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Experimental Investigation on the Reduction of Catalyst Costs in the Polyethylene Pyrolysis Process

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Abstract. In our earlier works, the catalyst USY zeolite was tested for the pyrolysis of High density polyethylene (HDPE). It yielded 71% liquid oil that could be separated into diesel and gasoline-like fractions [3]. However, the high cost of this catalyst led to the present study where the effects of different low-cost catalysts on catalytic cracking of HDPE were investigated. GC-MS analysis were performed to check the carbon distribution of each sample and to make theoretical gasoline/diesel quantification in the pyrolysis liquids. Products were compared by studying carbon distribution, condensable range, branching degrees and reaction speeds. According to all those parameters, none of them outperformed USY zeolite. The Second Part has been conducted to observe the regeneration of USY Zeolite and monitor its performance for its economic value. The regeneration was done 10 times and the performance was monitored after every experiment with respect to % of heavier compound yields, carbon distribution range, char deposition range and gasoline and diesel yields. It was found that the regenerated catalyst loses its capability very slowly and even after 10 regenerations products characteristics were not sensibly altered.

1. Introduction

The constant development in the polymerization industries and processing machines are producing cost-effective production which are replacing the conventional materials with the plastics. Continuous innovation explains that plastics production has increased by an average of almost 10% every year on a global basis since 1950. The total global production of plastics has grown from around 1.3 million tonnes (MT) in 1950 to 322 MT in 2016 [1].

Due to the much economic cost of the plastic and the middle - class development the consumption is rising up in the last few years. This high consumption has led to the generation of more and more plastic waste. Plastic poses a greater threat to the environment and thereby it has become very difficult for its direct disposal. Depending upon its area of application, the service life range life of expectancy of plastics lies from 1 to 35 years. Plastic in municipal solid waste streams makes up only 7–9% of the weight of the total waste stream, by volume they may represent 20–30%. Of the organic waste stream, that is, after removal of glass, metals, etc., plastics are about 9%–12% by weight. In addition to the presence of plastics in municipal waste streams, many wastes collected from manufacturing or service industries may contain much higher proportions of plastics [1]. There is a great economical challenge for the management this plastic waste to recover its potential source of energy while processing it through the thermal degradation.

Energy recovery via pyrolysis does not require sorted or clean feedstock and it could be feasible at smaller scales than recycling. Pyrolysis is the thermal degradation of polymers under the effect of temperature under inert atmosphere. Pyrolysis transforms plastics into liquid and gaseous products, with high heating values, that could be used as fuels. Pyrolysis is done using two methods that is thermal pyrolysis and Catalytic Pyrolysis. In thermal Pyrolysis, the degradation is completed through free radical exchange mechanism which results in statistical distribution of wide range of carbon chain [4]. On the contrary, Catalytic pyrolysis degrades the plastic through carbocation exchange



mechanism. This carbocation exchange results in the β -Scission of the hydrocarbon chain which results in the bi-functional conversion of the long chain into shorter chains in consecutive reactions [5].

Polyethylene and polypropylene which represent the major part of plastic wastes are composed of long chains of hydrocarbons and their thermal degradation results in shorter carbon chain products. In order to enhance reaction kinetics and to select a range of carbon chain length distribution, catalysts are used (zeolites, activated carbon, metallic oxides...). Depending on its chemical and physical characteristics, yield and characteristics of products can be impacted.

The objective of this experimental study is to investigate the thermal degradation of plastic waste by pyrolysis using different catalysts, regenerating the catalyst and to find the most effective catalyst based on thermal cracking performances and the economic value. In this work, the initiation was done by selectivity of different materials and parameters used in the pyrolysis process and characterizing the catalysts based on their chemical and physical properties. Furthermore, testing of different catalysts in plastic waste pyrolysis process and their regenerative capabilities has been conducted using a pilot pyrolysis plant.

The final aim of this work is to find a way to lower the catalyst part price in the catalytic pyrolysis process. Cheaper catalysts were tested and compared according to their liquid fuel yield. Moreover, regeneration test campaign was done with USY Zeolite.

