

# Effect of temperature, heating rate and zeolite-based catalysts on the pyrolysis of high impact polystyrene (HIPS) waste to produce fuel-like products

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Received: 4 May 2018, Accepted: 18 August 2018

## ABSTRACT

Pyrolysis of high impact polystyrene (HIPS) waste has been investigated under different process parameters, such as temperature, heating rate and types of zeolitic catalysts to produce valuable liquid products. Liquid, gas and coke as products of pyrolysis and aromatic, naphthene, olefin and paraffin as liquid components were obtained and their molecular weight distributions were studied with changing the process parameters in a stirred reactor. Aromatic-rich hydrocarbons within the gasoline range were the main pyrolysis products. Type of zeolitic catalysts, temperature and heating rate had significant effects on the products quality and quantity. Non-isothermal mass losses of high impact polystyrene were measured using a thermo-gravimetric analyzer (TGA) at heating rates of 5, 15, 30, 45 and 90°C min<sup>-1</sup> until the furnace wall temperature reached 600°C. The DTG (differential thermal gravimetric) curves showed that heating rate had no obvious effect on the degradation trends in the studied range, and by increasing heating rate, the activation energies were decreased obviously from 222.5 to 183.6 kJ mol<sup>-1</sup>. **Polyolefins J (2019) 6: 43-52**

**Keywords:** High impact polystyrene; temperature; heating rate; catalyst; TGA.

## INTRODUCTION

High impact polystyrene (HIPS) is the copolymer of polystyrene and butadiene rubber with improved toughness in comparison with polystyrene. Butadiene rubber as dispersed rubber phase in the polystyrene media with great increase in impact strength and environmental stress cracking resistance (ESCR) has led to a considerable growth in the range of applications for this polymer [1-2], including refrigeration cabinets, general packaging, electronics, toys, household appliances and disposables.

The increasing growth of HIPS waste can cause a lot of environmental problems in the related industries. On the other hand, HIPS waste has high volatile, fixed carbon and aromatic enriched content with heating value greater than the classic fuels. The understanding of effect of effective parameters on the thermal degradation processes, especially pyrolysis and gasification of various HIPS wastes can play an important role from the point of view of environment protection, and allowing to produce the valuable materials and energy [3-6].

Thermal degradation of natural and synthetic

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polymers at high temperatures in the absence of oxygen (pyrolysis) can be a reliable solution to dispose polymeric wastes [7-8]. In pyrolysis process under high temperatures, high molecular weight chains are broken down into low molecular weight ones. Depending on the polymer type, with acceleration of the secondary reactions and the formation of hot spots, some cokes are also produced. Coke, amount of liquid and gas and composition of products from pyrolysis process depend on the different structural and process parameters, such as polymer type, temperature, catalyst, reactor, carrier gas and maybe some other unknown parameters [8-11].

Degradation mechanisms, including chain-stripping, cross-linking, un-zipping and chain scission are the known mechanisms for the thermal degradation of polymers. It appears that all of the above mentioned 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 type and ratio can affect the degradation mechanism perfectly [12-15].

Catalytic degradation of polymeric materials can control the degradation mechanisms and the catalyst used can be a key parameter in determining the type and size of the final pyrolysis products. The catalytic products of the hydrocarbonic polymers like HIPS are highly useful and can be utilized as fuels or chemicals in the various applications. In pyrolysis, zeolite catalysts lower the required energy and time obviously. A narrow variety of products depending on the pore size of catalyst is another advantage of catalytic pyrolysis in comparison with the thermal cracking [16-18].

Temperature as a critical and key parameter of pyrolysis plays an important role in determining the pyrolysis products, and high pyrolysis temperatures can decrease the role of catalyst. In sum, a review of the literature showed strong dependence of carbonization products to process parameters, such as temperature, catalyst type and polymer/catalyst ratio, heating rate and residence time [19-20].

Thermo-gravimetric analysis (TGA) is one of the commonly used techniques for consideration of degradation trend in terms of different process parameters, such as temperature, heating rate and etc. The effect of real parameters on the degradation mechanisms and activation energy can be studied by using TGA measurements. TGA can especially be used for study of the degradation behavior of polymer

materials, including homo-polymers, copolymers and etc., [13-15].

