

# Original Article: Investigation of Heavy Polyethylene Catalytic Pyrolysis

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## ABSTRACT

Heavy polyethylene catalytic pyrolysis with 15% HZSM-5 catalyst was performed at 500 °C in a semi-continuous stirrer reactor under nitrogen gas. In the first experiment, about 46.7% of the liquid product, 29.2% of the gas product and 4.5% of coke was produced. In the second experiment, with the changes made on the reactor and condenser, the liquid product output increased by about 8%. In a similar study, the effect of HZSM-5 zeolite catalyst acidity on the catalytic degradation of heavy polyethylene was evaluated. To have HZSM-5 with different acidities, sodium nitrate solution with different concentrations was used. Displacement of protons in the original sample by sodium cations (at room temperature for 4 hours) reduces the acidity of the samples. By adding sodium to HZSM-5 and ion transfer, the acidity of the catalyst decreased and the degradation temperature increased from 390 °C to 555 °C. The gases released from pyrolysis were also analyzed by gas chromatography and it was concluded that the selectivity of volatile products changes with catalytic acidity.

## Introduction

### Investigation of Heavy Polyethylene Catalytic Pyrolysis System with HZSM-5 Catalyst

The change in acidity, followed by the change in catalyst activity, reflects the fact that the inner surface and cavities of the catalyst are involved in the reaction, despite the fact that

the reacting molecules are very large [1-3]. Thus HZSM-5 zeolite explicitly reduces the degradation temperature by reducing the activation energy and increasing the velocity [4-6]. Therefore, the energy required for the catalytic failure process must be much less than the energy required for the fully thermal failure process. Reducing the acidity of the zeolite has a significant effect on the performance of the

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catalyst, and on the other hand the acidic sites of the catalyst are located inside its micro pores, thus indicating that the catalyst process is more likely to occur inside the catalyst cavities and the external surface of the zeolite has an effect on the reaction [7-9].

### *Investigation of Heavy Polyethylene Catalytic Pyrolysis System with H-Mordenite Catalyst*

Heavy polyethylene catalytic pyrolysis with 15% H-Mordenite catalyst was performed at 555 ° C in a semi-continuous stirrer reactor under nitrogen gas [10-12]. According to the results, in the first experiment about 58.5% liquid product, 37% gas product and 4.5% of coke was produced. In the second experiment, 68% of the product was obtained as a hydrocarbon liquid by selecting a higher agitation. In one study, the effect of mordenite catalyst structure on pyrolysis of light polyethylene was investigated. In determining the quality of zeolite catalysts suitable for pyrolysis, a set of factors such as catalyst acidity, structure and rate of coke formation by the catalyst must be evaluated. In other words, not only the acidity of zeolite catalysts but also the

structure and size of their cavities are important in light polyethylene pyrolysis [13-15].

Mordenite catalyst with small pore size has little effect on lightweight polyethylene pyrolysis. In fact, Mordenite catalyst is a good catalyst in terms of acidity, but because its acidic sites are not available (due to the size of small pores), it does not perform well in the pyrolysis process [16].

### *Catalytic pyrolysis of heavy polyethylene with different catalysts*

In this section, the effect of different catalysts on pyrolysis of heavy polyethylene is investigated.

By adding 10% of FCC catalysts, compared to other catalysts, the most liquid product is produced with 99.5%. While heavy polyethylene pyrolysis with 15% HZSM-5 catalyst obtained 54.6% of the liquid product, degradation of heavy polyethylene with H-Mordenite catalyst resulted in the production of 80 g of liquid product. Table 1 shows the distribution of different compounds in the liquid product resulting from heavy polyethylene pyrolysis with 15% of FCC and HZSM-5 catalysts [17].

**Table 1:** Distribution of different compounds in the liquid product resulting from heavy polyethylene pyrolysis with 15% of FCC and HZSM-5 catalysts

HD/Z/15/2	HD/F/15/3	Sample Product components (Mole percentage)
27.8	7.5	Aromatic
29.3	7.51	Oil
24.1	37.53	Alfin
18.8	27.5	Paraffin

According to the results of experiments, in heavy polyethylene pyrolysis using FCC catalyst, olefins with more than 70% contain the highest percentage of liquid product. The reduced FCC catalyst in heavy polyethylene pyrolysis does not show a tendency to form aromatic compounds, and since up to 40% of aromatic compounds are allowed in gasoline, polyolefin pyrolysis products using the FCC catalyst itself can be used as fuel with due to the high level of olefins and low aromatics are not appropriate. This shortcoming can be compensated for by using other catalysts in addition to the FCC

catalyst and intensifying the Dills-Alders reactions [18].

