CHAPTER IV

RESULTS AND DISCUSSIONS

In this study, The attempt was done to reclaim TPA from used PET bottles. First, two methods: saponification and neutral hydrolysis have been studied to determine optimum conditions. Secondly, depolymerization of PET while that PET was mixed with another plastic, PVC, were done. Finally, the products from these experiments were characterized by FT-IR and NMR.

4.1 Saponification

PET was reacted with NaOH solution at various condition to provide ethylene glycol and an intermediate product, disodium terephthalate. The intermediate was then acidified with concentrated HCl causing TPA to precipitate. The reaction is shown in Figure 4.1.

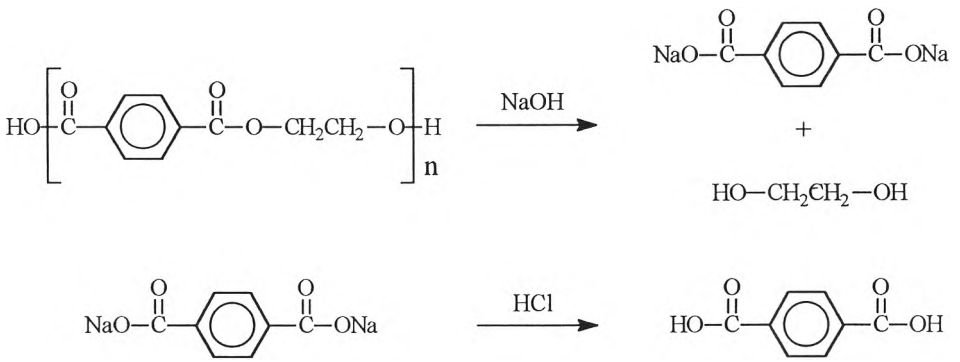

Figure 4.1 The saponification of PET

4.1.1 The effect of NaOH content

The results are shown in Table 4.1 and plotted to give the curve in Figure 4.2.

Table 4.1 %yield of PTA in saponification with various NaOH content

PTA	NaOH content (%w/w NaOH/PET)					
	25	40	50	60	75	100
weight (g)	5.33	11.49	12.35	12.33	12.32	12.31
yield (%)	41.1	88.6	95.2	95.1	95.0	94.9

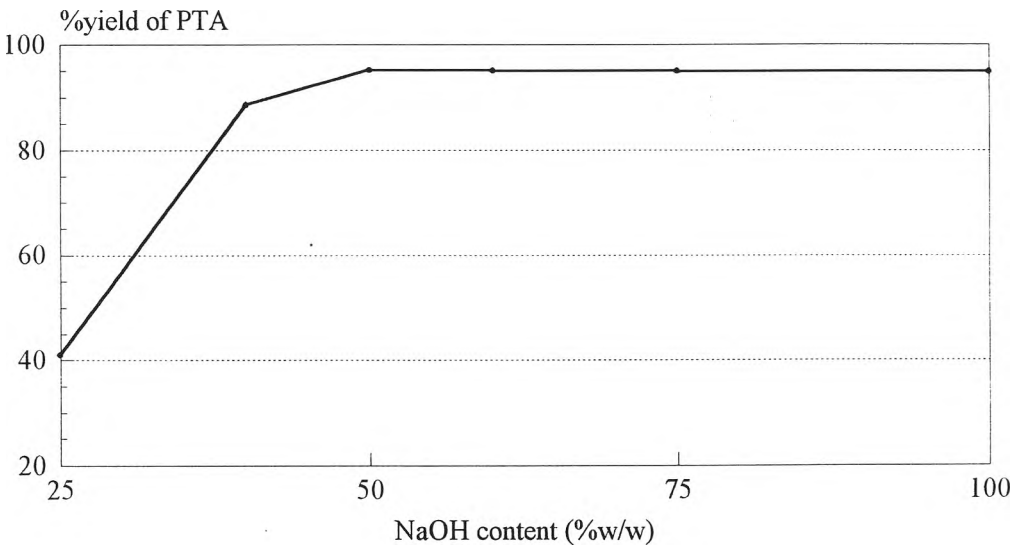

Figure 4.2 %yield of PTA versus NaOH content

The curve indicated that the 50% w/w (NaOH/PET) was the optimum content. At a content below 50% w/w, the reaction was not complete. In contrast with the higher NaOH content, the product might be carbonized resulting in a lower yield. **[23]**

4.1.2 The effect of temperature

The results are shown in the Table 4.2 and illustrated in Figure 4.3.

