

# Process Simulation of Terephthalic Acid Using Neutral Hydrolysis of Polyethylene Terephthalate Bottle Waste Method

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## Abstract

To mitigate the environment's unique challenges caused by polyethylene terephthalate [PET] bottle litter and to protect the petroleum feedstock. The chemical recycling technology was used to transform PET into practical items with a sizeable and successful industrial application. In order to model the chemical neutral hydrolysis depolymerization process of PET plastic wastes utilizing a continuous stir tank reactor for the synthesis of pure terephthalic acid [TPA] and EG for commercial use, this work used ASPEN PLUS V10. The data for the modeling came from an experimental chemical recycling project employing the neutral hydrolysis process to depolymerize PET bottle trash. PET waste was degraded using excess water [H<sub>2</sub>O] and zinc acetate [Zn [Ac]<sub>2</sub>] as the active catalyst. A mean PET particle size of 127.5 μm, 1000 kg/h of PET depolymerized at an H<sub>2</sub>O: PET [w/w] ratio of 8:1, 513.15 K temperature, 32.0 bar pressure, and 0.5 h residence time were the reaction's ideal working parameters. Regarding PET, it is a first-order reaction. The reaction yielded 782.72 kg/h of TPA, 292.43 kg/h of EG, and a depolymerization of PET of 90.54%. TPA and EG had selectivity of 0.7280 and 0.2720, respectively. Filtration, distillation, and crystallization techniques were used to separate the mixture of components. The heat from the conveyance, reaction, and separation processes was obtained. This effort increased the yield of TPA, the amount of water removed for reuse, the amount of EG generated, and the amount of processing heat required. The procedures and their operating circumstances can be used to scale up commercial processes in the future.

## Introduction

PET plastic is a cost-effective and long-lasting polymer that is used in a variety of products, including packaging, bottles, straws, bags, and much more, which keeps the plastic production and disposal cycle going nonstop. Due to increased urbanization, there is an increase in global population demand for extra PET bottle plastic use. PET bottles for soft drinks and water have a very short shelf life. They lack enough worth to be kept since they are so cheap and because their disposal is done improperly. They end up in landfills instead.

The production of PET packaging bottles has increased as a result of these products' attributes, which include good mechanical properties, ease of manipulation to fabricate any shape or product of interest, breadth of their products, and future promise in research for more products, combined with daily new innovation [1].

PET bottle trash is readily thrown out and is allowed to clog gutters and drains and leave behind litter everywhere. Due to its non-biodegradability and the potential for very slow disintegration caused by photochemical reactions, electrolyte corrosion, hydrolysis, microbes, and other factors. It builds up over

time and becomes a significant environmental issue globally [2]. Since the emergence of various environmental campaigns in recent years, the success of its industries in facilitating simple access to their products for consumption and preventing damage through the use of PET bottles with many superb functional properties has become a liability or problem for the industries to solve [3].

A significant amount of garbage is produced with limited PET recycling capabilities as a result of the expanding population, together with advancements in technology and PET bottle delivery services. Media studies indicate that plastic bottles disintegrate between 70 and 450 years old, demonstrating that plastics do not quickly biodegrade [4,5]. Another goal is to find a way to modernize, enhance, and develop PET bottle trash disposal techniques. This is necessary to meet the vision and insight that these practices must be environmentally sound and sustainable.

To address the difficulties caused by plastics, particularly PET, in the ocean and ecosystem, some researchers have acted. According to, just 9% of the 6,300 metric tons of plastic waste produced in 2015 was recycled, and 12% was burned. Instead, it was disposed of in landfills or the environment. If production

and waste management trends continue, by 2050 there will be around 12,000 metric tons of plastic waste in landfills or the environment [6]. The latest method used in managing PET bottle waste is recycling. The method itself has many issues if the right sub-method is not used and not handled properly [7].

