower specific surface area compared to the used FCC catalyst.

Table 1. The Specification of used FCC and Ga/used FCC Catalysts.

Specification	Used FCC	Ga/used FCC
Surface Area (m^2 g^{-1})	235.0	215.2
Si/Al	6.0	5.9
Ga (%)	0.00	0.82
Na (%)	0.30	0.29
Ca (%)	1.54	1.52
Fe (%)	0.20	0.19
V(ppm)	450	435
Ni(ppm)	180	175

The condensable products, solid residue and non-condensable as pyrolysis products plus the composition and specification of condensed products using used FCC & Ga/used FCC and different heating power are shown in Tables **2-13**. Furthermore, to study the degradation mechanisms, the degradation trend of HDPE: polystyrene mixture (50:50) was studied using TGA test method to consideration the pyrolysis mechanisms.

3.1. The pyrolysis of HDPE

The effect of HDPE content and used FCC/HDPE ratio on the pyrolysis of HDPE was considered using a semi-batch stirred reactor. The pyrolysis products of polyethylene under

Table 2. The Effect of Used FCC Catalyst on the HDPE Pyrolysis Products Yield and the Condensed Product

HDPE (g)	Used FCC (g)	Catalyst/ Polymer (%w/w)	Condensed product (%)	Gas (%)	Coke (%)	Paraffins (%)	Olefins (%)	Naphthenes (%)	Aromatics (%)	Olefin/ Paraffin
200	0	0	92.8	6.3	0.9	n.d.	n.d.	n.d.	n.d.	n.d.*
200	10	5	88.1	10.8	1.1	17.5	72.3	7.9	2.3	4.13
200	20	10	85.2	12.5	2.3	16.1	74.1	4.7	5.1	4.60
200	30	15	81.8	14.1	4.1	15.4	75.6	2.8	6.2	4.90
100	15	15	79.4	18.5	2.1	16.9	79.3	2.3	1.5	4.69
300	45	15	71.4	22.1	6.5	13.9	71.2	6.6	8.3	5.12

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W.

*Not determined.

Table 3. The Effect of used FCC Catalyst on the Carbon Number Distribution and Density of the HDPE Pyrolysis Condensed Product Composition.

HDPE (g)		200	200	200	100	300
Used FCC(g)		10	20	30	15	45
Carbon Number	C_4	4.2	6.6	7.1	9.3	6.7
	C_5	7.3	8.2	12.3	13.2	11.3
	C_6	12.5	13.4	15.1	17.2	12.8
	C_7	15.6	16.2	19.2	19.9	14.7
	C_8	12.4	12.5	13.4	14.2	11.8
	C_9	11.6	11.7	9.1	8.2	12.2
	C_{10}	14.1	13.2	10.5	9.8	14.1
	C_{10}^{+}	22.3	18.2	13.3	8.2	16.4
Sum(C_5-C_9)		59.4	62.0	69.1	72.7	62.8
Ave. Molecular weight		119.4	114.7	107.9	102.3	113.0
Density (kg m^{-3})		765	775	787	780	795

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W

different conditions are shown in the first section of Table **2**. Furthermore, by using GC–MS, the characterization of condensed products containing naphthenes, paraffins, olefins and aromatics are given in the next section of Table **2**. The carbon number distribution, gasoline range, average molecular weight and density of the condensed products are given in Table **3**.

With and without the catalyst, the main product fraction was condensed product up to 92.8%. Although the thermal pyrolysis produced the maximum condensed share compared to the catalytic pyrolysis but the produced liquid was waxy, more viscous and non-desirable.

The effect of increasing used FCC/HDPE ratio was investigated from 0- 15% on the pyrolysis products. The results showed that the condensed product yield decreased with catalyst increasing from 92.8 to 81.8% in the studied range. Meanwhile coke and non-condensable yields increased with catalyst content of 0.9 to 4.1% and 6.3 to 14.1% respectively. The increase of coke yield may be attributable to direct relation between secondary reactions such as aromatization and dehydrogenation with the catalyst surface [18, 28].