In heavy polyethylene pyrolysis with HZSM-5 catalyst compared to the case of FCC catalyst used, the increase of aromatics from 5.7% to 27.8% indicates an increase in dehydrogenation reactions and Dils Alder in pyrolysis. Considering that more than 90% of products are in the gasoline range using FCC catalysts, it can be concluded that although it is not suitable in terms of aromatics, it is a suitable catalyst in terms of carbon number of products in the pyrolysis process [2].

Looking at the results, using the FCC catalyst, the six-carbon compounds have the largest share of the liquid product, and with the HZSM-5 catalyst, the five-carbon compounds account for more than 22% of the bulk of the liquid product. In the study of heavy polyethylene pyrolysis with FCC catalyst compared to the case where HZSM-5 catalyst was used, the amount of product that is in the range of gasoline shows a slight increase and the average specific density of the product can be density decreases from 0.715 for the HD / Z / 2.15 sample to 0.672 for the HD / F / 3.15 sample. In cases where a catalyst is used, heat transfer inside the reactor is one of the effective factors and only in cases where heat transfer is appropriate, the product is produced with a high percentage of liquid and in the range of gasoline [18]. The higher the number of compounds with high carbon content as well as the aromatic content of the product, the higher the average specific density of the product. In the study of the distribution of liquid product resulting from heavy polyethylene pyrolysis with 15% of FCC and HZSM-5 catalysts, it is observed that the average specific density of pyrolysis product with HZSM-5 is higher than FCC, 0.043.

This is due to the high percentage of aromatics in the pyrolysis product with HZSM-5 (about 27.8%). Also, the percentage of high carbon compounds in pyrolysis product with HZSM-5 is higher than FCC [2]. The FCC catalyst is a catalyst with a pore size distribution of two peaks and 5-12 carbon chains that can easily pass through the pore. But because the catalyst is not the only factor influencing the degradation process and other factors such as temperature also affect, a very wide distribution of the liquid product is obtained [11].

#### *Investigation of polypropylene catalytic pyrolysis system with HZSM-5 catalyst*

Catalytic pyrolysis of polypropylene with 15% HZSM-5 catalyst was performed at 450 °C in a semi-continuous stirring reactor under nitrogen gas. In the first experiment, about 58% of the liquid product, 34.2% of the gas product and 7.8% of coke was produced [15].

#### *Investigation of polypropylene catalytic pyrolysis system with H-Mordenite catalyst*

Catalytic pyrolysis of polypropylene with 15% H-Mordenite catalyst was performed at 450 °C in a semi-continuous stirring reactor under nitrogen gas. In the first experiment, about 70% of the liquid product, 23.5% of the product Gas and 6.5% coke were produced.

#### *Catalytic pyrolysis of polypropylene with different catalysts*

In this study, the effect of different catalysts on pyrolysis of polypropylene was investigated. Catalyst after temperature is the most important factor in pyrolysis. One of the most important advantages of catalytic pyrolysis compared to the thermal process is the high selectivity of the product. Polypropylene pyrolysis results were evaluated with three catalysts FCC, HZSM-5 and H-Mordenite and without catalyst [36-38]. By adding 15% of FCC catalyst, compared to pyrolysis with other catalysts, the most liquid product is produced with 90.7%. Polypropylene pyrolysis under HZSM-5 catalyst produces the lowest amount of liquid product with 58.7%. To explain this phenomenon, it can be said that the HZSM-5 catalyst is a catalyst with a very small pore size, and the polymer chains break through the pores and the percentage of gaseous products from degradation increases, and so on. The percentage of hydrocarbon liquid resulting from pyrolysis decreases [10].

Pyrolysis of polypropylene using H-Mordenite catalyst also produces about 83.2% of the liquid product. In general, compared to HZSM-5 and H-Mordenite, FCC catalysts have a better effect on the degradation of polypropylene in terms of liquid product distribution. The results show that using polypropylene pyrolysis, olefins have the main share with more than 49% of products. According to the results of this study, the amount of olefins in the final product in pyrolysis of polypropylene is less than polyethylene's, which may be related to the structure of polypropylene and the presence of methyl groups. In polypropylene, due to the lower refractive energy compared to polyethylene's, the contact time of polypropylene chains with the catalyst surface is

reduced, and this causes the dehydrogenation reactions caused by the FCC catalyst is strengthened, reduced, and as a result the number of olefins decreases and the amount of paraffin's increases [11].

According to the results, catalytic pyrolysis of polypropylene with catalyst FCC and HZSM-5 both produces the same number of six-carbon hydrocarbons, while the number of groups nine and ten and higher is higher in pyrolysis with HZSM-5. On the other hand, the distribution of the pyrolysis liquid product by FCC is towards lighter hydrocarbons. In the liquid product resulting from catalytic failure, iso-alkanes and aromatics are present in the C5-C10 range.