The main issue with recycling is that it can only transform pure, uncontaminated plastic trash of one type back into its original shape during production. The issue of plastic trash at the disposal location is thus not addressed [8]. Only monolayer plastics are allowed for secondary [mechanical] recycling, which harms the environment and physically damages products. Additionally, did a study on the production of PET flakes and the mechanical recycling process [9]. The only byproducts of pyrolysis and gasification [tertiary recycling] that have undergone extensive research are gas and liquid fuel. Applying LCA allowed for the pyrolysis of PET bottle trash [10]. Enzymolysis [tertiary recycling by biodegradation] is a time-consuming process that can only partially decompose PET bottle waste. Solvolysis, or tertiary recycling via chemical depolymerization, is expensive, detrimental to the environment, and difficult to separate the end product. Recycling from the Quaternary recover's energy along with CO<sub>2</sub> emissions and other priceless materials. Recovering PET monomers is not covered by it [11].

There are several different types of hydrolysis for chemical recovery, including neutral, acid, and alkaline hydrolysis; alcoholics; aminolysis; glycolysis; and ammonolysis [12-16]. The steps of hydrolysis, alcoholics, and glycolysis convert PET bottle trash into TPA. In order to discover strategies to make PET bottle waste digestion into TPA innovative and industrially viable at a reasonable low cost of production, PET bottle waste was solvolysed [chemically recycled] in this study. A straightforward and effective separation technique was developed thanks to the planning, modeling, and simulation of the process. The life cycle inventory of recycling PET bottle waste into TPA was established to be used later. Quantifications of materials and energy offer hope for future research on environmental and economic implications. Through planning, modeling, and process simulation, a simple and efficient separation technique was created. It was designed to be utilized later to create a life cycle inventory of the recycled PET bottle waste converted into TPA. Further study of the effects on the environment and the economy can be found in the quantification of materials and energy.

#### **PET bottle waste-neutral hydrolysis design, modeling, and simulation [DMS] using Aspen Plus with the Aspen Polymer feature.**

In a reaction vessel developed and modeled by CSTR, PET [the reactant], H<sub>2</sub>O [the reactant and solvent], and Zinc Acetate [the catalyst] flow into the reactor while the product[s] of the reaction simultaneously exit the vessel. By allowing input and output streams to flow continuously, it becomes an effective tool

for continuous chemical processing. It has a tank reactor, feed and exit pipes, an embedded impeller, and is meant to handle an extremely viscous PET material. To ensure that the reactants are thoroughly mixed, enough room should be provided to create a vortex. Given that PET is a solid material, it was chosen for its well-known capacity for scaling up and excellence in robust solid handling. Residence time distribution control is enhanced by CSTR cascades' pseudo-plug flow characteristics, because they have better heat transmission capabilities. It is a possible option for PET and superheated water reactions, which need extremely high temperatures. Additionally, they have greater resistance to stronger reactions and higher reagent concentrations. They can operate for extended periods of time and produce large volumes of product per unit of time, making them ideal for reactions with fast kinetics. They have greater conversion per unit mass of catalyst than other catalytic reactors, as well as lower operating costs and continuous operation. The amount of zinc acetate utilized demonstrates this. It runs in a steady state with a constant flow of reactants and products, and the feed adopts a uniform composition throughout the reactor. The exit stream also has the same composition as the material in the tank. Heat may be removed from the reaction mixture more quickly and efficiently using CSTRs than batch reactors because they have better heat transfer characteristics. This can speed up reaction times and reduce the chance of overheating. Continuous stirred-tank reactors are used most frequently in homogeneous liquid-phase flow operations in industrial processing where continuous agitation is required, such as in the polymer [PET] industry. They can be utilized alone, sequentially, or as a component of a battery. As the control aim of CSTR, the temperature of the reacting mixture, T, should remain constant at the appropriate value. The only variable that can be altered is the coolant's temperature. Both the temperature control system and the method used by CSTR are innovative and logically constructed. They are favorable for energy savings and consumption reduction because of their quick control speed, high control precision, high heat exchange efficiency, and low heat-carrying agent consumption. They are very easy to utilize and put into practice. It is used in the chemical industry to make mixes with similar chemical compositions at the input and output and to assure perfect mixing of materials that are continuously supplied into the reactor.

