

## **Optimization of Catalytic degradation of Plastic to Aromatics Over HY Zeolite**

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### **Abstract**

Feedstock recycling methods to convert plastic waste into liquid hydrocarbons products are becoming an important issue since dumping plastic waste into landfill and incineration are not appropriate methods due to legislative and environmental problems. Catalytic degradation of plastics into high quality liquid hydrocarbons is one of the more accepted and promising methods.

In this study HY zeolite is used as catalysts and polyethylene as feedstock. The polyethylene melt heated at degradation reaction under a nitrogen atmosphere in the melter was pressed out by pressurized nitrogen (0.11–0.15MPa) into the reactor loaded with 1 - 3 gram of catalyst through a capillary. Nitrogen was flowed as a carrier gas at a rate of 10 ml/min. The product distribution, the yield of liquid products and liquid composition are further investigated. The effects of temperature and weight of zeolite Y on product distribution and composition of liquid products are investigated. The optimum conditions and model are also estimated by Statistica 6.0 software.

The Pareto chart indicated that the variable with the largest effect was temperature ( $X_1$ ). From the response surface methodology (RSM) results the optimal liquid yield of 13.3%, which 49.7% aromatics content, at the optimized reaction condition (412°C and 2.25 gram HY catalyst) was obtained.

## **Introduction**

There has recently been a growing interest in plastics recycling because of serious environmental problems caused by waste plastics as well as their potential for use as resources. Plastics can be recycled by three different methods: mechanical recycling, chemical recycling (otherwise termed feedstock recycling or tertiary recycling) and energy recovery. Catalytic degradation of plastics into fuel oil is one of the more accepted and promising methods.

Various kinds of techniques to convert plastic wastes into either solid or liquid fuels have been proposed. In the middle of the 1970s, thermal degradation of plastic wastes into fuel oils was studied extensively, but the oils obtained showed a wide distribution of carbon atom numbers and contained a significant fraction of olefins [2]. Since olefins are easily polymerized into unusable compounds during storage and transportation, the oils obtained by a thermal degradation were not fit for fuel oils [5].

The catalytic degradation of plastic wastes was studied using solid acids and bases as catalysts [5–7]. It was found that the oils obtained by catalytic degradation over those solid acids contained lower amounts of olefins and were rich in aromatics compared to the oils obtained by a thermal degradation.

Plastic wastes treated by catalytic degradation processes are mainly limited to waste polyolefins and polystyrene (PS). Waste polyvinyl chloride (PVC) has been excluded because of the emission of hazardous gases [9]. Now, the catalytic conversion of polyolefins into fuels is one of the most significant options of the plastic recycling technologies. However, there is not much research work being done on the optimization of catalytic degradation of plastic.

In this study the thermal and catalytic degradations of polyethylene (PE) are carried out in a quartz reactor by utilizing a batch operation. The product distribution, the yield of liquid products and liquid composition are further investigated. The effects of temperature and weight of zeolite Y on product distribution and composition of liquid products are investigated. The optimum conditions and mathematical model are also estimated by Statistica 6.0 software.

## **Experimental**

Commercially available polyethylene sample with a low density of  $0.915 \text{ g/cm}^3$  was obtained from Aldrich Chemical Co. and used without further treatment. They were pressed into disks, crushed and sieved to give particle sizes ranging from 16 to 32 mesh. Zeolite HY obtained from Zeolyst Co. were used as catalysts. The catalysts were then calcined in air at  $550^\circ\text{C}$  for 3 h.

Figure 1 shows the fixed-bed tubular flow reactor system used in the present study. Briefly, the polyethylene melt heated at degradation reaction under a nitrogen atmosphere in the melter was pressed out by pressurized nitrogen (0.11–0.15 MPa) into the reactor loaded with 1 - 3 gram of catalyst through a capillary. Nitrogen was flowed as a carrier gas at a rate of 10 ml/min. The degradation reaction was carried out at a temperature of  $300 - 500^\circ\text{C}$

The amounts of the liquid and the wax produced were measured by weighing. The coke which deposited on the catalyst surface was determined from the increase in catalyst weight before and after the reaction. The liquid samples collected were analyzed on a Perkin Elmer Gas Chromatograph equipped with a flame ionization detector and a HP-1 column.

The low, middle and high levels of all the independent variables were temperature reaction,  $X_1$ ; and weight of catalyst,  $X_2$ . Accordingly, 300°C, 400°C and 500°C were chosen for variable  $X_1$  and 1.0 g, 2.0g and 3.0 g for  $X_2$  (Table 1). Allowances for extreme measures are designated as  $-\alpha$  and  $+\alpha$  in the central composite design.