The goal of this paper is to elucidate the effect of temperature, heating rate and different zeolite-based catalysts on the pyrolysis of high impact polystyrene to produce the valuable products. Hence, we have reported the effect of zeolitic catalysts, such as used FCC (fluid catalytic cracking), HZSM-5 (hydrogen form Zeolite Socony Mobil-5) and Ga/used FCC, temperature and heating rate on the pyrolysis yield and the composition of the condensed products as well as the effect of heating rate on the degradation trend of HIPS using TGA method. Our results show that the studied parameters have a significant effect on the residence time, amount of produced styrene, the distribution of molecular weight, and the composition of condensed product. Also, the trend of degradation of HIPS does not change significantly in the range of studied heating rates.

## EXPERIMENTAL

### Materials

HIPS (7240 grade) was supplied by Tabriz Petrochemical Company, nitrogen gas (purity 99.99%) by Roham Co and spent FCC catalyst by Abadan FCC Refinery. Ga(NO<sub>3</sub>)<sub>2</sub> was purchased from Merck Chemical, and HZSM-5 catalyst was supplied by Sudchemi Company.

### Instruments and methods

#### *Catalyst preparation*

The spent FCC catalyst was regenerated at 650°C and steamed slightly for 4 hours. 0.78g Ga(NO<sub>3</sub>)<sub>2</sub> was dissolved in distilled water (100g) under slow stirring at 90°C. The Ga/used FCC catalyst was prepared by the wetness incipient method. The Ga solution was added to the regenerated used FCC (30g) in a laboratory rotary dryer (RV8 model). The rotary temperature and rotation speed were raised step-by-step to obtain a dry mixture. Then, the Ga/used FCC was dried in an oven at 120°C for 16 hours, and then calcined for another 4 hours at 650°C prior to the experiment.

#### *EDX*

A Quantax 200 energy-dispersive X-ray spectrometer (EDX) at a WD of 23.00 and 15 kV was used to detect the metals on the surface of used FCC, Ga/used FCC

and HZSM-5 catalysts. Furthermore, Si/Al ratio was calculated after detection of Al and Si elements.

#### BET

BET (Brunauer–Emmett–Teller) method (Quantachrome Corp. Nova2200, Version 7.11) was used to calculate the surface area of the catalysts from the adsorption isotherms of nitrogen at 77K.

#### TGA

Thermogravimetric analysis was performed on a Netzsch TG 209 thermo-balance. The initial mass of all the samples was 12.0–13.0 mg at the same sizes. The experiments were carried out in a nitrogen atmosphere (99.99% minimum purity) with a flow rate of 30 ml min<sup>-1</sup>.

Generally for polymer degradation, it is assumed that the rates of conversion are proportional to the concentration of reacted material. The rate of conversion can be expressed by the following basic rate equation:

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

Where " $\beta$ " is the heating rate and " $x$ " is the degree of advance defined by:

$$X = \frac{W_0 - W}{W_0 - W_f} \quad (2)$$

Where  $W$  is the weight of the sample at a given time  $t$ ,  $W_0$  and  $W_f$  refer to values at the beginning and the end of the weight loss event of interest, respectively.  $f(x)$  and  $K(T)$  are functions of conversion and temperature, respectively.

For each heating rate, the kinetic parameters, activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) of HIPS pyrolysis were determined by the integral method [21]. Many investigators assumed that solid fuel pyrolysis is a first-order reaction [22–24].

#### GC/MS

Identification of varied compounds in the condensed products was carried out by a gas chromatograph mass spectrometer (GC/MS) of model GC–MS–QP5000. The analysis was performed on a 60 m × 0.32 mm capillary column coated with a 1  $\mu$ m film of DB-1. The oven temperature was programmed as follow: a

40°C hold for 10 min, ramp to 300°C at 5°C min<sup>-1</sup>, and hold for 10 min. Pure helium was used as the carrier gas at a rate of 1.4 ml min<sup>-1</sup>. The injector/transfer line/trap temperatures were 220/250/200°C, respectively. Compounds were identified by means of the NIST12 and NIST62 library of mass spectra and subsets HP G1033A.

