Optimization of the Recovery Parameters of Poly (Ethylene Terephthalate) Depolymerization through Aminolysis in the Presence of an Organotin Catalyst

Edsel B. Calica
Instructor III, Chemical Engineering Department
University of Santo Tomas
Manila City, Philippines

Jude Anthony O. Billiones
Student, Chemical Engineering Department
University of Santo Tomas
Manila City, Philippines

Allan Joseph V. Jumaquio
Student, Chemical Engineering Department
University of Santo Tomas
Manila City, Philippines

Viel E. Villalon
Student, Chemical Engineering Department
University of Santo Tomas
Manila City, Philippines

Abstract—**Plastics had been of good use in various industries. However, poly(ethylene terephthalate) (PET) plastic take a long time to decompose, hence, need to recycle PET waste must be taken into consideration. Chemical recycling is one of the most effective methods of plastic recycling and one type of this is aminolysis which yields terephthalic diamines which are used as stabilizers for the manufacture of Low Density Polyethylene (LDPE). This study aimed to optimize the recovery parameters of PET depolymerization through aminolysis by total reflux condensation with ethanolamine (EA) in the presence of an organotin catalyst specifically Dibutyltin Oxide (DBTO) by varying the catalyst-PET ratio, PET-Ethanolamine molar ratio and reaction time. A mathematical model that would predict the yield of Bis(2-hydroxy ethylene) terephthalamide (BHETA) was deduced. The product was subjected to Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC) in order to confirm the identity of BHETA. The generated model was given as Yield (%) = 204.8 − 40.7 (Time) + 29.7 (Catalyst-PET ratio) − 1040 (PET-Ethanolamine ratio + 212.9 (Time) (PET-Ethanolamine ratio) and optimized values of the chosen parameters were 6 hours of reaction time, 0.75 w/w catalyst-PET ratio and 0.25 molar ratio of PET-Ethanolamine. Recovery using the optimum values produced a 42.184% BHETA yield. The FTIR spectra confirmed the presence of peaks corresponding to functional groups that comprise BHETA and DSC results show that the melting point of the product sample was within the range of BHETA compound.**

Keywords— Chemical recycling, Depolymerization, Aminolysis, Ethanolamine, Bis(2-hydroxy ethylene) terephthalamide, Dibutyltin Oxide (DBTO)

I. INTRODUCTION

Due to its versatility, plastics had provided our generation with convenience through varied applications. Plastics are generally inexpensive, lightweight materials having good strength and durability, and offer a good resistant against gases and other chemicals. Moreover, thermoplastics are plastics that may be reformed after heating. Because of these physical and mechanical properties, plastics became one of the most widely used packaging materials for food and beverages. However, PET plastics take a long time to decompose in an ecosystem due to its molecular structure; hence, the PET waste quantities are increasing dramatically [1]. This problem motivated the researchers to explore the possible recycling strategies that would help lessen pollution brought about by plastic wastes.

PET recycling can be classified into four categories according to the manner of recycling namely primary, secondary, tertiary and quaternary. Primary recycling simply is re-using the material without altering the product. Secondary recycling, also known as mechanical recycling, is achieved by cutting or grinding, melting, and reforming the plastic waste mixtures. Chemical recycling involves completely breaking down a product into its monomers by means of chemical processes. Lastly, quaternary recycling uses combustion or incineration to recover energy from plastic products [2].

Chemical recycling, also known as depolymerization, should be promoted among other recycling techniques because it conforms to the principles of sustainable development by being able to produce raw materials. Furthermore, chemical recycling also lessens the production of virgin polyethylene for the manufacture different thermoplastic products, thus, reducing the potential amount of plastic waste generated.

Aminolysis is a method of depolymerization of PET which, compared to other depolymerization techniques, has been least investigated [3]. This technique involves the degradation of PET by an aqueous amine in the presence or absence of an organotin catalyst [4]. This process yields terephthalic diamines which are used as stabilizers for low density polyethylene (LDPE).

In this study, post-consumer PET bottles were reacted with ethanolamine with organotin oxide catalyst in order to produce the yield, bis(2-hydroxy ethylene) terephthalamide (BHETA).The main objective of this study was to determine the effectiveness of ethanolamine (EA) in the aminolysis of poly(ethylene terephthalate) in the presence of Dibutyltin Oxide as an organotin catalyst.