The overall effect of increasing the HDPE content of 100 to 300 g at constant used FCC/HDPE on the pyrolysis product is shown in Table **2**. The condensed products showed a peak with HDPE content increasing while the coke increased with HDPE increasing. The results showed that for each pyrolysis reactor with a specific geometry and heating power, the amount of polymer inside the reactor will definitely affect the degradation mechanism and the results of pyrolysis. The low polymer content inside the reactor leaded to increase the chain scission and gas production. By increasing the amount of polymer from the reactor power, the material began to pyrolysis in the vicinity of the reactor body, while the material

Table 4. The Effect of used FCC Catalyst on the Polystyrene Pyrolysis Products Yield and the Condensed Product.

Polystyrene (g)	Used FCC (g)	Used FCC/ Polystyrene (w/w %)	Condensed (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffins (%)	Naphthenes (%)	Aromatics (%)	Styrene (%)
200	0	0	95.5	4.4	0.1	0.2	0.0	0.0	99.8	65.2
200	10	5	93.7	4.0	2.3	0.4	0.0	0.0	99.6	61.2
200	20	10	92.2	3.6	4.2	0.5	0.0	0.0	99.5	54.7
200	30	15	91.1	3.5	5.4	0.6	0.0	0.0	99.4	52.8

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W

in the reactor core had much lower temperature and the reactor showed a broaden temperature distribution. In general, the heat and temperature heterogeneity and the increase in residence time inside the reactor intensified the secondary reactions and produced more gas and coke.

With increasing of used FCC/HDPE in the studied range, the varied components of condensed product were olefins (72–80%), paraffins (15–18%), naphthenes (2–8%) and aromatics (2–7%). The rate of Diels-Alder reaction accelerates in the presence of zeolite catalysts with suitable size channel and acidity and the reaction activity increases with the catalyst content in the pyrolysis process [18, 26]. The results also indicated that the olefin/paraffin ratio increased with the increasing of used FCC/HDPE ratio. Meanwhile with increasing of HDPE content in the reactor at constant used FCC/HDPE ratio, olefins decreased (79.3-71.2%) and paraffins showed the same trend (16.9-13.9%). The cyclic products containing naphthenes and aromatics increased with HDPE content increasing obviously.

As shown in Table **3**, the molecular weight of condensed products decreased mildly when the used FCC/HDPE ratio increased while the yield of gasoline range increased with the catalyst content of 59.4 to 69.1%. Furthermore, in accordance with the results of polyolefin pyrolysis, the size selectively of the HDPE pyrolysis and gasoline range increased as the catalyst/polymer ratio [11, 18, 21].

The results showed that the density of condensed product increased with catalyst increasing from 765 to 787 kg m-3 and it may be depended on the increase of aromatic and cyclic compounds with catalyst increasing. The results showed that the increase of HDPE content broadened the molecular weight distribution of the pyrolysis product. In the studied range of polymer content, the gasoline range decreased (72.7-62.8%), average of molecular weight increased (102.3-113.0 g gmole-1) and the density experienced the increasing (780 to 795 kg m-3).

3.2. The Pyrolysis of Polystyrene

The effect of increasing the used FCC/polystyrene ratio from 0 to 15% on the pyrolysis products is given in Table **4**. The maximum condensed product yield was achieved without catalyst though the pyrolysis of polystyrene with and without the catalyst produced the condensed products more than 90%. The high condensed product is in relation with the nature of polystyrene and phenyl groups in the polystyrene structure and in accordance with the same documents [29, 30]. Generally, the different catalysts have no very important effect on the polystyrene pyrolysis compared to polyolefins [5, 15]. Meanwhile the coke and non-condensables had low shares though they increased with catalyst increasing. The composition of paraffins, naphthenes, olefins, aromatics and styrene yields in the condensed fraction, as a function of catalyst content are given in the next part of Table **4**. The results showed that the main component was aromatics (>99%) and the other hydrocarbons were negligible. In accordance with the same works, unzipping and/or monomer recovery was the main mechanism of polystyrene pyrolysis [31] though monomer recovery and styrene production decreased mildly with catalyst increasing (43.2-37.8%).