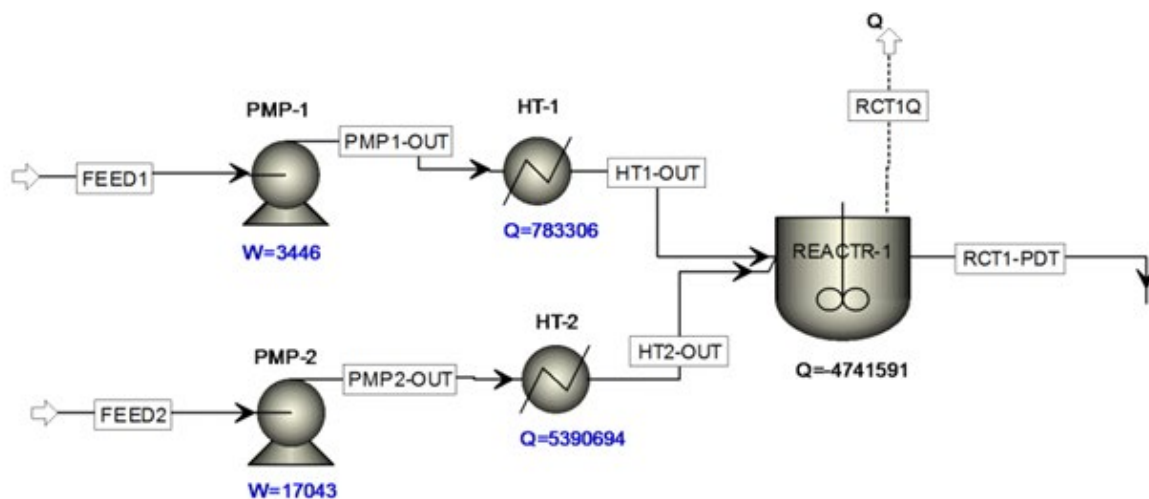
#### **DMS of PET bottle waste neutral hydrolysis depolymerization process**

In its DMS processing, information from the PET bottle waste neutral hydrolysis depolymerization experimental study was employed. The Aspen Plus with Polymer feature's CSTR used for the reaction component had all of its reaction modeling equations pre-built in the program. Due to the effectiveness of the software, the component properties have a tolerance of 0.001. Table 1 displays data from the PET neutral hydrolysis depolymerization experiment and CSTR.

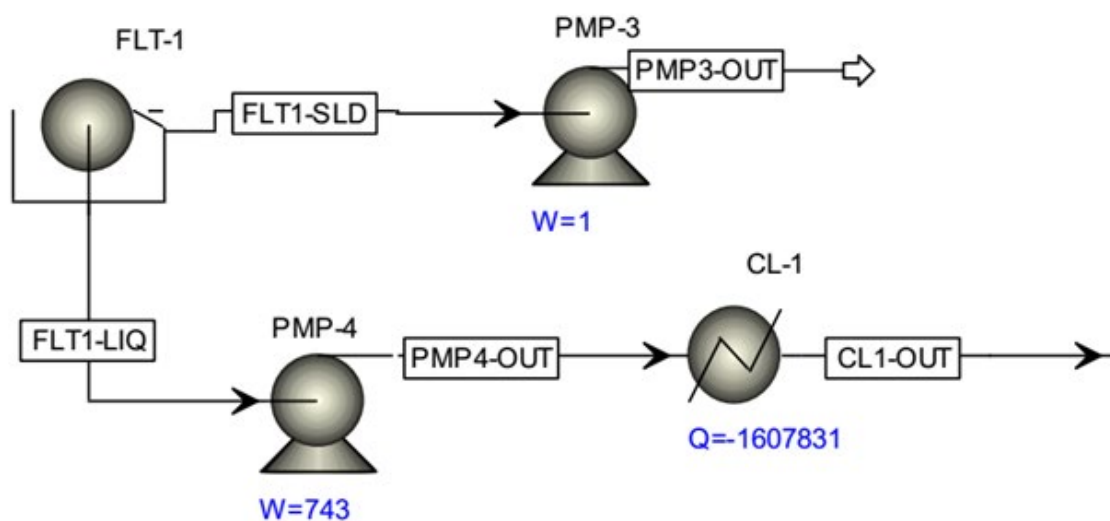
**Table 1: PET neutral hydrolysis and depolymerization reaction operating conditions**