Specifically, the study aimed to:

- chemically recycle PET through laboratory scale aminolysis under ambient conditions;
- confirm the presence and purity of BHETA in the end product; and
- deduce a mathematical model on the process parameters considered such as PET-catalyst ratio, PET-EA ratio, and reaction time to identify the optimal recovery of BHETA.

II. METHODOLOGY

Raw Materials

A. PET Bottles

Approximately 30 pieces of empty post-consumer 350 ml nature's spring bottles, collected inside the vicinity of the University of Santo Tomas, were used in the study. Labels and caps were removed. After collecting, the bottles were washed with dishwashing liquid and water, and were sun-dried for 30 minutes. The bottles were cut approximately to one mm by one mm (1mm x 1mm) chips.

B. Ethanolamine solution

Concentrated solution ($\geq$ 99%) of ethanolamine was purchased at Belman Laboratories in Quezon City, Philippines. The concentration of the aqueous solution prepared was 20% by volume. It was done by adding 2.52 ml, 3.36 ml and 5.04 ml of water to 0.63 ml, 0.84 ml and 1.26 ml of ethanolamine, respectively.

C. Dibutyltin oxide (DBTO)

The catalyst was also purchased at Belman Laboratories. The amount used for the experiment was based on the desired catalyst-PET weight ratio which varied from 0.25, 0.50 and 0.75, the same weight ratios as with those used by Parab et al. (2012).

D. Formulation of the Solution for Depolymerization

Depolymerization of PET was performed with varying PET-ethanolamine molar ratio, DBTO-PET ratios and reaction time. Half a gram of PET was used for each reaction. All reaction formulations for the 17 runs are shown in Table 1. The reaction time varies from four, five and six hours. The catalyst-PET weight ratio varies from 0.25, 0.5 and 0.75 and the PET-ethanolamine molar ratio varies from 0.125, 0.1875 and 0.25. As an example, the reaction parameters for the first run were five hours of reaction time, 0.25 grams of catalysts and 0.84 milliliter of pure ethanolamine.

Two pre-set combination runs were required by Box Behnken as base line for the 17 runs. The first reference run has a combination of four hours reaction time, 0.125 grams of catalysts and 0.84 ml of ethanolamine. The second reference run has a combination of six hours reaction time, 0.125 grams of catalyst and 0.84 ml of ethanolamine. Half a gram of PET was used for both reactions.

Experimental Procedure

A. Depolymerization (Aminolysis)

The PET flakes, ethanolamine solution, and the catalyst were mixed together in a three-neck flask under total reflux condensation. The mixture was subjected to heating at 120-130 degrees Celsius and constant stirring of the oil bath at 500 rpm for homogeneity purposes. Two ml of water was added and the temperature was recorded in 30-minute intervals with respect to the reaction time.

B. Cooling of the mixture.

At the end of every reaction, the mixture was allowed to cool under room temperature until the mixture reached temperatures between 50-60 degrees Celsius. The cooled mixture was then subjected inside a household refrigerator for 24 hoursFirst, confirm that you have the correct template for your paper size. This template has been tailored for output on the A4 paper size. If you are using US letter-sized paper, please close this file and download the file "MSW_USltr_format".

C. Filtration and precipitation of product

The reaction mixture was filtered using a pre-weighed grade 40 Whatman filter paper and the product was obtained by precipitation.

Primary Residue. The residue obtained from the first filtration process contained the unreacted PET flakes. It was washed twice with five ml distilled water and oven dried at 80 degrees Celsius for two hours.

Primary Filtrate. The primary filtrate contained the BHETA, ethylene glycol, water and catalyst. The main product, bis(2-hydroxy ethylene)terephthalamide (BHETA), was precipitated in powdered form by freezing the mixture inside a household refrigerator at 0°C for 24 hours. The precipitate obtained was again filtered to separate BHETA from the water, ethylene glycol and catalyst.

Secondary Residue. The secondary residue contained the product BHETA that underwent the determination of the yield.