The carbon number distribution, molecular weight, gasoline range and density of the condensed hydrocarbons at different catalyst ratios are given in Table **5**. The results showed that C8 as the main component of the condensed products was increased with the catalyst increasing (69.7-77.4%). The results indicated that the size selectivity increased with the catalyst increasing and the gasoline range increased obviously of 75.9 to 90.7% while the C10+ share decreased with increase in the catalyst significantly (20.9-6.3%). The results showed that with the increase in catalyst content, the produced dimer, trimer and tetramer have been significantly reduced and more products were in the gasoline range. The average molecular weight of the condensables tended to decrease with the FCC catalyst increasing (127.0-117.0 g gmol-1) and density of the condensed products showed a decrease with catalyst increasing mildly of 895 to 888 kg m^{-3}.

3.3. The Effect of Ga/used FCC on the Pyrolysis of HDPE and Polystyrene

Many studies have reported some gallium-containing zeolite catalysts that convert polyolefins to aromatic hydrocarbons, mainly benzene, toluene, and xylene (BTX) in acceptable yields [32, 33]. Table **6** reports the effect of Ga/used FCC at 15% catalyst/polymer ratio on the pyrolysis products of HDPE, polystyrene and the 50:50 mixtures of them. The results showed the acceptable yield of condensed product though it seemed that the Ga/used FCC catalyst tended to produce more coke compared to the used FCC catalyst. It may be related with the more aromatization and poly-aromatic production on the surface of Ga/used FCC catalyst compared to the used FCC catalyst [11, 18]. With Ga/used FCC catalyst,

Table 5. The Effect of used FCC Catalyst on the Carbon Number Distribution and Density of the Polystyrene Pyrolysis Condensed Product Composition.

Polystyrene (g)		200	200	200	200
Used FCC/ Polystyrene (w/w%)		0	5	10	15
Carbon Number	C_4	0.0	0.0	0.0	0.0
	C_5	0.0	0.0	0.0	0.0
	C_6	0.3	0.9	1.1	1.5
	C_7	3.1	3.2	4.1	4.7
	C_8	69.7	72.2	75.2	77.4
	C_9	2.8	5.2	6.3	7.1
	C_{10}	3.2	2.3	2.5	3.0
	C_{10}^+	20.9	16.2	10.8	6.3
Sum(C_5-C_9)		75.9	81.5	86.7	90.7
Ave. Molecular Weight		127	123.7	120	117
Density (kg m^{-3})		895	892	890	888

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W

Table 6. The Effect of Ga/used FCC Catalyst on the Polystyrene, HDPE and their Mixture Pyrolysis Products Yield and the Condensed Product.

Polymer			Condensed (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffin (%)	Naphthenes (%)	Aromatics (%)
polystyrene (g)	HDPE (g)	Ga/used FCC (g)							
0	200	30	83.9	9.9	6.2	63.2	13.2	4.3	19.3
200	0	30	89.6	4.7	5.7	0.2	0.0	0.0	99.8
100	100	30	86.8	7.1	6.1	8.8	4.5	5.4	81.3

olefins was the main pyrolysis product of HDPE while aromatics had acceptable portion compared to the other hydrocarbons. The catalytic pyrolysis of polystyrene with Ga/used FCC showed no significant difference with the used FCC catalyst and it's related with the polystyrene structure. The Ga/used FCC pyrolysis of the HDPE: polystyrene mixture was a bit different. The products yields were almost like the pyrolysis using the used FCC catalyst while under Ga/used FCC catalyst, aromatics in the condensed product with 81.3% showed a significant difference about 10% with the resultant aromatics of used FCC pyrolysis. Generally the type and amount of catalyst can strongly affect the pyrolysis results containing the products share and composition [11, 12].