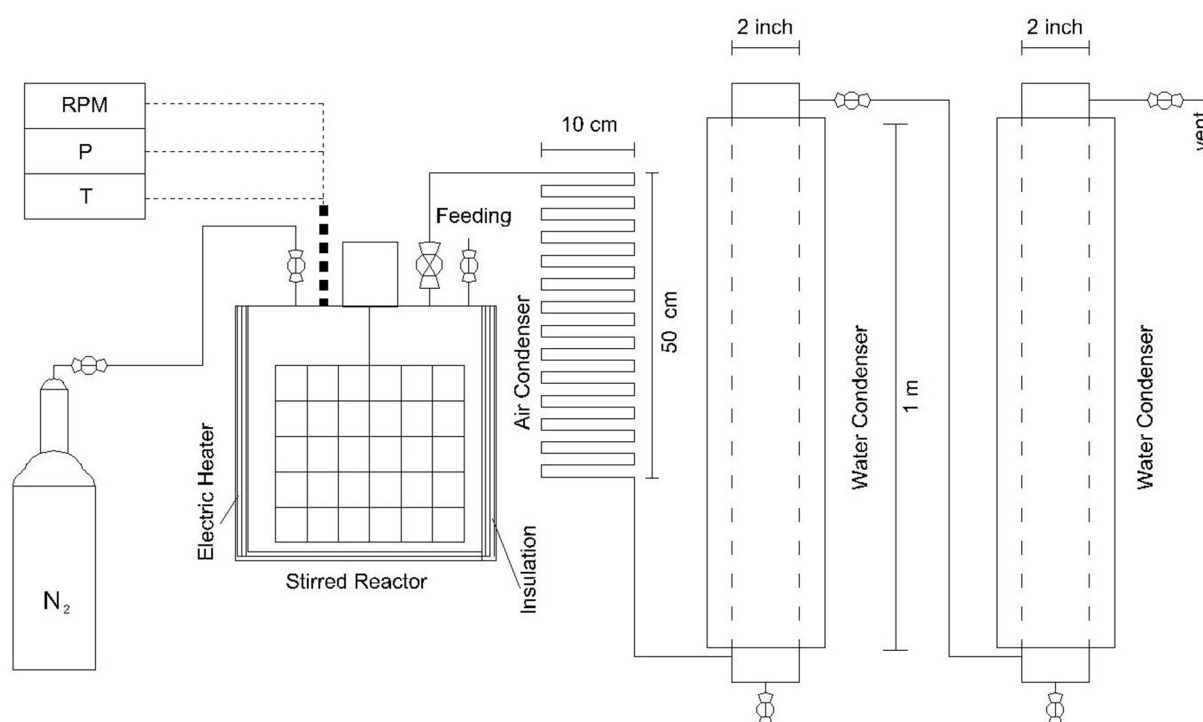
#### Pyrolysis process

Pyrolysis experiments were carried out in a 1 L stirred semi-batch reactor (buchi pilot plant with a custom built pressure reactor, temperature control by using a K-type thermostat with electrical heating and special paddle stirrer) under atmospheric pressure. The schematic diagram of pyrolysis system is shown in Figure 1. The fixed experimental conditions were as follows: 100g of shredded HIPS in the reactor, 300 ml min<sup>-1</sup> of nitrogen stream as carrier gas, and 50 rpm of agitator speed. At first, the mixture of HIPS and catalyst was added to the reactor and then the reactor heater was turned on. Under nitrogen atmosphere as carrier gas, the pyrolysis vapors were passed through three condensers including an air condenser and two water condensers (mixture of ice and water, 0°C).

The liquid product condensed in the water condensers and the non-condensable product vented from the condensers. The non-condensable products were not analyzed, and after cooling, vented through the three condensers and the condensed hydrocarbons products were stored in glass sampling bottles. The components of total condensed hydrocarbons (residue in the condensers contained C<sub>4</sub> to C<sub>10</sub><sup>+</sup>) were quantified by GC/MS and the non-condensable products were not analyzed. The solid char yield was determined gravimetrically after completion of the reaction and the non-condensable yield was calculated by subtracting the weight of the condensed hydrocarbons and solid products from the sample weight.