2. Materials and methodology

The Experiment was done using Batch type reactor of stainless steel. The reaction chamber was protected by Thermal resistance cover to avoid the reflux of the process. The Plastic used for the Experiment was High Density Polyethylene (HDPE). Catalysts were mixed with the plastics and introduced to the cold reactor. To create Inert Atmosphere, the nitrogen gas was purged for about 5-8 minutes. In condensing system, the direct flow of Tap water was continuously supplied throughout the whole experiment. The exhaust system was connected to a blower which was connected to general ventilation of the laboratory. The Catalysts that was used for conducting the experiments were CaO, Activated Carbon, Activated Carbon Sulphonated, Red Mud and Industrial Zeolite USY. The Red mud was from the origin of solid waste clay of Cameroon and the other catalysts were either taken or prepared in the laboratory.

The limit of the reactor temperature was controlled at 500°C with the heating rate of 21°C/min. Catalyst was added in 1:10 that is 20g of catalyst was taken for the pyrolysis of 200g of plastic. The liquid product was collected in a glass bottle with the measurement of volume in ml. The Time was recorded corresponding to the temperature and volume obtained at that particular time. Digitally, The Data of the process was registered using the software LabVIEW 7 Express.

The samples were analyzed by the machine PERKIN ELMER CLARUS 680 which is coupled with (GC/MS-FID). A column SLB - 5MS (30m x 0.250 mm; 0.25 μ m film thickness) was used to pass the helium at the flow rate of 1ml/min. The temperature commenced at 40°C for 10mins followed by 3°C/min to 170°C and then 10°C/min to 330°C, which was hold for 6mins. The peaks of the spectra was identified by NIST Library or attributed according to their molecular peak.

2.1 Catalyst regeneration

In this Study, the Regeneration was done for the USY Zeolite Catalyst. USY Zeolite has very high BET surface of about 617 m²/g [2] and high Si/Al ratio which make it highly acidic in nature. The hypothesis has been made on the basis of its activity in different parameters. The experiments were all conducted at the same quantity ratio 1:10 and was controlled at same temperature limit of 550°C. The Images were taken at 3 different phases before the experiment, after experiment, and after regeneration which can be seen in figure 1.

The regeneration was done by taking the residue after the experiment in a ceramic bowl and heating it inside the oven with the presence of air. The oven configuration was set for an increasing rate of temperature from ambient temperature to 550°C for 47 mins and then holding at the same

temperature of 550°C for the next 3 hrs. It was observed that in the regenerated catalyst, char is completely removed and visibly it is little pale yellow as compared to the white color of fresh catalyst. After each regeneration, the catalyst was weighted and the lost catalyst was completed according of the ratio of 1:10 with fresh catalyst.



Figure 1. Images of Catalyst (A) Before Experiment (B) Residue after Experiment (C) After Regeneration