Table 1. Reaction Formulations for the Aminolysis of PET

Run	Time (hours)	Catalyst-PET Ratio (w/w)	PET-Ethanolamine molar ratio	Weight of Catalyst (grams)	Volume of Pure Ethanolamine (mL)
1	5	0.50	0.1875	0.250	0.84
2	5	0.75	0.2500	0.375	0.63
3	5	0.50	0.1875	0.250	0.84
4	4	0.75	0.1875	0.375	0.84
5	5	0.50	0.1875	0.250	0.84
6	6	0.50	0.2500	0.250	0.63
7	5	0.50	0.1875	0.250	0.84
8	5	0.25	0.1250	0.125	1.26
9	4	0.50	0.1875	0.250	0.63
10	5	0.25	0.2500	0.125	0.63
11	5	0.75	0.1250	0.375	1.26
12	5	0.50	0.1875	0.250	0.84
13	6	0.50	0.1250	0.250	1.26
14	4	0.50	0.1250	0.250	1.26
15	4	0.25	0.1875	0.125	0.84
16	6	0.75	0.1875	0.375	0.84
17	6	0.25	0.1875	0.125	0.84
Pre-set 1	4	0.25	0.1875	0.125	0.84
Pre-set 2	6	0.25	0.1875	0.125	0.84

D. Yield recovery

The primary filtrate was boiled for 30 minutes in a water bath. Crystals of BHETA were produced by freezing the boiled primary filtrate inside a household refrigerator at 0°C for 24 hours.

E. Determination of the yield.

The secondary residue was dried in an oven dryer at 80 degrees Celsius. The weight of the empty filter paper and the dried filter paper containing the secondary residue were determined using an Ohaus PA214 Pioneer analytical balance. The yield estimate was determined by weighing by difference and using the equation 1 below.

$$BHETA\ yield\ (\%) = \frac{W_{BHETA}}{W_{BHETA,o}} \, x100 \quad (Eqn.1)$$

F. Characterization of the product

A sample of BHETA was subjected to characterization through Fourier Transform Infrared Spectroscopy (FTIR) analysis and Differential Scanning Calorimetry to determine the compound present and the melting point of the polymer, respectively. Both tests were done at Thomas Aquinas Research Center in the University of Santo Tomas.

G. Model fitting and Analysis of Variance

A stepwise multiple regression analysis was used for determining the mathematical model that can predict the recovery of the desired product. The yield response from the experiment was plotted with its corresponding reaction time, catalysts-PET ratio and PET-ethanolamine molar ratio for 17 runs using Design Expert 7.0 Box Behnken. The simulation and statistical diagnostic tests were performed using Minitab.

III. RESULTS AND DISCUSSION

H. Aminolysis

Post-consumer Nature's Spring PET flakes were subjected to aminolysis in ethanolamine solution with dibutyltin oxide catalyst to produce bis(2-hydroxyethylene) terephthalamide and ethylene glycol.

In this reaction, two nucleophilic centers were found in ethanolamine, nitrogen and oxygen, with nitrogen being less electronegative than oxygen. Since the carbon atom in the ester linkage is highly positive, the less electronegative nitrogen attacks this carbon to form a more stable bond which forms BHETA and by-products ethylene glycol and water.

For the degradation of PET in ethanolamine solution, 0.5 grams of post-consumer PET flakes were reacted. The catalyst to PET ratio, molar concentration of ethanolamine to PET ratio, and the reaction time were varied within the considered range in order to determine the optimal yield solution of the synthesis.

Table 2. % PET Degradation and % BHETA yield

Run	% Degraded	% Yield
1	25.655	7.983
2	58.088	34.557
3	42.546	17.273
4	26.564	11.051
5	52.347	37.225
6	45.437	32.847
7	22.308	17.197
8	21.378	15.881
9	16.101	14.944
10	33.641	22.284
11	81.525	41.066
12	62.411	10.753
13	48.252	0.000
14	46.270	35.321
15	9.551	8.799
16	37.396	25.272
17	5.929	5.600
Preset 1	11.614	8.616
Preset 2	59.120	40.554

In order to determine the percent degradation of PET, Equation 2 below was used.

$$PET_{\deg redation}(\%) = \frac{W_{PET,0} - W_{PET,f}}{W_{PET,0}} x100 \qquad (Eqn.2)$$

The yield of BHETA was calculated using Equation 3 shown below.

$$BHETA_{yield}(\%) = \frac{W_{BHETA}}{W_{BHETA,o}} x100 \qquad (Eqn.3)$$

Where:

$W_{PET,0}$ = initial weight of PET
$W_{PET,f}$ = final weight of PET
W_{BHETA} = experimental weight of BHETA
$W_{BHETA,0}$ = theoretical weight of BHETA

Using the given equations, % PET Degradation and % BHETA yield was computed for each run given by Box-Behnken design. Table 2 shows the summary of the data calculated as well as sample calculations. The highest % degradation and % yield was 81.525% and 41.066% respectively. Both of which were obtained from run 11 having five hours of reaction time, 0.75 Catalyst-PET ratio, and 0.125 PET-Ethanolamine molar ratio.