## RESULTS AND DISCUSSION

According to the previous studies [7–10], temperature, catalyst and heating rate as the key process parameters were considered to determine the optimal points of the pyrolysis of high impact polystyrene. By using a laboratory semi-batch stirred reactor, the effect of temperature (420–510°C) and heater power (1000–4000 W) as a function of heating rate and type of zeolite-based



**Figure 1.** Flow scheme of the pyrolysis system.

catalysts, including used FCC, Ga/used FCC and HZSM-5 were considered on the pyrolysis products. To calculate the mass balance and residue (char and the catalyst), the reactor vessel was weighted before and after the runs. The pyrolysis products are grouped together as non-condensable product (gas), condensed products (liquid) and char.

### Effect of temperature

Temperature as a key process parameter plays an important role in the thermal degradation [7-9]. Table 1 shows yield of different products and the composition of condensed liquid of high impact polystyrene pyrolysis at different degradation temperatures. In the studied range, the condensed liquid similar to other hydrocarbonic polymers [7-9] showed a maximum yield of 94.9% at 450°C, and the char yield increased with increasing temperature from 0.3 to 1.1% and the

non-condensable product had no obvious trend with the temperature (4.7-7.1%). The increase in char yield can be related to the enhancement of Diels-Alder reactions and polycyclic production with temperature [25]. The pyrolysis of high impact polystyrene produced the acceptable liquid shares (91.8-94.9%) in the studied temperature range as the applied range for the pyrolytic liquid production [7-9].

The composition of condensed pyrolysis products was identified using GC/MS as a function of temperature and the obtained results are given in Tables 1 and 2. Naphthenes (cycloalkanes), paraffins (alkanes), olefins (alkenes) and aromatics as the main structural components of hydrocarbons, carbon numbers, molecular weight and gasoline range are shown in the mentioned tables. Aromatics (93.4-95.2%), olefins (2.9-3.6%), paraffins (2.3-0.8%), naphthenes (1.4-0.4%) as components of the pyrolytic condensed

**Table 1.** Effect of temperature on the HIPS product yield and liquid composition.

T (°C)	Liquid (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffins (%)	Naphthenes (%)	Aromatics (%)	Styrene (%)	Residence time (min)
420	93.2	6.5	0.3	2.9	2.3	1.4	93.4	39.8	56
450	94.9	4.7	0.4	3.2	1.6	1.1	94.1	38.5	47
480	92.9	6.4	0.7	3.4	1.4	0.6	94.6	36.2	41
510	91.8	7.1	1.1	3.6	0.8	0.4	95.2	33.9	36

Catalyst/HIPS: 0, Carrier gas: Nitrogen, Agitator speed: 50 RPM, Heating Power: 2000W

**Table 2.** Effect of temperature on the carbon number distribution of the HIPS condensed product composition.

Temperature(°C)		420	450	480	510
Carbon Number	C <sub>4</sub>	0.2	0.1	0.1	0.2
	C <sub>5</sub>	0.5	0.4	0.8	1.6
	C <sub>6</sub>	3.4	4.2	5.4	6.4
	C <sub>7</sub>	3.5	4.3	5.7	7.3
	C <sub>8</sub>	65.2	64.5	63.1	61.2
	C <sub>9</sub>	2.5	3.2	4.2	6.8
	C <sub>10</sub>	4.9	4.6	4.8	4.7
	C <sub>10</sub> <sup>+</sup>	19.8	18.7	15.9	11.8
Sum(C <sub>5</sub> -C <sub>9</sub> )		75.1	76.6	79.2	83.3
Ave. Molecular Weight		127.4	124.5	121.0	116.7

Catalyst/HIPS: 0, Carrier gas: Nitrogen, Agitator speed: 50 RPM, Heating Power: 2000W

liquid were affected by degradation temperature obviously. The results indicated that the aromatics were the main component, and in this regard the structural parameter could limit the role of temperature in the studied range [19], nevertheless, the aromatics increased with increasing temperature moderately. The results showed that the dehydrogenation was accelerated with temperature and paraffins content decreased moderately [7-9]. Temperature had no obvious effect on the polystyrene segments and aromatics were almost the only pyrolytic product, while the pyrolysis of polybutadiene segments showed a reduction in aliphatic yield and an increase in the cyclic products with temperature increasing. This could be related to the enhancement of Diels-Alder reactions and cross-linking mechanism [8-9]. As a result, the un-zipping mechanism had a key role in the thermal degradation of HIPS and styrene had a significant share in the condensed products, however, styrene content decreased with temperature (39.8-33.9%).