Therefore, by selecting the appropriate catalyst, the distribution of the product can be controlled.

#### *Polybutadiene rubber catalytic pyrolysis system with FCC catalyst*

Catalytic pyrolysis of polybutadiene rubber with 15% FCC catalyst was performed at 450 °C in a semi-continuous stirring reactor under nitrogen gas. In the first experiment, about 21.6% of the liquid product, 69.9% of the gas product and 8.5% of coke was produced. In subsequent experiments, the amount of liquid product increased almost fourfold due to the changes made. The results of these experiments are shown in table (2).

**Table 2:** Percentage of thermal and catalytic pyrolysis products of polybutadiene rubber in different experiments

Specific density	Percent of coke	Percentage of gas product	Percentage of liquid product	Product % the experiment
0.76	1.3	8.1	90.6	PBR/1
-	8.5	69.9	21.6	PBR/F/15/1
-	4.3	15.04	80.66	PBR/F/15/5
0.665	2.2	12.6	85.2	PBR/F/15/6
0.698	2.9	10.7	86.4	PBR/M/15/2

#### *Investigation of polybutadiene rubber catalytic pyrolysis system with HZSM-5 catalyst*

Catalytic pyrolysis of polybutadiene rubber with 15% HZSM-5 catalyst was performed at 450 °C in a Buchi stirrer reactor under nitrogen gas.

#### *Investigation of catalytic pyrolysis system of polybutadiene rubber with H-Mordenite catalyst*

Catalytic pyrolysis of polybutadiene rubber with 15% H-Mordenite catalyst was performed at 450 °C in a semi-continuous stirrer reactor under nitrogen gas. In the first experiment, about 70% of the liquid product, 26.9% of the product gas and 3.1% of coke were produced [2].

#### *Investigation of styrene butadiene pyrolysis system with HZSM-5 catalyst*

Catalytic pyrolysis of styrene butadiene rubber was performed with 15% HZSM-5 catalyst at 450°C in a Buchi stirrer reactor under nitrogen

gas. The products of this degradation included 78.7% liquid, 17% gas and 4.3% coke. Due to the significant percentage of distilled liquid product and its reproducibility, the mentioned test conditions were considered suitable.

#### *Investigation of styrene butadiene pyrolysis system with H-Mordenite catalyst*

Catalytic pyrolysis of styrene butadiene rubber with 15% H-Mordenite catalyst was performed at 450 °C in a semi-continuous stirring reactor under nitrogen gas.

#### *Investigation of the effect of different catalysts on pyrolysis of styrene butadiene rubber*

In this study, the effect of different catalysts on pyrolysis of styrene butadiene rubber was investigated. The effect of catalyst agent on pyrolysis has been investigated using three catalysts FCC, HZSM-5 and H-Mordenite. By pyrolysis of styrene butadiene rubber with 15% of FCC catalyst, about 93.2 g of liquid product

was produced, which is exactly equal to the amount of liquid product obtained from thermal pyrolysis. However, by adding 15% of FCC catalyst to the pyrolysis system, the amount of coke left increased from 1.4 to 1.7. In the pyrolysis of styrene butadiene rubber under the HZSM-5 catalyst, 17% of the products are released as gases. It produces about 17% more than other catalysts, but due to the effect of the cage and the lack of access of the catalyst to all the chains, the effect of the catalyst on the product is less than plastics and the amount of liquid with HZSM-5 catalyst is more than plastics.

Also, in the catalytic degradation of styrene butadiene rubber with H-Mordenite catalyst, about 90.1% of distillate products and 2.4% of coke were obtained. The coke formed during the pyrolysis process of the tires has a three-dimensional and closed structure and by settling on the surface of the catalyst, it blocks the cavities and reduces its activity drastically. As the results show, in pyrolysis of styrene butadiene rubber with FCC and HZSM-5 catalysts, aromatics have more than 50% of the main share in the liquid product. Due to the presence of styrene in the structure of styrene butadiene rubber and the possibility of Dils Alder reactions, the percentage of aromatics in the compressible product is higher than other cases.

During pyrolysis of tires, due to the presence of many double bonds in the structure of styrene butadiene rubber and the possibility of creating polymer networks during the degradation process, it is likely that the rubber will be degraded on the catalyst surface before it can enter the catalyst cavities. Therefore, the role of catalyst in pyrolysis of tires is less than that of plastics. It is noteworthy that in the pyrolysis of styrene butadiene rubber with H-Mordenite catalyst, the major part of the liquid product is olefins with more than 37%.