Operating conditions	Values	Units
H <sub>2</sub> O : PET	8:1	
Temperature	513.15	K
Pressure	32.0	bar
Residence time	0.5	h
Catalyst /PET (w/w) ratio [Zn(Ac) <sub>2</sub> : PET]	1:67	
Total reactor volume, V <sub>t</sub>	242.0525	m <sup>3</sup>
Total reactor actual volume, V <sub>a</sub>	266.2578	m <sup>3</sup>
Order of reaction	1 <sup>st</sup> order	Based on PET
Reaction rate constant, k	23.0259	s <sup>-1</sup> (or sec <sup>-1</sup> )
Activation energy (E <sub>a</sub> )	80.94	kJ/mole

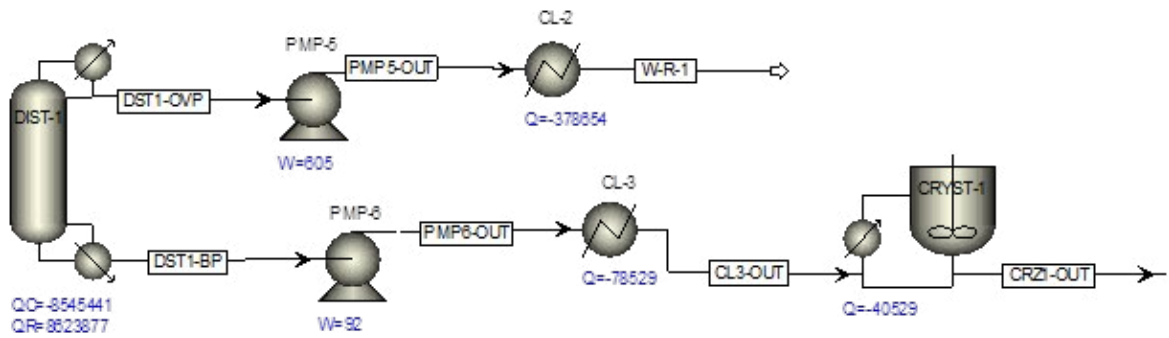
The simulation was done based on the computational flow diagram [CFD] shown in Figures 1[a-d] below:



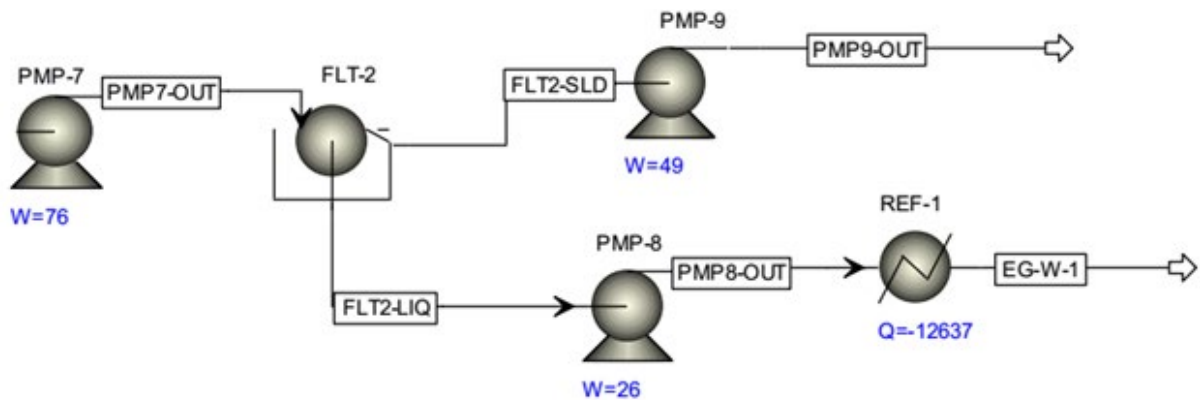
**Figure 1a:** Process flow diagram of neutral hydrolysis of polyethylene terephthalate bottles waste chemical recycling into terephthalic acid



**Figure 1b:** Process flow diagram of neutral hydrolysis of polyethylene terephthalate bottles waste chemical recycling into terephthalic acid



**Figure 1c:** Process flow diagram of neutral hydrolysis of polyethylene terephthalate bottles waste chemical recycling into terephthalic acid