Table 2 shows the distribution of C<sub>4</sub>-C<sub>10</sub><sup>+</sup> condensed hydrocarbon products, molecular weight and gasoline range with pyrolysis temperature. With temperature increasing, more chain scission occurred and the products tended toward low molecular weight (127.4-116.7 g mol<sup>-1</sup>) products and also a tendency toward a lower content of C<sub>10</sub><sup>+</sup> (19.8-11.8%). Like polystyrene

**Table 4.** Effect of catalysts on the HIPS products yield and condensed product.

Catalyst	Liquid (%)	Gas (%)	Coke (%)	Olefins (%)	Paraffins (%)	Naphthenes (%)	Aromatics (%)	Styrene (%)	Residence time (min)
no catalyst	94.9	4.7	0.4	3.2	1.6	1.1	94.1	38.5	47
used FCC	93.5	5.8	0.7	2.9	1.0	0.8	95.3	34.1	35
Ga/FCC	93.3	5.8	0.9	0.8	0.4	0.7	98.1	33.9	33
HZSM-5	90.2	8.6	1.2	1.6	0.9	1.6	95.9	32.2	29

Catalyst/HIPS: 0.15 w/w, Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450°C, Heating Power: 2000W

**Table 3.** Specification of catalysts used in the catalytic degradation of HIPS.

Catalyst	Used FCC	Ga/FCC	HZSM-5
Surface Area (m <sup>2</sup> g <sup>-1</sup> )	235.0	215.2	381.3
Si/Al	6.0	5.9	20.0
Ga (%)	0.00	0.82	0.00
Na (%)	0.30	0.29	0.18
Ca (%)	1.54	1.52	0.00
Fe (%)	0.20	0.19	0.00
V(ppm)	450	435	0
Ni(ppm)	180	175	0

pyrolysis [19], although temperature had no clear effect on the product components but the carbon number distribution of the products showed the obvious difference under the studied temperature range. Meanwhile, the gasoline range yield showed a significant increase with temperature (75.1-83.3%). The pyrolysis of HIPS could produce the aromatic enriched liquid with acceptable gasoline range as auxiliary fuel to enhance the octane number in the studied temperature range [26]. The results also indicated that like the other polymers [7, 9], the residence time of HIPS in the reactor decreased obviously with increasing temperature (56-36 min).

#### Effect of different catalysts

The structural information of different zeolite-based catalysts was identified using energy dispersive X-ray spectroscopy (EDX) analysis and BET test method (Table 3). The results showed a little difference between the Si/Al atomic ratio of Ga/used FCC and that of used FCC. It has been reported that the residue metals on the used FCC can affect the polymer degradation and pyrolysis products [27].

The effects of different types of zeolitic catalysts (catalyst/HIPS: 0.15 w/w) on the percentage of condensed liquid, non-condensables and coke as the pyrolysis products and the components of the condensed liquids in comparison with the thermal degradation are shown in Table 4. Table 5 shows the carbon number distribution of C<sub>4</sub> to C<sub>10</sub> and C<sub>10</sub><sup>+</sup>, molecular weight

**Table 5.** Effect of catalysts on the carbon number distribution of the HIPS condensed product composition.

	no catalyst	used FCC	Ga/used FCC	HZSM-5	
<b>Carbon Number</b>	C <sub>4</sub>	0.1	0.1	0.1	1.2
	C <sub>5</sub>	0.4	0.7	0.7	3.3
	C <sub>6</sub>	4.2	4.7	5.2	5.9
	C <sub>7</sub>	4.3	5.3	5.8	6.2
	C <sub>8</sub>	64.5	69.1	70.1	68.8
	C <sub>9</sub>	3.2	3.9	3.7	7.1
	C <sub>10</sub>	4.6	3.4	3.1	1.4
	C <sub>10</sub> <sup>+</sup>	18.7	12.8	11.3	6.1
<b>Sum(C<sub>5</sub>-C<sub>9</sub>)</b>	76.6	83.7	85.5	91.3	
<b>Ave. Molecular Weight</b>	124.5	119.8	118.4	112.9	

Catalyst/HIPS: 0.15 w/w, Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450°C, Heating Power: 2000W

and gasoline range as a function of catalytic and thermal pyrolysis of HIPS.