3. Results and discussions

3.1 Gasoline and diesel yields

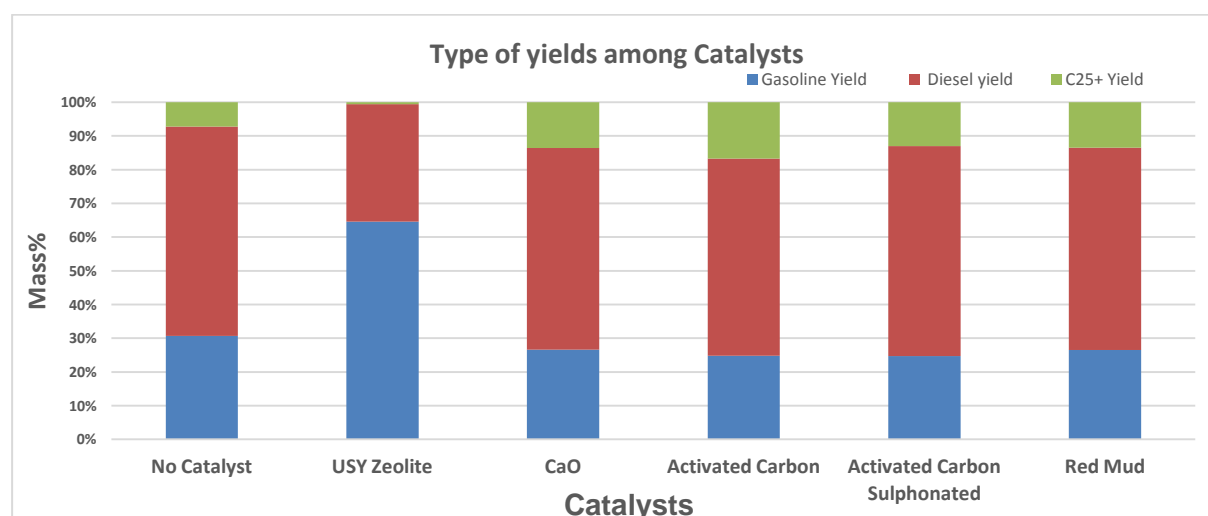


Figure 2. Comparison of Types of yield among the catalysts

The analyses of gasoline and diesel yields were monitored to find the maximum amount of different products that can be recovered after pyrolysis using different catalysts. The monitoring was done on the basis of hydrocarbon ranges which varies from C₅-C₁₂ (Gasoline), C₈-C₂₄ (Diesel) and C₂₅₊ (Other products) [6].

According to the Hydrocarbon ranges, Gasoline and Diesel share very small distribution of carbon range but this proportion can be separated further by distillation processes. It can be seen in figure 2, that the Maximum yield of gasoline is given by USY Zeolite and the rest of the catalyst has very low ranges of gasoline. This was due to the effect of internal structure that plays an important role in determining the cracking capability of catalyst. No catalyst also yielded a good amount gasoline and diesel but the quality of the fuel is very low. All the Catalyst except USY Zeolite are amorphous in internal structure that's why, it become difficult to crack long hydrocarbon chains. Whereas, the

Zeolite USY is crystalline in structure, which provides better cracking with higher rate of ion exchange activity.

3.2 Carbon distribution comparison

The carbon distribution shows the mass% and retention time of each type of compounds which are varied by the different catalyst that can be seen in figure 3. The graph with no catalyst has been considered as the reference while comparing with other catalyst. The shortening of carbon chains by the catalyst shows the active phase while cracking.