The scattered plot of PET degradation versus yield of BHETA on Figure 2 shows that most of the trials performed have relatively higher %PET degradation rather than %Yield. Given that all of the points lied just above the diagonal line, most results show that the recovery of BHETA from the solution was inadequate.

I. Characterization of Products

In order to confirm that the identity of the product was BHETA, the purified sample was subjected to FTIR analysis. The results were compared to the FTIR spectrum of BHETA presented by Achilias (2007), et al.

According to the characteristics of the spectra, BHETA compound was identified from the significant peaks. Wavelengths approximately at 3365 cm^{-1} and 1050 cm^{-1} indicated the presence of hydroxyl particularly of a primary alcohol (-CH$_2$-OH); wavelengths observed at 3300, 1650, 1550 and 1320 cm^{-1} represented a N-substituted benzamide; the peaks appearing at 2850, 2880, 2950 and 3000 cm^{-1} corresponded to stretches of alkyl groups such as –CH$_2$-CH$_2$-. Therefore, the wavelengths identified above would correspond to the chemical compounds that comprise BHETA. All spectra obtained are similar to the FTIR spectrum presented by Achilias (2007), which confirmed the presence of the recovered BHETA.

Optimization

A. Mathematical Modeling

In order to determine the optimal conditions to maximize the BHETA recovery, the gathered experimental data were subjected to multiple regression analysis using Minitab. The candidate variables for the stepwise selection of terms were set as Time, Catalyst-PET ratio, PET-Ethanolamine ratio, Time*Time, Catalyst-PET ratio*Catalyst-PET ratio, PET-Ethanolamine ratio*PET-Ethanolamine ratio based from the Box Behnken design. Performing a stepwise selection of terms that maintains a hierarchical model at each step, the selected terms with their corresponding P-values are shown in Table 3.

Table 3. Stepwise Selection Results

Terms	1st model		2nd model	
	Coefficient	P-value	Coefficient	P-value
Constant	20.67		20.67	
Time	-0.80	0.841	-0.80	0.841
PET-Ethanolamine ratio	1.55	0.700	1.55	0.700
(Time)(PET-Ethanolamine ratio)	13.31	0.036	13.31	0.036
Catalyst-PET ratio			7.42	0.086
R-sq	32.70%		49.18%	
R-sq(adj)	11.80%		28.85%	
Mallows' Cp	6.83		5.15	

The Mallows' CP was evaluated in order to determine which among the two generated models would be the better equation to predict the future responses, as desired. It should be close to the numbers of predictors in the model which includes the constant. In this regard, the Mallows' CP should be close to five taking into account the constant and the considered terms in the model which are Time, PET-Ethanolamine ratio, (Time)(PET-Ethanolamine ratio) and Catalyst-PET ratio. The second model has a Mallows' CP of 5.15 which is closer to 5.00 as compared to the first model that has a Mallows' CP of 6.83; thus, the second model is relatively precise and unbiased in estimating the true regression coefficients and predicting the future responses

Further analyzing the 2nd model using ANOVA in order to obtain the P-values of the predictors, the results show that the Catalyst-PET ratio has a P-value that is significant at 5% level of significance whereas a two-way interaction of Time and PET-Ethanolamine ratio has a P-value that is significant at 10% level of significance. The summary of the results is shown in Table 4.

By default, Minitab analyzes designs using coded units. Although it is convenient to think of the data in uncoded units, it is better to analyze the data using coded units. Coding simplifies comparisons of factors with different measurement scales. For example, Time versus Catalyst-PET ratio. In addition, using uncoded units often leads to multicollinearity among the terms in the model. This inflates the variability in the coefficient estimates and makes them difficult to interpret. Using coded units help to eliminate this problem.