#### *Investigation of the effect of FCC catalyst percentage on pyrolysis of styrene butadiene rubber*

According to studies, the FCC catalyst produces the highest amount of liquid product among other catalysts, including HZSM-5 and H-Mordenite, and has been one of the main reasons for its selection for this study. One of the salient features of this catalyst is that it has a two-peak pore distribution that allows it to produce products in the gasoline range. The effect of catalyst content on pyrolysis of styrene butadiene rubber in five percent different from zero to sixty percent compared to styrene butadiene rubber is investigated in table (3).

**Table 3:** Effect of FCC catalyst percentage on pyrolysis of styrene butadiene rubber

Percent of coke	Percentage of gas product	Percentage of liquid product	Product% the experiment
1.4	5.4	93.2	SBR/F/0
1.7	5.1	93.2	SBR/F/15/6
1.9	2.4	95.7	SBR/F/30/1
2.1	0.1	97.8	SBR/F/45/1
3.8	3.8	92.4	SBR/F/60/1

Pyrolysis of styrene butadiene rubber with 45% FCC catalyst produces the most liquid product with 97.8%. The amount of liquid product with increasing percentage of FCC catalyst first increases (maximum value in catalyst ratio 45%) and then decreases. With increasing the amount of catalyst, the necessary ground for increasing the coke is provided and

with increasing the amount of catalyst from zero to sixty percent, the amount of coke increases from 1.4 to 3.8 percent.

It should be noted that gaseous compounds also decrease and then increase as the amount of catalyst increases, so that the catalyst ratio reaches a minimum of 45%. In general, the



catalyst reduces the pyrolysis temperature and activation energy required for bond failure, and in this respect has a significant impact on the economic costs of the design.

### *Investigation of the effect of FCC, HZSM-5 and H-Mordenite catalysts on pyrolysis of rubbers and plastics*

The FCC catalyst consists of a zeolite crystal and a non-zeolite acidic compound (usually a silica-alumina and a binder). For the past forty years, zeolite Y has been the mainstay of this group of catalysts, mainly due to its high thermal resistance and the optimal selectivity of its product. Alumina, clay, and binder compounds are used in FCC catalysts to increase the mechanical and thermal resistance required for pyrolysis. These catalysts are commercially available in the form of powder or tablets, the type of sheet of which has an average diameter of 60 microns and the type of powder has a smaller size. The method of preparation and the type of compounds used have a great impact on the performance of the catalyst. During various experiments, the effect of FCC, HZSM-5 and H-Mordenite catalysts on pyrolysis of tires and plastics was investigated [9].

It should be noted that all experiments were performed with 15 g of catalyst and 100 g of polymer and under nitrogen gas in a semi-continuous reactor with appropriate agitation.

### Conclusion

It should be noted that if we have a combination of polymers, it is better to use FCC catalyst for pyrolysis, because in this case we get more liquid product for all polymers. In styrene butadiene rubber using HZSM-5 catalyst, both more liquid product and higher aromatic percentage are obtained. Aromatics are the most expensive petrochemical products. The permissible aromatic concentration in gasoline is 35 to 37%. In fact, aromatics are high-octane products that increase the octane number of gasoline. The FCC is a catalyst with a pore size distribution of two peaks.

So, it is suitable for passing both small chains and large chains into its cavities. 5-12 carbon

polymer chains are able to easily pass through its pores and do not allow the chain to turn into gas with further failure. Therefore, it works well for all the polymers we study, and regardless of the type of polymer, a significant liquid product is obtained. Therefore, the amount of liquid product in pyrolysis of different polymers with FCC catalyst has a more uniform process than HZSM-5 catalyst. Pyrolysis of tires using HZSM-5 catalysts gives a more liquid product than plastics. And three-dimensional coke interpreted this phenomenon, and therefore the reason that catalysts are ineffective in pyrolysis of tires is that the multidimensional networks formed contain catalyst particles and prevent rubber chains from entering the catalyst cavities. Dual bonding is the main cause of crosslinking in tires, which is why crosslinking is rare in plastics. During the pyrolysis process, the parts between the networks are broken and released and become a liquid product without reaching the catalyst surface. In fact, network connections do not allow rubber chains to enter the catalyst holes. But plastic chains that operate individually enter the catalyst cavities and fail. If we want to compare different catalysts, with two catalysts FCC and H-Mordenite, the percentage of liquid product is high percent and with HZSM-5 catalyst in pyrolysis of tires, more liquid product than plastic has been obtained. As mentioned earlier, catalysts do not have much effect on tires, but the smaller the size of the catalyst holes, the more gaseous product and less liquid product is produced.

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