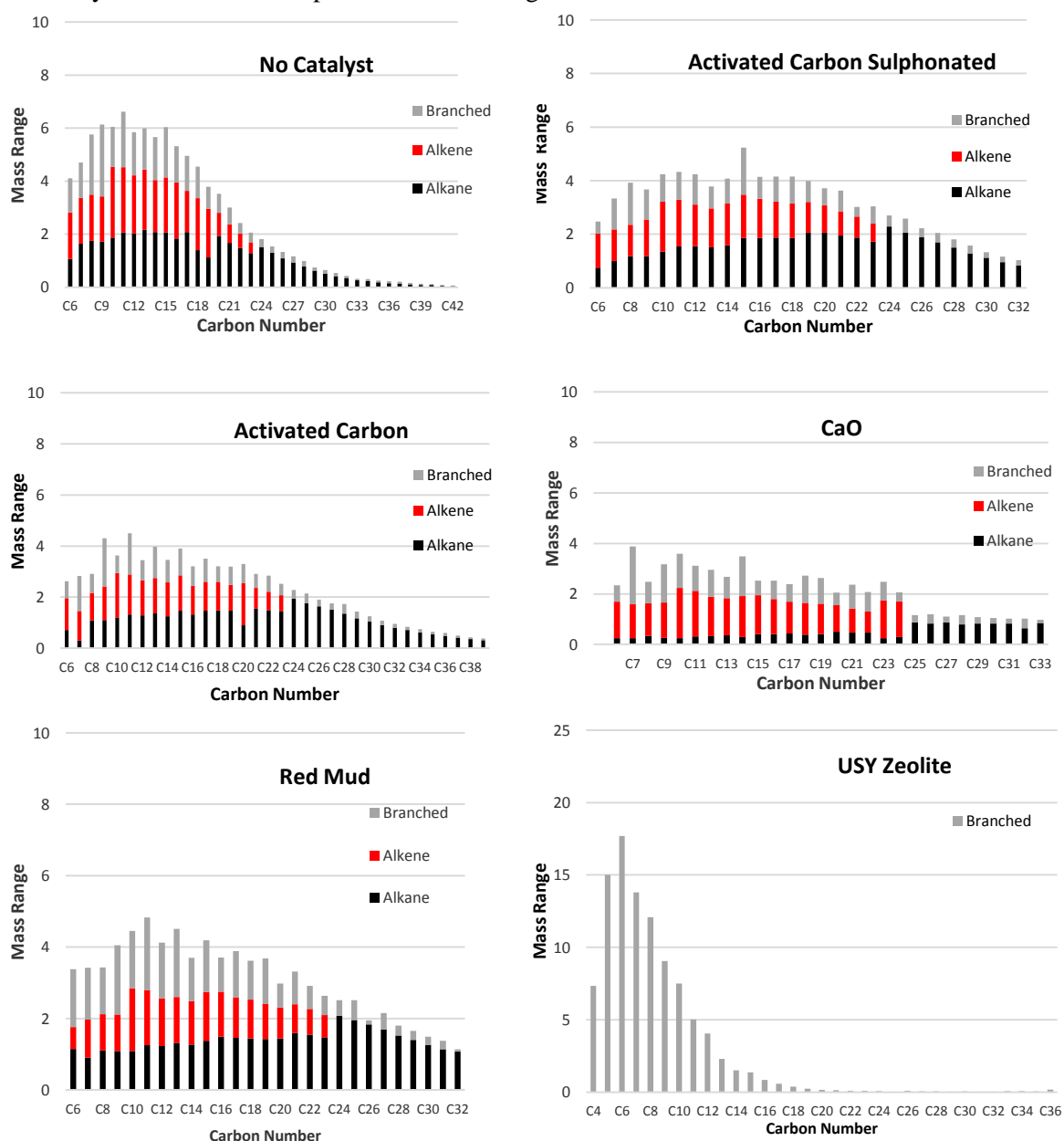


Figure 3. Carbon distribution comparison of catalysts

The phase of product yield in all the catalyst except USY Zeolite was obtained in wax phase while the product of USY Zeolite was in liquid phase. The wax formation in the products was due to the

alternation in the catalytic cycle. It can be seen that the high % of the formation of heavier compounds in other catalysts results in the absorption of lighter compounds by the heavier compounds. On the other hand USY Zeolite produces high % of lighter compounds in comparison to others. This is due to the high presence of active acid sites and higher reaction degree mechanism of USY Zeolite.

3.3 Kinetics of different catalysts

The kinetics of catalysts were monitored by the consideration of the reference with the limit time in mins to the volume of 150 ml. The comparison was done with No catalyst which was our base point and then the order of kinetic was observed with catalysts. The variation was observed according to the increasing order that was **No Catalyst** (90mins) < **Activated Carbon Sulphonated** (68mins) < **CaO** (66mins) < **Red Mud** (65mins) < **Activated Carbon** (61mins) < **USY Zeolite** (31mins).

No catalyst surpasses the performance of Zeolite USY which is due to the absence of active bronsted acid sites in the other catalysts. This gives us a conclusion that the activity depends upon the crystalline structure and the acidic sites in the materials.

3.4 Regeneration of USY Zeolite

3.4.1 Relative difference in regenerations. The regeneration experiments were monitored by the relative difference in their carbon distribution. The experiments was conducted till 10 times but to observe the difference, the comparison was done between the 5th and 10th experiment. It can be seen from the figure 4 that the formation of heavier compounds are increasing at the 10th experiment from C₁₈. This might be due to the after effect of the increasing number of regenerations done which deactivates the acidic sites in the catalyst and destruct the internal structure. This makes the catalyst incapable to crack large hydrocarbons and thus produces heavier compounds.