According to central composite design, the total number of experiment combinations is  $2^k + 2k + n_0$ , where  $k$  is the number of independent variables and  $n_0$  is the number of experiments repeated at the center point [1,3,4,8]. In this case,  $n_0 = 2$ . The actual experimental design for optimization is shown in Table 2. It was found that a total of 10 runs were needed to optimize the yield of liquid. The result for the design of experiment was obtained by using the Statistica version 6.0.

## Results and Discussion

### *Optimization of Yield of Liquid by Regression Analysis*

The result for yield of liquid according to the experimental design is given in Table 2. The application of response surface methodology yielded the following regression equation, which is an empirical relationship between yield of liquid and the test variable in coded unit as given in equation (1).

$$Y_p = - 56.2855 + 0.2628 * X_1 + 10.9571 * X_2 - 0.0003 * X_1^2 - 2.4375 * X_2^2 - 2.7339 * 10^{-15} * X_1 * X_2 \dots\dots\dots (1)$$

The fitting of the model can be checked by several criteria. The Analysis of Variance (ANOVA) tabulated in Table 3 pertains to the response of the liquid yield. The determination of coefficient  $R^2 = 0.98$  indicates that only 2% of the total variation

did not fit the model. Each of the observed values,  $Y_o$  is compared with the predicted value,  $Y_p$  calculated from the model, as tabulated in Table 2.

Pareto Chart (Figure 2) indicated that the most significant parameters are clearly the temperature, ( $X_1$ ) than weight of catalyst, ( $X_2$ ). The interaction between the temperature and weight of catalyst, ( $X_1X_2$ ) did not seem to have affected the liquid yield.

### ***Optimization of Yield of Liquid by Analyzing the Response Surface Contour Plots***

The yield of liquid can also be predicted from the respective contour plots. Each contour curve represents an infinite number of two test variables and others are maintained at their respective zero level. The maximum predicted liquid yield is indicated by the surface confined in the smallest ellipse in the contour diagram [1,4,8].

It is evident from the plot that liquid yield reached its maximum at a combination of coded level 412°C of temperature and 2.25 gram of catalyst weight. The model predicted a maximum liquid yield of 13.38% within this range (Figures 3 and 4).

The results from Response Surface Method (RSM) using Statistica software indicated that the optimum point for liquid yield is 13.38 when reaction temperature = 412°C and weight of catalyst = 2.25 gram. The catalytic reaction test at the optimized reaction condition is 13.0 for liquid yield.

The composition of liquid product over HY catalyst at the optimized reaction condition (412°C and 2.25 gram HY catalyst) is shown in Table 4. The liquid composition has a low aliphatic and high aromatics content, at 12.4% and 49.7%, respectively however the majority is still wax at 58.4%.

## Conclusions

The liquid yield from degradation of plastic was optimized over HY zeolite catalyst using Statistica version 6.0 software. The two independent variables involved in the optimization are temperature and weight of catalyst. The Pareto chart indicated that the variable with the largest effect was temperature ( $X_1$ ). This is followed by weight of catalyst ( $X_2$ ). The interactions between two of the independent variables can be neglected. From the RSM results the optimal liquid yield of 13.3%, which 49.7% aromatics content, at 412°C and 2.25 gram catalyst was obtained. The adequacy of this model is confirmed by means of variance analysis and additional experiment.

## References

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Table 1. Experimental Range and Levels of Independent Variables

X, Variables	Variable Level			Step Change Value $\Delta X$
	$-\alpha$	0	$\alpha$	
X <sub>1</sub> , Temperature	300	400	500	100
X <sub>2</sub> , Wt. Catalyst	1.0	2.0	3.0	1.0

Table 2. Fractional factorial central composite design two variable with the observed responses (Y<sub>o</sub>) and predicted values (Y<sub>p</sub>)

Run	X <sub>1</sub>	X <sub>2</sub>	Y <sub>o</sub>	Y <sub>p</sub>	(Y <sub>o</sub> -Y <sub>p</sub> )
1	300	1.0	3.0	2.4	0.6
2	300	3.0	5.0	4.8	0.2
3	500	1.0	4.0	3.9	0.1
4	500	3.0	6.0	6.4	-0.4
5	400	2.0	10.0	10.0	0.0
6	259	2.0	2.0	2.5	-0.5
7	541	2.0	5.0	4.7	0.3
8	400	0.6	3.0	3.4	-0.4
9	400	3.4	7.0	6.8	0.2
10	400	2.0	10.0	10.0	0.0