Table 4.2 % yield of PTA in saponification with various temperature

PTA	Temperature (°C)				
	150	180	210	240	270
weight (g)	7.14	12.49	12.44	12.41	12.35
yield (%)	55.1	96.3	95.9	95.7	95.2

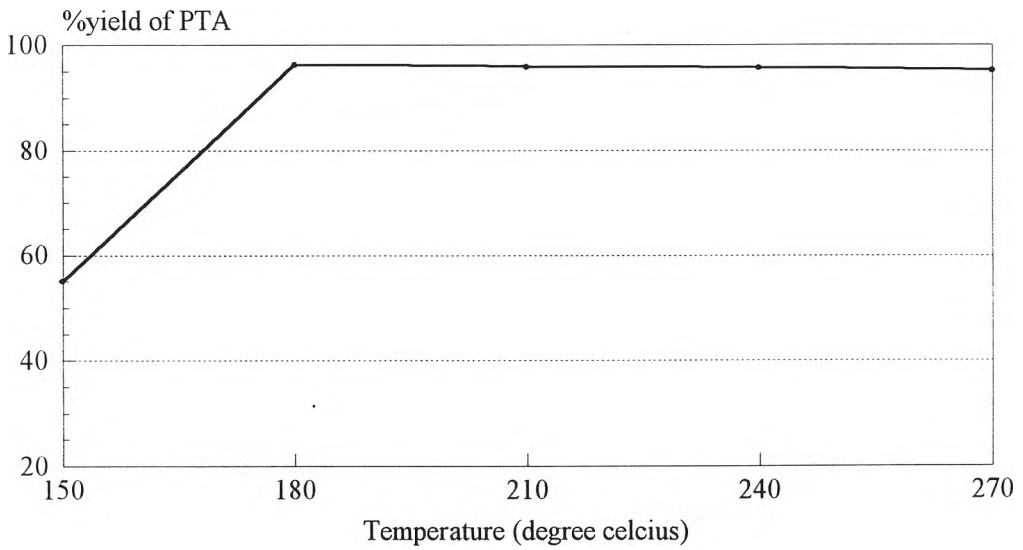

Figure 4.3 %yield of PTA versus temperature

By the same consideration as before, the curve showed that the optimum temperature was 180°C.

4.1.3 The effect of time

Table 4.3 and Figure 4.4 shows the results of varying reaction time.

Table 4.3 % yield of PTA in saponification with various reaction time

PTA	Time (minutes)				
	5	15	30	45	60
weight (g)	9.57	12.16	12.41	12.63	12.49
yield (%)	73.8	93.8	95.7	97.4	96.3