Like other hydrocarbonic polymers [7-9], the condensed liquid was the main fraction of HIPS pyrolysis (93.5-90.2%). The volatile products from the catalytic pyrolysis had narrower molecular weight distribution and lower viscosity than those from the thermal degradation. In the catalytic pyrolysis, used FCC had better operation in the liquid production (93.5%) and HZSM-5 with attention to the small size channel [9-10, 15] produced the lower amount in comparison with the others (90.2%).

Hot spots, the enhancement of secondary reactions such as Diels-Alder reactions on the catalyst pores can increase the coke production on the catalyst surface and channels. The catalytic pyrolysis of HIPS resulted in higher percentage of coke (0.7-1.2%) in comparison with the thermal degradation (0.4%). HZSM-5 with smaller channel size is more prone to coke formation [9-10].

The catalytic pyrolysis of HIPS showed an acceptable operation in the gasoline range of 83.7-91.3% and the yield of C<sub>10</sub><sup>+</sup> as non-desirable product from the catalytic process (12.8-6.1%) was lower than yield of that from the thermal degradation process (18.7%).

The catalysts were less likely to follow the un-zipping mechanism and styrene production (34.1-32.2%) in comparison with the thermal degradation (38.5%).

The results also showed that the presence of catalyst decreased the residence time significantly and HZSM-5 - 29 min- had the best performance in comparison with the thermal degradation (47 min).

The composition of the condensed liquid produced from thermal degradation was composed of cyclic hydrocarbons (94.1% aromatics and 1.1% naphthenes) and aliphatic hydrocarbons (3.2% olefins and 1.6% paraffins). The composition of the condensed products from catalytic pyrolysis using Ga/used FCC was composed of aromatics (98.1%), olefins (0.8%), paraffins (0.4%) and naphthenes (0.7%). The results also showed that the zeolite-based catalysts had no different effect on the degradation mechanisms in comparison with the thermal degradation, which may be related to the special structure of HIPS [3]. Whereas, the zeolite catalysts can affect strongly the non-aromatic hydrocarbonic polymers [7-9].

Also with the used FCC catalyst, the results were a little different from those obtained with Ga/used FCC. The condensed product was composed of aromatics (95.3%), olefins (2.9%), paraffins (1.0%) and naphthenes (0.8%) and its yield was 90.4%. The content of the condensed hydrocarbons produced with using HZSM-5 catalyst was lower than those produced with the other catalysts and the yield was 90.2%. Aromatics (95.9%), olefins (1.6%), paraffins (0.9%) and naphthenes (1.6%) are the main components of the condensed product produced with using this catalyst.

### Effect of heating rate

Heaters with different powers were used to study the HIPS degradation at different heating rates. The effect of heating power ranged from 1000 to 4000W on the pyrolysis products including condensable, non-condensable and coke as well as the composition of liquid products is shown in Table 6. The results show that the condensed (91.9-94.9%) and non-condensable

**Table 6.** Effect of heating power on the products yield, the condensed product composition and residence time.

Heating power (w)	Liquid (%)	Gas (%)	Coke (%)	olefins (%)	paraffins (%)	naphthenes (%)	aromatics (%)	Styrene (%)	residence time (min)
1000	91.9	7.4	0.7	2.7	1.7	0.4	95.2	40.6	62
2000	94.9	4.7	0.4	3.2	1.6	1.1	94.1	38.5	47
3000	93.5	6.2	0.3	3.9	1.4	1.5	93.2	37.2	39
4000	93.1	6.7	0.2	4.1	1.1	2.0	92.8	35.6	33

Catalyst/HIPS: 0, Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450°C.