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W Table **7** shows the carbon number distribution, molecular weight, gasoline range and density of the condensed products of HDPE, polystyrene and the mixture pyrolysis. The results showed that C6, C7 and C8 were the main components of the HDPE pyrolysis while C8 was the main component of polystyrene and the polystyrene: HDPE mixture pyrolysis. C8 in polystyrene pyrolysis with 68.7% had significant difference compared to the polystyrene: HDPE mixture pyrolysis (54.1%).

The results indicated that polystyrene pyrolysis tended to produce the hydrocarbons in the gasoline range. By using Ga/used FCC catalyst, polystyrene pyrolysis produced the most gasoline range with 90.5%. The presence of 50% HDPE in the mixture decreased the gasoline range to 86.0% and the catalytic pyrolysis of pure HDPE just produced about 77.1%.

The average molecular weight of the condensables tended to increase with polystyrene content increasing (108.3-115.0 g gmol-1). While the density of the condensed products showed a significant increase with polystyrene increasing of 0 to 100% (810-845-896 kg m^{-3}).

3.4. The Pyrolysis of Polystyrene: HDPE Mixture (50: 50%).

In terms of the pyrolysis of polystyrene: HDPE mixture (50: 50), it can be seen from Table **8** that with increasing used FCC catalyst from 0 to 30 g, the condensed liquid decreased about 6.5% (91.8-85.3%) and the coke content (0.7-4.7%) and non-condensables (7.5-10.0%) tended to increase. The results showed that used FCC catalyst affected the product yields mildly and it may be depended on the polystyrene presence in the feed and low difference of catalyst content in the studied catalyst range. Aromatics as the main component of the

Table 7. The Effect of Ga/used FCC Catalyst on the Carbon Number Distribution and Density of the Polystyrene, HDPE and their Mixture Pyrolysis Condensed Product Composition.

Polymer (g)	HDPE	200	0	100
	Polystyrene	0	200	100
	Ga/used FCC	30	30	30
Carbon Number	C_4	3.2	0.0	1.1
	C_5	8.9	0.0	3.5
	C_6	18.8	8.7	7.9
	C_7	22.6	6.3	9.8
	C_8	16.9	68.7	54.1
	C_9	9.9	6.8	10.7
	C_{10}	11.2	2.8	8.1
	C_{10}^{+}	8.5	6.7	4.8
Sum (C5-C9)		77.1	90.5	86.0
Ave. Molecular weight		108.3	115.0	113.3
Density (kg m^{-3})		810	896	845

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W.

Table 8. The Effect of Used FCC Catalyst on the Pyrolysis Products of Polystyrene and HDPE Mixture and the Condensed Products.

Polymer		catalyst	Condensed (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffin (%)	Naphthenes (%)	Aromatics (%)
polystyrene (g)	HDPE (g)	Used FCC(g)							
100	100	0	91.8	7.5	0.7	n.d.	n.d.	n.d.	n.d.
100	100	10	90.3	7.8	1.9	14.5	19.6	1.6	64.3
100	100	20	87.9	8.8	3.3	15.3	16.2	2.1	66.4
100	100	30	85.3	10.0	4.7	17.6	8.1	3.2	71.1

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W.

condensed products indicated that the present of polystyrene in the feed could affect the condensed product composition obviously. The results showed that aromatics (64.3-71.1%), olefins (14.5-17.6%) and naphthenes (1.6-3.2%) increased with the catalyst increasing while paraffin (19.6-8.1%) tended to decrease.

The carbon number distribution, molecular weight, gasoline range and density of the condensed products of the mixture pyrolysis at differing used FCC catalyst ratios are given in Table **9**. The results showed that C8 with more than half of the condensed product was the main component. The results indicated that the gasoline range (78.4-84.0%) increased with the catalyst increasing while as another desirable result, the C10+ share decreased obviously (12.3-5.5%). The average molecular weight of the condensables tended to decrease (120.0-113.0 g gmol-1) and density of the condensed products showed a mild increase (823-833 kg m^{-3}) with catalyst increasing.