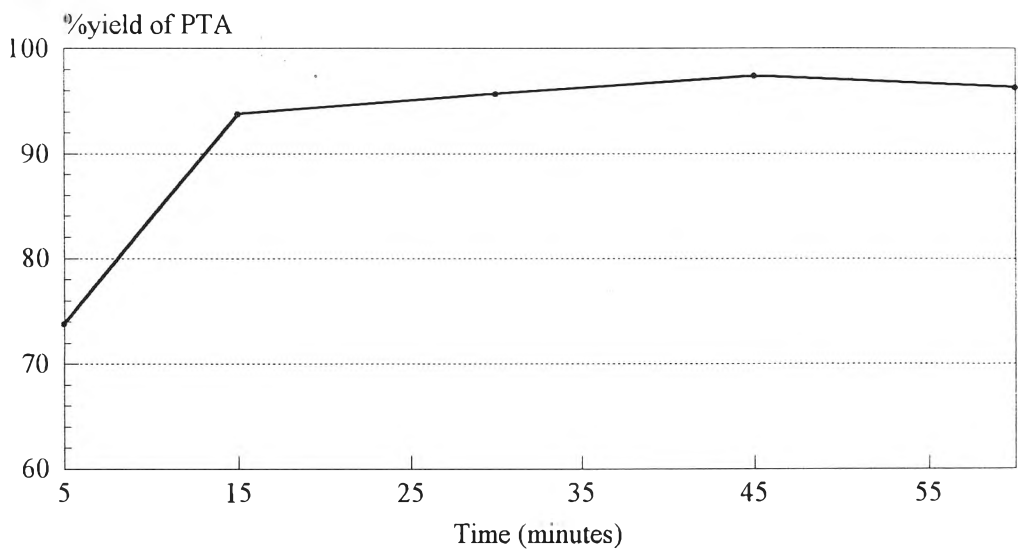

Figure 4.4 %yield of PTA versus reaction time

As discussed before, the optimum reaction time was 45 minutes.

For economic aspects, the shortest time is necessary. The optimum reaction time, in this study, was 45 minutes. It is a long time, hence, it should be decreased to increase economic efficiency.

To obtain the optimum time for economic practices, the reaction temperature should be increased from 180°C to 210°C and NaOH content held at 50% w/w (NaOH/PET). The reaction pressure was increasing to 230 psig corresponding to the increasing temperature. The results of various operating times of 1, 5, 15, 30, 45, and 60 minutes are shown in Table 4.4 and Figure 4.5.

Table 4.4 % yield of PTA in saponification with various reaction time (on economic aspects).

PTA	Time (minutes)					
	1	5	15	30	45	60
weight (g)	12.63	12.61	12.59	12.55	12.50	12.44
yield (%)	97.4	97.2	97.1	96.8	96.4	95.9

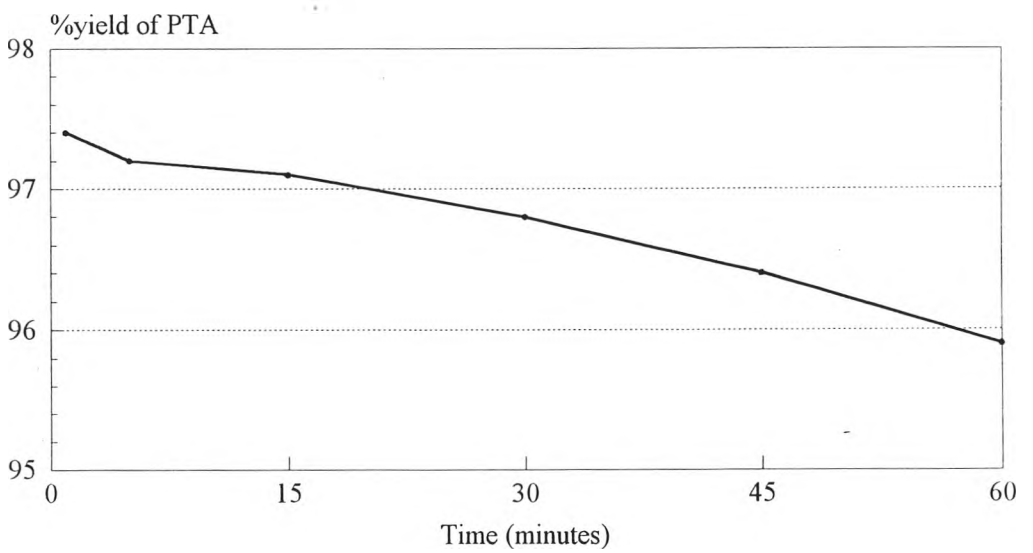

Figure 4.5 %yield of PTA versus reaction time (on economic aspect)

The curve denoted that the optimum operation time was 1 minute at 210°C. Longer period of time, higher carbonization caused lower yields, although, the differences may not be statistically significant.

For the reclamation of TPA by saponification, the optimum conditions are as follows:

NaOH content	50	%w/w (NaOH/PET),
Temperature	210	°C (at 230 psig),
Time	1	minute.