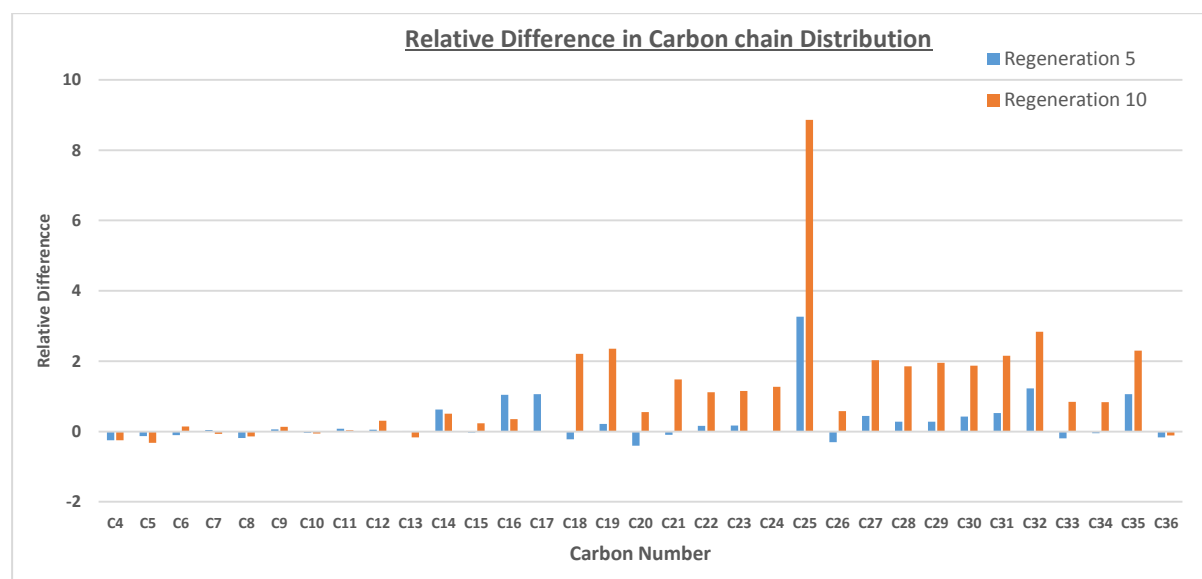


Figure 4. Difference between regenerations

It is also interesting to see that the formation of lighter compounds (till C₁₇) from the 5th and 10th experiment carries a very low relative difference. This gives a very strong indication that in both the experiments there was almost same percentage of formation of lighter compounds which follows the same carbon distribution range of USY Zeolite. It can also be noted that there is still the active presence of acidic sites in the catalyst till the 10th experiment.

3.4.2 Char deposition. According to the proximate analyses, the plastic contains the ash content and due to this, there is the formation of char in the residue of the pyrolysis process. While in the pyrolysis process, due to the polymerization reaction, there is no formation of the coke at the bottom of the reactor or less than 1% of the HDPE. The coke gets to stick to the internal structure of the surface of the catalyst. In the analyses it showed that, the mass% of char deposited has varied between 1.5% - 2.25 % of the total weight of the plastic. The activation state of the catalyst can be concluded from the char yield %. It can be concluded from that the catalyst shows little variation of char deposited throughout the experiments conducted and it is still in the active state.

4. Conclusion

It can be concluded from the experimental study that the catalytic cracking is far more advantageous than thermal cracking which is due the different type of cracking mechanisms. The variation in the activities of different catalyst are strongly dependent upon the presence of its acidic sites and the type of internal structure. In order to improve the performance of the catalyst, there can be treatment with acids to increase their overall strength.

The Pyrolysis process also yields the gases such as H₂, CH₄ etc. which can be further used for the energy production.

On the regeneration part of USY Zeolite, we observe that there is still presence of active acid site till the 10th experiment which shows that it is an economic method for the usage of the same catalyst. Industrial manufactured Zeolites like USY Zeolite are highly efficient and are very expensive but they can go through regeneration process to be economical while in continuous process of pyrolysis.

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