Using uncoded units provides estimated regression coefficients in the original factor scales. However, it may change the results of the statistical tests of hypotheses used to determine whether each term is a significant predictor of the response. Table 5 shows the summary of coded coefficients used to derive the mathematical model.

On the other hand, the generated regression equation in uncoded units is:

$Yield(\%) = 204.8 – 40.7(Time) + 29.7(Catalyst\text{-}PET\ ratio) – 1040(PET\text{-}Ethanolamine\ ratio + 212.9(Time)(PET\text{-}Ethanolamine\ ratio)$ (Eqn. 4)

Lastly, multicollinearity test was performed through variance inflation factor. As per rule of thumb, the value of the VIF must be less than the value of 5 to depict that the variables considered were truly independent. The results of the VIF for the four respective models showed less than the value of 5. Hence, there was no multicollinearity among the variables.

B. Diagnostic Check

Performing a diagnostic check on the deduced mathematical model, the residuals generally appear to follow a straight line as shown in Fig 1. Given the said figure, there is no evidence of an outlier, skewness and non-normality. Moreover, evaluating the test for normality using Kolmogorov-Smirnov, the residual is normal at 5% level of significance with p-value > 0.150. Therefore, the error terms were normally distributed and this assumption check did not violate the normal distribution assumption.
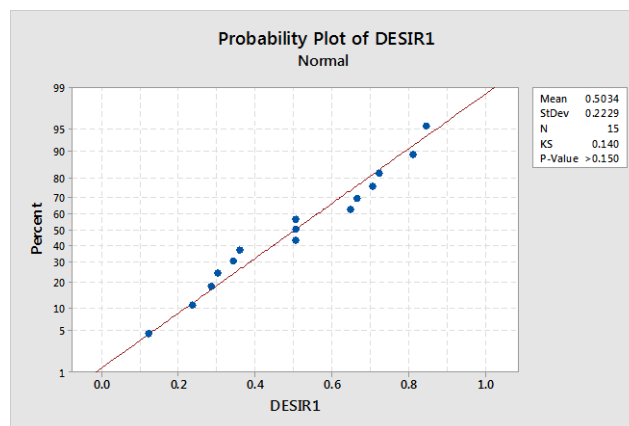

Fig 1. Normality Test

Table 4. Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	4	1173.19	293.298	2.42	0.117
Linear	3	465.01	155.005	1.28	0.334
Time	1	5.11	5.114	0.04	0.841
Catalyst-PET ratio	1	440.79	440.787	3.64	0.086 *
PET-Ethanolamine ratio	1	19.11	19.113	0.16	0.700
2-Way Interaction	1	708.18	708.179	5.84	0.036
(Time)(PET-Ethanolamine ratio)	1	708.18	708.179	5.84	0.036 **
Error	10	1212.47	121.247		
Lack-of-Fit	8	765.96	95.745	0.43	0.841
Pure Error	2	446.51	223.253		
Total	14	2385.66			

*Significant at 10% level of significance
**Significant at 5% level of significance
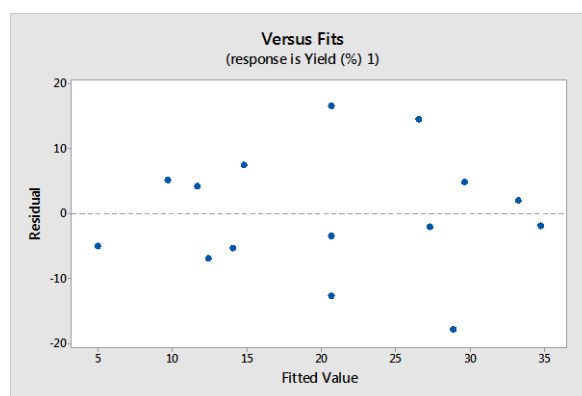
Fig 2. Plot of Residuals vs. Fitted Value

Table 5. Coded Coefficients

Term	Effect	Coefficient	T-Value	P-Value	VIF
Constant		20.67	7.27	0.000	
Time	-1.60	-0.80	-0.21	0.841	1.00
Catalyst-PET ratio	14.85	7.42	1.91	0.086	1.00
PET-Ethanolamine ratio	3.09	1.55	0.40	0.700	1.00
(Time)(PET-Ethanolamine ratio)	26.61	13.31	2.42	0.036	1.00

Fig 2 shows the plot of Residuals vs. Fitted Value. Based from the said plot, the residuals appear to be randomly scattered about zero. Therefore, there is no evidence of non-constant variance or outlier exists.