The conversion of PET was 100%, whereas the yield of TPA was found to be 97.4%.

These results were shown that the result can be achieved by heating PET in NaOH solution. It was not necessary to use another solvent in contrast to a previous report using DMSO **[22]**. Furthermore, the reaction time of this study was less than in a related report using 30 minutes **[23]**.

Nevertheless, the recovery of TPA by neutralization of the salts with acid was wasteful because acid and base were consumed and salts were created. Disposal of the salts would have a negative effect on the environment.

4.2 Neutral hydrolysis

PET depolymerization was carried out in the presence of water at elevated temperature. TPA and ethylene glycol were reclaimed by one-step reaction as shown in Figure 4.6.

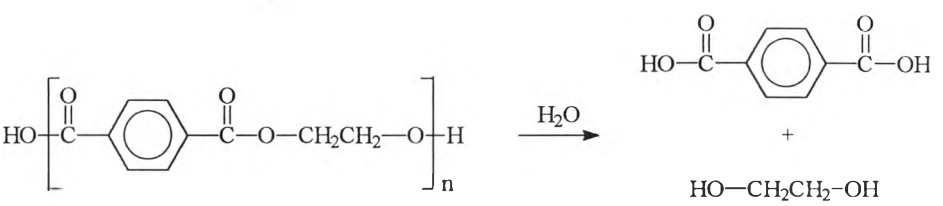

Figure 4.6 The neutral hydrolysis of PET

4.2.1 The effect of temperature

The results are shown in Table 4.5.

Table 4.5 % yield of PTA in neutral hydrolysis with various temperature

PTA	Temperature (°C)		
	210	240	270
weight (g)	ND	ND	12.48
yield (%)	ND	ND	96.2

Note : ND means not detected because of incomplete reaction.

The data showed that lower temperatures generally caused slow hydrolysis rates and gave incomplete reaction over reasonable time periods. It was determined that the optimum temperature was 270°C.

4.2.2 The effect of reaction time

The results are shown in Table 4.6.

Table 4.6 % yield of PTA in neutral hydrolysis with various reaction time

PTA	Time (minutes)				
	1	3	5	15	30
weight (g)	ND	ND	12.52	12.48	12.45
yield (%)	ND	ND	96.5	96.2	96.0

Note : ND means not detected because of incomplete reaction.

The above data showed that the optimum reaction time was 5 minutes. There was no significant difference with longer reaction times.

4.2.3 The relation of Temperature and Reaction Time

As discussed before, the shorter reaction time corresponded to the higher temperature. Figure 4.7 displays the relation between temperature and reaction time.

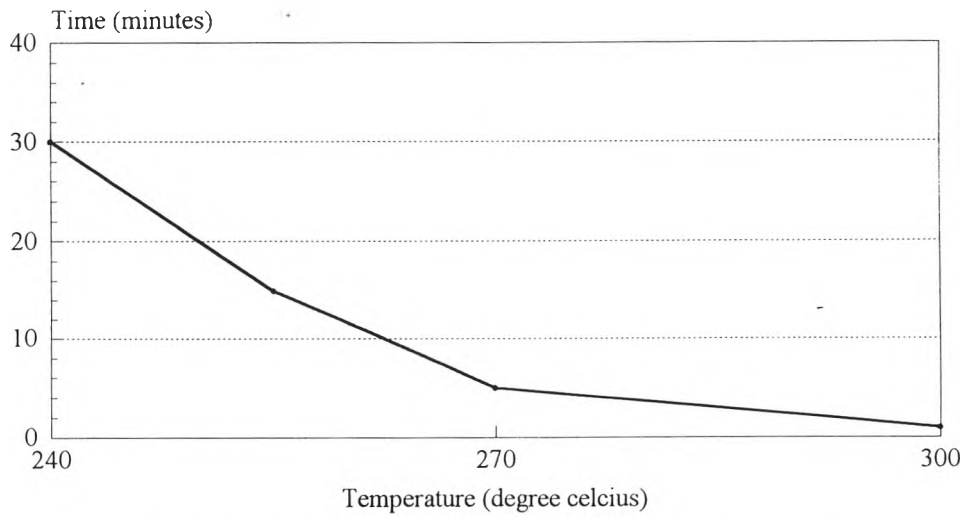

Figure 4.7 Temperature versus Reaction Time

From the above curve, it was concluded that the reclamation of TPA by neutral hydrolysis has the optimum condition as follows:

Temperature	270	°C (at 700 psig)
Time	5	minutes

The yield of terephthalic acid was determined to be 96.5%, whereas the conversion of PET was 100%.