3.5. The Effect of Heating Rate

The effect of element heaters with different powers as function of heating rate was studied on the HDPE and polystyrene degradation. The pyrolysis products plus the composition of condensed liquids of HDPE and polystyrene were considered under different heater powers from 1000 to 4000 W in a semi-batch pyrolysis system (Tables **10** & **12**). The results of polyethylene pyrolysis show that the condensed (80.2-85.2%) as the main product and non-condensable products (12.5-18.4%) had a peak with increasing heater power while the coke yield decreased with increase of heater power in the studied range (3.8-1.4%).

The pyrolysis of HDPE at temperatures below 500oC follows the chain scission mechanism and the results are also in line with literature review [10]. By increasing the heating power as function of heating rate, the number of scission increases and pyrolysis exhibits less tendency towards aromatic and

Table 9. The effect of used FCC Catalyst on the Carbon Number Distribution and Density of Condensed Product Composition of Polystyrene and HDPE Mixture Pyrolysis.

Catalyst (g)		10	20	30
Carbon Number	C_4	1.1	1.4	2.3
	C_5	3.1	3.7	4.3
	C_6	5.3	5.9	7.1
	C_7	6.7	7.2	8.2
	C_8	51.2	53.6	55.9
	C_9	12.1	9.1	8.5
	C_{10}	8.2	7.8	8.2
	C_{10}^+	12.3	11.3	5.5
Sum (C_5-C_9)		78.4	79.5	84.0
Ave. Molecular weight		120.0	118.1	113
Density (kg m^{-3})		823	828	833

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Heating power: 2000W

Table 10. The Effect of Heater Power on the Products Yield and Condensed Product Composition of HDPE Pyrolysis.

Heater power (W)	Liquid (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffins (%)	Naphthenes (%)	Aromatics (%)	olefin/paraffin
1000	82.3	13.9	3.8	73.0	14.5	5.3	7.2	5.0
2000	85.2	12.5	2.3	74.1	16.1	4.7	5.1	4.6
3000	83.8	14.3	1.9	74.2	16.7	4.3	4.8	4.4
4000	80.2	18.4	1.4	74.7	17.8	3.6	3.9	4.2

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Used FCC/HDPE: 0.15

Table 11. The Effect of Heater Power on the Carbon Number Distribution and Density of the HDPE Pyrolysis Condensed Product Composition.

Heating Power (W)		1000	2000	3000	4000
Carbon Number	C_4	6.9	6.6	6.2	5.2
	C_5	8.4	8.2	10.8	12.3
	C_6	11.0	13.4	14.1	14.6
	C_7	14.8	16.2	17.6	18.2
	C_8	11.7	12.5	13.8	16.2
	C_9	11.9	11.7	12.4	14.9
	C_{10}	13.9	13.2	9.8	7.5
	C_{10}^+	21.4	18.2	15.3	11.1
Sum(C_5-C_9)		57.8	62.0	68.7	76.2
Ave. Molecular weight		119.6	116.6	112.5	109.0
Density (kg m^{-3})		778	775	771	770

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Used FCC/HDPE: 0.15.

Table 12. The Effect of Heater Power on the Products yield and Condensed Product Composition of Polystyrene Pyrolysis.

Heater Power (W)	Liquid (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffins (%)	Naphthenes (%)	Aromatics (%)	Styrene (%)
1000	90.9	3.8	5.3	0.3	0.0	0.0	99.7	59.3
2000	92.2	3.6	4.2	0.5	0.0	0.0	99.5	54.7
3000	93.2	3.8	3.0	0.6	0.0	0.0	99.4	52.4
4000	95.6	1.9	2.5	0.6	0.0	0.0	99.4	51.6