Optimization

In order to determine the optimal conditions in attaining the maximum recovery of BHETA, the contour plot as shown in Fig 3 was established. It shows the distribution of the yield, while holding the catalyst ratio level at 0.5 as the center point. A greener hue signifies higher yield. Based on the contour plot, the combination of PET-Ethanolamine ratio and Time that will give the highest yield would be at the area where the PET-Ethanolamine ratio is at 0.14 and Time at 4 hours and PET-Ethanolamine ratio at 0.24 and Time at 6 hours.
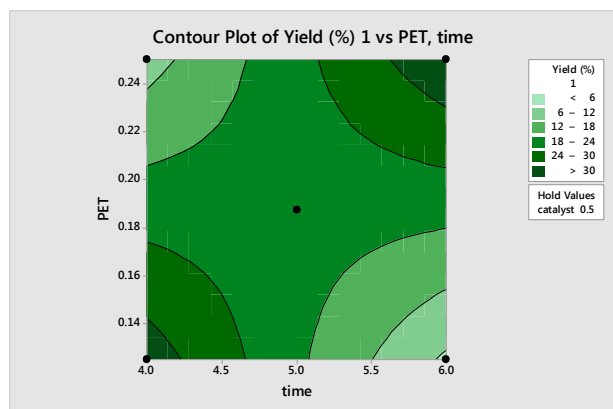
Optimization plot on Fig 4 shows the graph of predicted yield in each variable. The dash line indicates the target requirements. Red line indicates the intersection of the predicted yield line and the target requirements. The intersection shows the optimum level of each variable.

Several diagnostic checks above show that the model is viable in estimating the yield based from the given variable settings. Table 6 shows the optimum solutions based on the model derived.

Optimization uses the model to estimate the optimal variable settings. As the predicted responses to the target requirements would be closer, the value of the desirability would approach 1. Hence, based on the deduced model, the determined maximum yield are Time at 6 hours, Catalyst-PET ratio at 0.75 and PET-Ethanolamine ratio at 0.25.
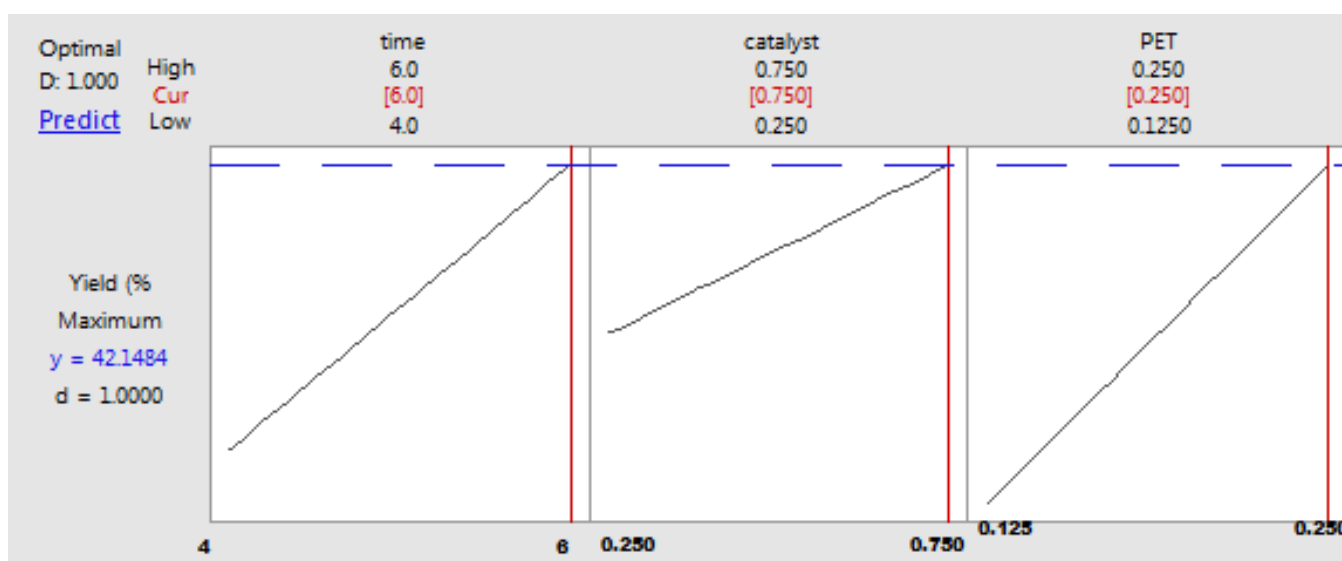