**Table 7.** Effect of heating power on the carbon number distribution of condensed products.

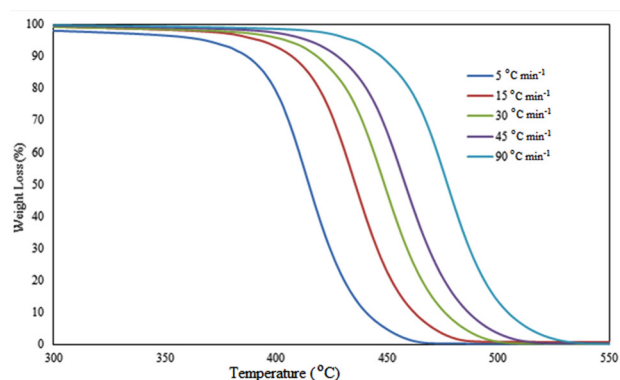
	1000 W	2000 W	3000 W	4000 W	
Carbon Number	C <sub>4</sub>	0.4	0.1	0.2	1.2
	C <sub>5</sub>	0.6	0.4	4.3	4.3
	C <sub>6</sub>	1.2	4.2	6.1	8.1
	C <sub>7</sub>	1.5	4.3	6.7	7.2
	C <sub>8</sub>	66.1	64.5	62.7	61.1
	C <sub>9</sub>	3.9	3.2	2.3	3.2
	C <sub>10</sub>	3.1	4.6	2.9	2.8
C <sub>10</sub> <sup>+</sup>	23.2	18.7	14.8	12.1	
Sum(C <sub>5</sub> -C <sub>9</sub> )	73.3	76.6	82.1	83.9	
Ave. Molecular Weight	128.1	124.5	118.6	115.7	

Catalyst/HIPS: 0, Carrier gas: Nitrogen, Agitator speed: 50 RPM, Temperature: 450°C

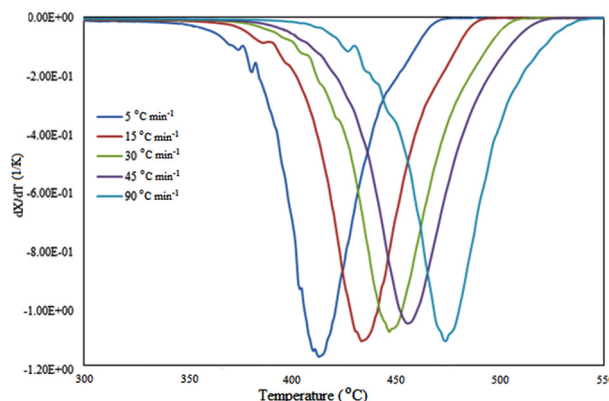
products (4.7-7.4%) had a peak with increasing heater power, while the coke yield decreases with increasing heating power in the studied range (0.7-0.2%).

The results showed that styrene had a significant share in the condensed products and the degradation tended to follow the un-zipping mechanism, and styrene content decreased with heating power in the studied range (40.6-35.6%). Aromatics containing styrene as the main and only component decreased with increasing heating power (95.2-92.8%), while the other components with less than 10% share acted as raffinate and had no significant role in the products. The results indicated that the residence time decreased with heating power obviously (62-33 min).

The carbon number distribution, molecular weight and gasoline range of the condensed product at different heating powers are shown in Table 7. The results show that the molecular weight of the liquid products is clearly decreased with increasing heating power.



**Figure 2.** TGA curves of HIPS at different heating rates (5, 15, 30, 45 and 90°C min<sup>-1</sup>).



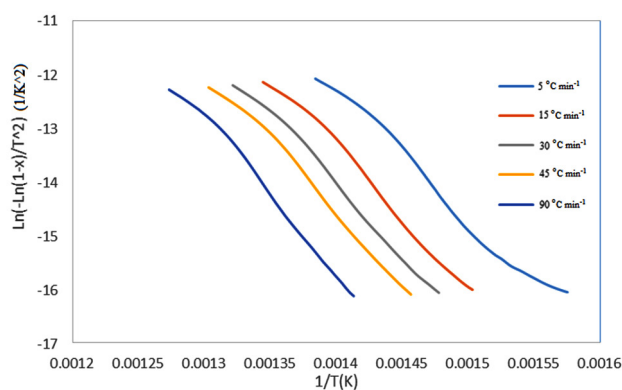
**Figure 3.** DTG curves of HIPS at different heating rates (5, 15, 30, 45 and 90°C min<sup>-1</sup>).