Table 3. ANOVA for the yield of liquid

Source	Sum of square	Degree of freedom	Mean square	F- value	R <sup>2</sup>
S.S. Regression	69.71	5	13.942	50.2414414	0.98432646
S.S. Error	1.11	4	0.2775		
S.S. Total	70.82	9			

Table 4. The yield of products and composition of liquid from catalytic degradation of plastics over HY catalyst at 412°C and 2.25 gram of HY catalyst

Yield (wt.%)	Thermal	Zeolite HY
Gas	7.6	28.2
Liquid	3.1	13.0
Wax	89.2	58.4
Coke	0.1	0.4
Distribution of Liquid (wt.%)		
Aliphatic	Trace	12.4
Aromatics	Trace	49.7
Others	Trace	37.9

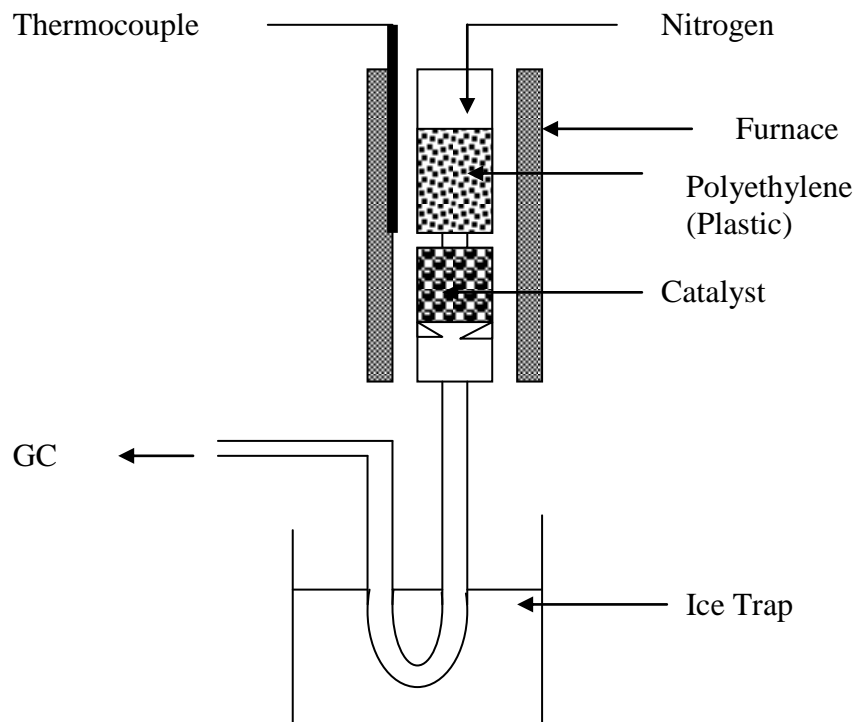


Figure 1. The fixed-bed tubular flow reactor system.