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Used FCC/polystyrene: 0.15

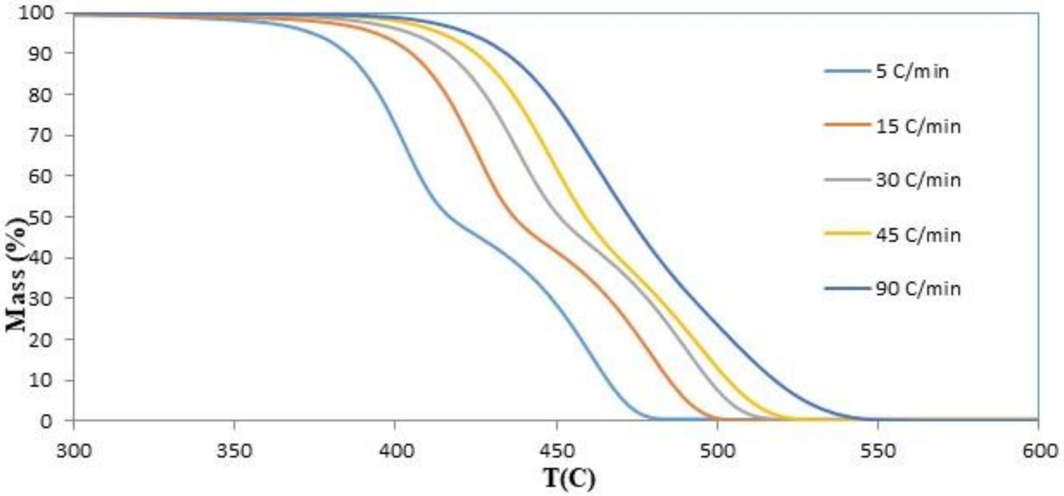

Fig. (2). TGA curves of the 50:50 mixture of HDPE and polystyrene at different heating rates (5, 15, 30, 45 and 90 oC min-1).

naphthene products. With decrease in heating power, the effect of cross-linking and chain stripping mechanisms and secondary reactions such as Diels-Alder is further increased and tends to produce more cyclic products. Olefins (73.0-74.7%) as the main component and paraffin (14.5-17.8) increased with increasing heating power moderately while the cyclic products containing aromatics (7.2-3.9%) and naphthenes (5.3-3.6%) showed the decrease in the studied heating power range. The results showed that density of the condensed products decreased with heating power (778-770 Kg m^{-3}) and it can be related to the significant difference between the cyclic and aliphatic hydrocarbons densities.

Table **11** shows the carbon number distribution of the condensed product of HDPE pyrolysis under different heating power in the reactor. The results showed that the amount of product in the gasoline range (57.8-76.2%) had increased significantly with increasing heating power while the molecular weight of products decreased with heating power increasing (119.6-109%). In general, the heating power can significantly affect the pyrolysis of HDPE and lead to produce the valuable hydrocarbons.

The effects of heater powers from 1000 to 4000 W on the pyrolysis products containing condensable, non-condensable and coke plus the composition of liquid products are shown in Table **12**. The results showed that the effect of heating on pyrolysis of polystyrene was completely different from pyrolysis of polyethylene, which could be due to the different structure of these two polymers. The results showed that by increasing the heating power, the condensed product (90.9-95.6%) increased and almost the amount of produced coke (5.3-2.5%) and gas (3.8-1.9%) decreased obviously. The heating power had no obvious effect on the liquid compounds and aromatics at all heating powers accounted for more than 99% of the condensed product. The amount of produced styrene significantly decreased with increasing heating power (59.3-51.6%). Table **13** shows that the heating power had no obvious effect on the carbon distribution of products.

3.6. The Trend of Degradation

Fig. (**2**) shows the non-isothermal mass losses of HDPE: polystyrene mixture (50: 50) using a thermo-gravimetric analyzer (TGA) at heating rates of 5, 15, 30, 45 and 90oC min^{-1}. The results indicated that with increase in the heating rate, the mixture tended to degrade at higher temperatures. Fig. (**3**) shows the related DTG graphs with the TGA curves at the previous figure. The DTG curves showed two obvious degradation peaks while 90 oC min-1 as fast pyrolysis almost showed a unimodal DTG curve.