### TG study of HIPS pyrolysis

Figure 2 shows the non-isothermal mass losses of HIPS measured using a thermo-gravimetric analyzer (TGA) at heating rates of 5, 15, 30, 45 and 90°C min<sup>-1</sup>. The results show that the sample tends to degrade at higher temperatures with increase heating rate. Figure 3 shows the DTG graphs obtained from the TGA curves presented in Figure 2. The DTG curves show a unimodal degradation curve though the next peak tended to eliminate with heating rate increasing.

The typical plots of ln [-ln (1-x)/T<sup>2</sup>] versus 1/T, indicating that for all of the heating rates, a single first-order reaction should be used to describe the pyrolysis process (Figure 4). An integral method [22-24] was applied separately to each of the stages. Therefore, the conversion x was recalculated for each reaction. From the slope of each line, the value of E<sub>a</sub> and A could be obtained for different stages.

The activation energies and pre-exponential factors obtained at different heating rates using the integral method are listed in Table 8. The results show that ac-



**Figure 4.** Plot of ln(-ln(1-x)/T<sup>2</sup>) vs 1/T of HIPS at different heating rates.

**Table 8.** Effect of heating rate on the kinetic parameters and characteristic temperatures.

$\beta$ (°C min <sup>-1</sup> )	Conversion range (%)	$E_a$ (KJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$R^1$	$T_5$ (°C)	$T_{95}$ (°C)	$\Delta T$ (°C)
5	5-95	222.5	$3.4 \cdot 10^{13}$	0.989	367.8	449.4	81.6
15	5-95	215.4	$6.7 \cdot 10^{12}$	0.998	391.1	471.2	80.1
30	5-95	206.1	$4.6 \cdot 10^{12}$	0.994	404.3	484.7	80.4
45	5-95	199.7	$1.9 \cdot 10^{12}$	0.993	415.2	494.9	79.7
90	5-95	183.6	$2.2 \cdot 10^{11}$	0.993	434.7	512.8	78.1

tivation energy is decreased with increasing heating rate (222.5-183.6 kJ mol<sup>-1</sup>). The kinetic parameters were calculated in the range of  $x = 5$  to 95%, 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. Table 11 also indicates the temperature interval for the decomposition of the HIPS defined between the temperatures  $T_5$  and  $T_{95}$  and their difference. These two temperatures are defined, respectively, as the temperatures at which the reaction starts ( $T_5$  at 5% conversion) and ends ( $T_{95}$  at 95%). The results indicated that the difference between  $T_5$  and  $T_{95}$  as function of DTG breadth, decreased moderately with heating rate increasing. It could show that the heating rate had no obvious effect on the degradation mechanism in the studied range.

It seemed that the related effective pyrolysis mechanisms (i.e. chain scission, un-zipping and a little cross-linking) and their shares in the degradation were changed with heating rate and degradation temperature. According to the results obtained with using the pyrolysis reactor and those obtained from the TGA tests, it was revealed that unzipping and chain scission were the effective mechanisms, and un-zipping over chain scission decreased with increasing temperature and heating rate. The cross-linking mechanism had a little role in the degradation process, and the role of cross-linking mechanism increased with temperature and decreased with heating rate.

## CONCLUSION

A laboratory stirred reactor and a TGA instrument were used to study and measure HIPS degradation and pyrolytic products using different types of zeolitic catalysts and at different temperatures and heating rates. The fuel-like and aromatic enriched products in the gasoline range can be produced under catalytic degradation of high impact polystyrene over zeolite-

based catalyst. According to this study, the pyrolysis products changed with changing heating rates and temperature. The results showed that the faster pyrolysis and high degradation temperatures tended to decrease the molecular weight in the gasoline range. Styrene as the main product of high impact polystyrene pyrolysis produced up to 40%. The catalysts used, heating rate and temperature tended to decrease styrene content and the role of un-zipping mechanism. The DTG curves obtained at different heating rates were almost the same due to the structural similarity between the performances of chain scission and un-zipping as main degradation mechanisms in the pyrolysis. The activation energy of the degradation reaction was decreased with increasing heating rate and temperature. Thus, the catalytic pyrolysis of high impact polystyrene using zeolitic catalysts at higher heating rates and temperatures appeared to be more economically favorable in terms of cost efficient operation.

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