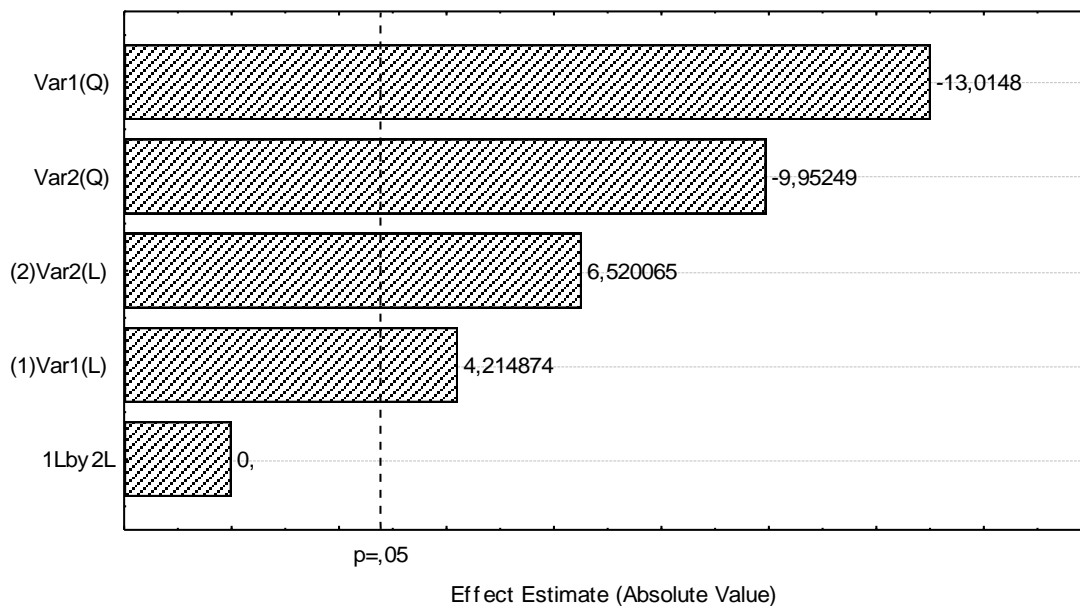


Figure 2. Pareto chart of standardized effects of liquid yield



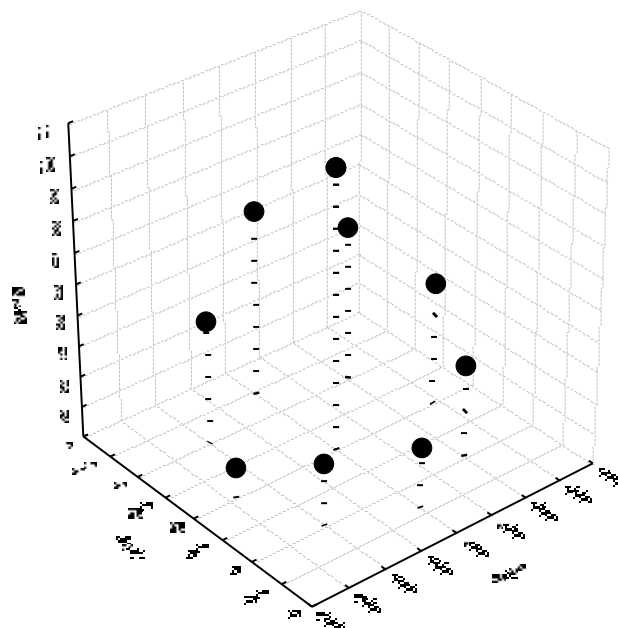


Figure 3. Three-D graphic surface optimization of liquid yield versus temperature (Var 1) and weight of catalyst (Var 2)

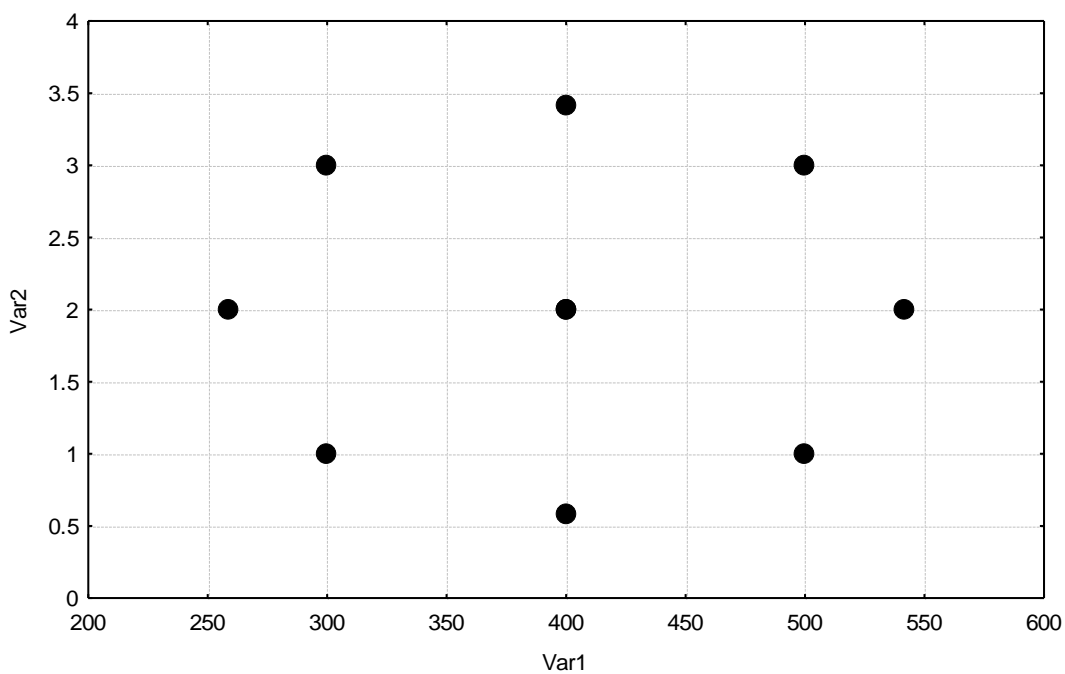


Figure 4. Contour surface plot of liquid yield as a function temperature (Var 1) and weight of catalyst (Var 2)