It seems that the related pyrolysis mechanisms (i.e. chain scission and unzipping) and their shares in the degradation were changed under different heating rates and degradation temperature. Under low heating rates, the low supplied energy could control the degradation selectivity. The unzipping and chain scission of polystyrene chains needed to lower energy compared to polyethylene degradation and the obvious two peaks were seen using the slow pyrolysis. The first peak was

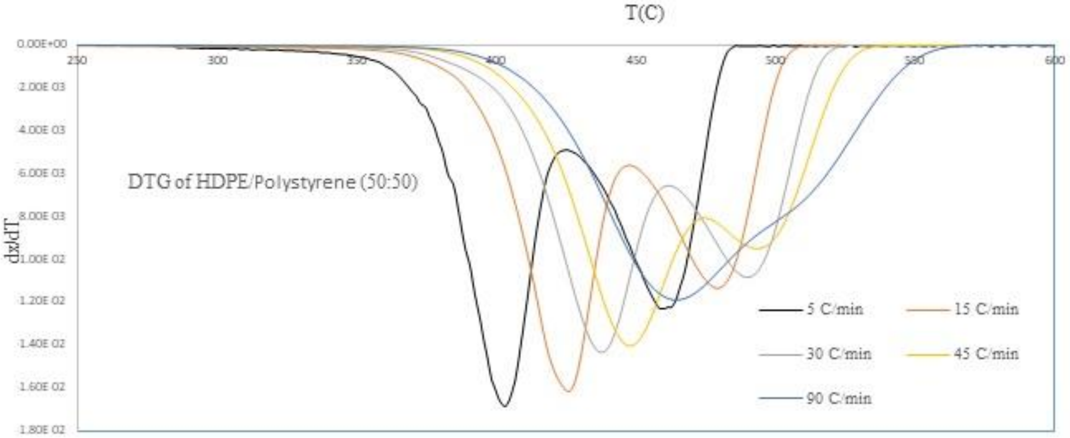

Fig. (3). DTG curves of the 50:50 mixture of HDPE and polystyrene at different heating rates (5, 15, 30, 45 and 90 oC min-1).

Table 13. The Effect of Heater Power on the Carbon Number Distribution and Density of Polystyrene Pyrolysis Condensed Product Composition.

Heating power (W)		1000	2000	3000	4000
Carbon Number	C_4	0.1	0.0	0.0	0.0
	C_5	0.2	0.0	0.0	0.0
	C_6	1.3	0.9	0.8	0.8
	C_7	3.3	3.2	3.0	3.9
	C_8	74.1	72.2	71.9	70.8
	C_9	3.1	5.2	7.6	8.2
	C_{10}	1.6	2.3	2.8	3.2
	C_{10}^{+}	16.3	16.2	13.9	13.1
Sum(C_5-C_9)		82.0	81.5	83.3	83.7
Ave. Molecular Weight		123.0	123.7	122.7	122.2
Density (kg m^{-3})		897	892	889	886

Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450oC, Used FCC/polystyrene: 0.15.

almost the degradation of polystyrene and the next showed the pyrolysis of polyethylene chains. The heating rates of 5, 15, 30 and 45 oC min-1 followed this trend while with increase in the heating rate, the second peak got smaller.

At heating rate of 90 oC min-1 as fast pyrolysis, the high supplied energy was the most important factor and the degradation of both polymers almost occurred simultaneously and the degradation of the mixture showed a unimodal peak.

The typical plots of ln[−ln(1−x) T-2] versus T-1, indicating that for the heating rate of 90 oC min-1, single first order reaction should be used to describe the pyrolysis process, whereas two independent first order reactions were in accordance with the other heating rates. The integral method [24, 25] was applied separately to each of the stages. To do so, the conversion x was recalculated for each reaction. From the slope of each line, the value of Ea and A could be obtained for different stages.