The neutral hydrolysis is a perfect method for reclaiming TPA. This method was effective without the use or production of organic reagents, products or inorganic salts that would harm the environment.

According to the results of this study, the reaction time was less than in the work of Mendoki **[24]** which had residence time of the process more than 30 minutes. Furthermore, it was not necessary to operate under nitrogen pressure as the work of Tustin et.al. **[25]**. Thus, the neutral hydrolysis in this study could be operated in a continuous manner as illustrated in Figure 4.8.

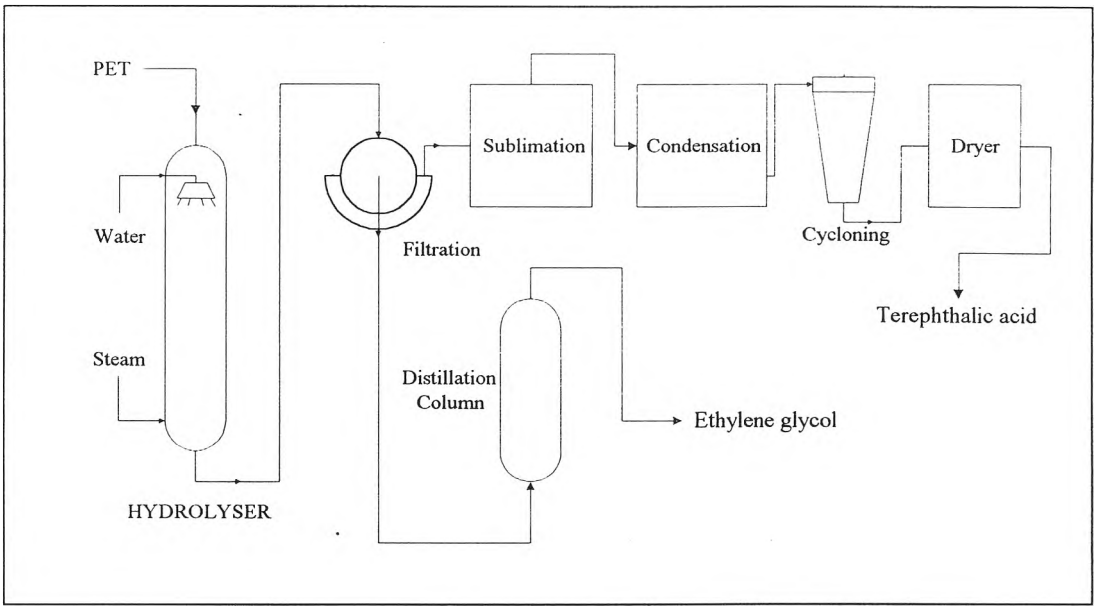

Figure 4.8 Schematic diagram for reclaiming PTA in continuous process

Firstly, PET would be chopped into a particular size and fed continuously into the hydrolyzer. The steam would agitate the PET to provide heat transfer and to maximize contact between the PET and the hot water in the hydrolyzer. The hydrolysis temperature might be 270°C and the vapor pressure of water would corresponding to the reaction temperature. According to this study, the residence time in the hydrolyzer would be five minutes.

Next, the mixture of solid and liquid portion would be taken apart at a filtration unit. The liquid component containing water and ethylene glycol would be sent to a distillation column for the recovery of ethylene glycol. The solid would be transferred to the sublimation unit as a TPA-purification step.