Fig 3. Contour Plot of Yield vs and PET-Ethanolamine ratio and time

Fig 4. Optimization Plot

Table 6. Optimum solutions based on the model

Solution	Time	Catalyst-PET Ratio	PET-Ethanolamine Ratio	Yield (%) Fit	Composite Desirability
1	6	0.75	0.25	42.1484	1.00000
2	5.91346	0.75	0.25	41.0661	1.00000
3	4	0.75	0.125	40.6560	0.99002
4	6	0.309112	0.25	29.0578	0.70759
5	4	0.321898	0.125	27.9451	0.68049
6	4.72984	0.75	0.207107	27.6696	0.67378
7	5.14943	0.75	0.180973	27.6079	0.67228
8	5.38632	0.661409	0.196799	26.1519	0.63682

II.   CONCLUSION

A laboratory scale experiment was performed in order to determine the effectiveness of ethanolamine (EA) in the aminolysis of poly(ethylene) terephthalate (PET) depolymerization with the presence of dibutyltin oxide (DBTO) as an organotin catalyst. Process parameters such as PET-catalyst ratio, PET-EA ratio and reaction time were varied throughout the investigation. The reaction was in total reflux at temperatures ranging from 120 - 130˚C. The gathered experimental data show that BHETA recovery is inadequate because the % PET degradation is relatively higher than the % yield. The identity of BHETA was verified through FTIR analysis and DSC spectroscopy. The significant peaks present in the FTIR analysis consists of the compounds that make up BHETA.

a) Based on the generated multiple regression equation yield = 204.8 – 40.7(Time) + 29.7(Catalyst-PET Ratio) - 1 040(PET-Ethanolamine   Ratio)   +212.9(Time)(PET-Ethanolamine Ratio)*, maximum yield can be obtained when Time is at 6 hours, Catalyst-PET ratio at 0.75 and PET-Ethanolamine at 0.25. These optimal variables shall result to a 42.148 4% yield*.

REFERENCES

[1] Khalaf, H., & Hasan, O. (2012).Effect Of Quarternary Ammonium Salt As A Phase Transfer Catalyst For The Microwave Depolymerization Of Polyethylene Terephthalate Waste Bottles.Chemical Engineering Journal 192, 45-48.

[2] Bartolome, L., Imran, M., Cho, B.G., Al-Masry, W., Kim, D.H (2012). Recent Developments In The Chemical Recycling Of PET, Material Recycling - Trends And Perspectives, 66-84

[3] Hoang, C.N., Dang, Y.H. (2013) Aminolysis Of Poly(Ethylene   Terephthalate)   Waste   With Ethylenediamine And Characterization Of A,Ω-Diamine Products. Polymer Degradation And Stability, 98, 697-708.

[4] Tawfik, M. E., & Eskander, S. B. (2010). Chemical Recycling Of Poly(Ethylene Terephthalate) Waste Using Ethanolamine.Sorting Of The End Products. Polymer Degradation And Stability, 95, 187-194.

[5] Liu, Y., Wang, M., & Pan, Z. (2012). Catalytic Depolymerization Of Polyethylene Terephthalate In Hot Compressed Water. The Journal Of Supercritical Fluids 62, 226-331.

[6] Parab, Y. S., Pingale, N. D., & Shukla, S. R. (2011). Aminolytic Depolymerization Of Poly (Ethylene Terephthalate) Bottle Waste By Conventional And Microwave Irradiation Heating. Journal Of Applied Polymer Science, 125(2), 1103-1107.

[7] Achillias, D., Tsintzou, G., Nikolaidis, A., Bikairis, D., & Karayannidis, G. (2010, November 17). Aminolytic Depolymerization Of Poly(Ethylene Terephthalate) Waste In A Microwave Reactor. Polymer International(60), 500-506.

[8] Shukla, S. R., & Harad, A. M. (2006). Aminolysis Of Polyethylene   Terephthalate   Waste.   Polymer Degradation And Stability, 91(8), 1850-1854.