The activation energies and pre-exponential factors were obtained by different heating rates using integral method are shown in Table **8**. The results indicated that activation energy was decreased with increase of heating rate obviously (243.0-192.5 kJ mol-1). The kinetic parameters were calculated in the range of x=2 to 99%, which represented the main pyrolysis region. The good correlation coefficient indicated that the corresponding independent first order reaction model fitted the experimental data very well. At 5oC min-1, the two stages of the pyrolysis process showed the activation energies of 198.7 kJ mol-1 and 287.3 kJ mol-1 respectively. In the first subinterval of temperatures (about 345–425 °C), the polystyrene as weaker bonds degraded and needed to lower energy while the polyethylene chains as strong bonds consumed more energy in the next subinterval (425–485 °C) stage. Under heating rate of 15 oC min-1, the temperature region of 362-449 oC as first interval with the activation energy of 183.6 kJ mol-1 and the next temperature range (449-505 oC)

Table 14. The Effect of Heating Rates on the Kinetic Parameters and Characteristic Temperatures.

β (^{o}C min^{-1})	Temperature (^{o}C)	Conversion range (%)	E_a (kJ mol^{-1})	Average E_a (kJ mol^{-1})	A(min^{-1})	R^{1}
5	345-425	2-50	198.7	243.0	3.2*10^{9}	0.978
	425-485	50-99	287.3		4.7*10^{16}	0.992
15	362-449	2-50	183.6	222.2	1.1*10^{10}	0.985
	449-505	50-99	260.8		1.6*10^{16}	0.989
30	370-462	2-50	179.7	216.4	3.5*10^{9}	0.992
	462-521	50-99	253.1		7.4*10^{9}	0.987
45	380-476	2-50	161.6	203.4	2.3*10^{9}	0.990
	476-533	50-99	245.2		8.6*10^{9}	0.995
90	377-561	2-99	192.5	192.5	1.7*10^{10}	0.973

1R: correlation coefficient

with 260.8 kJ mol-1 showed the bimodal degradation curve. With the heating rate of 30 and 45 oC min-1, the second peak tended to get smaller and the heating rate of 90 oC min-1 as fast pyrolysis had almost unique trend compared to the slower heating rates. Generally based on Table **14**, the activation energy was increased with increase of degradation conversion and temperature in a specified heating rate.

4. CONCLUSION

A laboratory catalytic system has been used to obtain a range of volatile hydrocarbons by degradation of HDPE, polystyrene and their 50:50 mixture with used FCC and Ga/used FCC under different heating rates. The pyrolysis of HDPE without catalyst tended to produce the waxy product while used FCC and Ga/used FCC produced the light oil in the gasoline range as the main product. HDPE pyrolysis showed that Ga/used FCC had more activity in aromatization reaction and liquid production compared to the used FCC catalyst. The different amounts of HDPE inside the pyrolysis reactor indicated that the products were changed with the polymer content. The higher polymer contents tended to increase the cyclic and aromatic products while the lower contents increased the non-cyclic products. In the pyrolysis of polystyrene, the polymer structure was the effective parameter and the catalysts had no significant effect on the products. Styrene was the main product of polystyrene thermal pyrolysis while the catalysts decreased the produced styrene obviously. The results showed that heating power as function of heating rate had significant effect on the HDPE pyrolysis while the heating power had less impact on the polystyrene pyrolysis. The degradation of 50:50 mixture of HDPE and polystyrene was studied using TGA instrument. By using the medium and low heating rates and the controlled supplied energy, the pyrolysis had degradation selectivity and the polymeric mixture almost degraded separately and showed obvious bimodal DTG curves. While the heating rate of 90 oC min-1 as fast pyrolysis with high supplied energy degraded all of the polymer bonds in the mixture without degradation selectivity and created the unimodal degradation curve. The activation energy was decreased with increase of heating rate while increased with the degradation temperature and the higher heating rates appeared to be the more economically favorable in terms of cost efficient operation.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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