There were many techniques for sublimation. One of the best techniques is the sublimation/condensation method **[25]**. In this method, the solid is heated to a temperature above its dew point. The dew point varies as a function of the pressure and mole ratio of water to TPA. For example, when the water:TPA ratio is 3:1 at about 0.1 atmosphere pressure, then the

dew point is 315°C. This technique can also be considered as steam distillation.

Next, the heated vapor stream ensuing from the sublimation unit would be cooled to a temperature below its dew point in the condensation unit. A condensation temperature below about 230°C is preferred for condensation of TPA from the vapor in the one atmosphere process.

The white solid of TPA contained in a condensation vessel would mostly be floating on the top of the condensed water. Cycloning and filtration are the preferred means of collecting the products. A portion or all of the water used in the sublimation/condensation process could be returned to the hydrolyzer or portions might also be reverted to the sublimation/condensation operation.

4.3 Study of terephthalic acid reclamation from mixed PET and PVC

PET and PVC was mixed in various ratios, 100:0 75:25 50:50 and 25:75 by weight. The reaction was studied under the optimum condition of each method, 50%w/w (NaOH/PET), 210°C, 1 minute for saponification and 270°C, 5 minute for neutral hydrolysis, to determine the effect of PVC on reclamation of TPA from mixed plastics.

The results are presented in Table 4.7.

Table 4.7 % yield of PTA in neutral hydrolysis and saponification of Mixed PVC and PET.

%yield of Terephthalic acid	Ratio of PET/PVC (%by weight)			
	100:0	75:25	50:50	25:50
Saponification	97.4	97.3	97.2	97.2
Neutral hydrolysis	96.5	96.3	96.2	96.2

No significant differences in terephthalic acid yield was found. It can be said that PVC did not affect either of the reclamation methods.

However, in neutral hydrolysis, the pH of PET/PVC mixed solution compared with the pH of PET solution decreased from 7 to 1. It could be said that PVC was decomposed at the reaction temperature. The decomposition of PVC was first noted at temperature near 100°C **[26-27]**, by molecular weight and thermal conditions. As dehydrochlorination occured and hydrogen chloride was evolved, the PVC become discoloured. Temperature-sensitive allylic groupings and tertiary chlorine were formed and unzippering occurred, leading to the formation of polyene structures which led to discoloration.

Both saponification and neutral hydrolysis methods could generate hydrochloric acid; hence, the saponification method was safe for this case. Sodium hydroxide used in the method would trap the acid that formed.

4.4 Product characterisation

4.4.1 Functional groups

The FT-IR spectrum of TPA from each optimum condition was the same as displayed in Appendix A1. It was similar to the IR spectrum of Aldrich Library **[28]**. The spectrum indicated the presence of a very broad O-H stretching in the region of 3,300-2,500 cm^{-1}. The peak at 1,702 cm^{-1} corresponds to C=O stretching. The C-O stretching is at 1,298 cm^{-1}. Asymmetric and Symmetric carboxylate anion stretching are apparent at 1,580 and 1,430 cm^{-1}, respectively. It is also aromatic C-H stretching at 3,100 cm^{-1}, whereas the peaks at 943 cm^{-1} results from para-substituted out-of-plane ring bending.

4.4.2 The structure

TPA form each optimum condition was characterised by ^{13}C-NMR as shown in Appendix A2. The spectrum, supported by Sadtler standard **[29],** showed signals with chemical shifts at 130, 135, and 168 ppm with the ratio of 2:1:1 corresponding to the structure of TPA, especially.

4.4.3 Acid number

The acid number was determined by back-titration and calculated by the equation shown in 3.2.4.3.

The results are shown in Table 4.8.

Table 4.8 acid number in mg KOH/g of terephthalic acid

Sample	acid number (mg KOH/g)
1	675.75
2	674.79
3	675.75
Average	*675.43*

The acid number is an overall purity measurement of TPA. A perfectly pure sample would have an acid number of 675.5 mg KOH/g, but the low impurity levels made the acid number meaningless as a quantitative indication of purity, and it was being phased out. The acid number of TPA that was more than 673 mg KOH/g would be commercially acceptable**[18]**. Hence, the product from this study was sufficiently pure for the preparation of high quality PET.