**Figure 1d:** Process flow diagram of neutral hydrolysis of polyethylene terephthalate bottles waste chemical recycling into terephthalic acid

### PET neutral hydrolysis depolymerization chemical reaction model

A kinetic Segment-based power law reaction model was used in the simulation of PET neutral hydrolysis chemical recycling into TPA, which is consistent with research on that simulated and

$$r = kT^n e^{-Ea/RT} \Pi(C_i)^{\alpha_1} \quad (1)$$

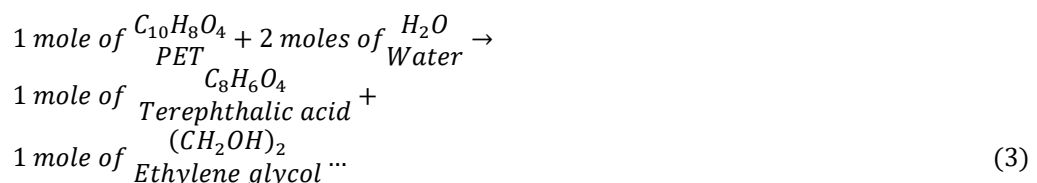
If the reference temperature  $T_0$  is not stated, the above equation (1) is appropriate. Otherwise, if a reference temperature  $T_0$  is supplied, the equation (2) below is appropriate.

$$r = k \left( \frac{T}{T_0} \right)^n e^{\left( \frac{-Ea/R}{\left[ \frac{1}{T} - \frac{1}{T_0} \right]} \right)} \Pi(C_i)^{\alpha_1} \quad (2)$$

Where T is temperature in degrees K,  $T_0$  is reference temperature in degrees K, r is reaction rate, and n is the exponential factor, Ea stands for activation energy, R for the universal gas law constant, C for molarity [kg mol/m<sup>3</sup>], i for component index, and  $\Pi$  for the product operator. Relevant and suitable models can also be developed for the work, as was done by, who developed mathematical models for continuous biodiesel reactors that can be used for economic analysis of supply changes in continuous processes of biodiesel [18].

measure the recovery efficiency of copper in leaching process of copper oxide in H<sub>2</sub>SO<sub>4</sub> solution CSTR in Aspen Plus. As stated in the following equation (1), a power law representation of the molarity concentration basis [C<sub>i</sub>] was utilized [17].

It should be noted that the first order reaction involving the digestion of PET is the depolymerization of PET utilizing H<sub>2</sub>O to generate TPA. PET conversion was 90.54%, TPA [monomer] yield was 90.54%, and selectivity was 0.7280. The EG yield and selectivity were 90.54% and 0.27, respectively. In Eq. (3), the reaction route is illustrated.



## Chemical Recycling of PET Bottles Waste Using Neutral Hydrolysis Method: Process Design, Modeling, and Simulation Procedure.

To model the chemical depolymerization of PET into TPA using the neutral hydrolysis method, experimental data from the [19]. PET bottle waste neutral hydrolysis digesting into TPA work was used. The Aspen Plus v10 with polymer function was utilized for CSTR with agitation. Table 1 above displays the data that was used.

### Neutral Hydrolysis of PET Bottles Waste Process Description

This project's basis is a 1000 kg/h PET waste bottle. Simulation and modeling were done using Figures 1(a)–(d). In Feed 1, PET powder and water were mixed in a 1:1 mass ratio at 298.15 K and 1.01325 bar at ambient operating conditions. The transport medium for PET was water. Pump 1 was operating at 33.00 bars, and heater 1 was operating at 513.15 K to move it into reactor 1. 7000 kg/h of feedwater [feed 2] was carried into reactor 1 by pump 2 running at 33.00 bars, through heater 2 (pre-heating), which heated the water to 513.15 K. In reactor 1, the mass proportion of water to PET was 8:1. Water was overly present to encourage PET's full conversion to TPA and the TPA product's better selectivity over EG.

The input at Reactor 1 [the CSTR reactor] was a mixture of 1000 kg/h of PET and 8000 kg/h of water at a temperature and pressure of 513.15 K and 33.00 bar, respectively. 266.257792 m<sup>3</sup> was its volume, and it operated at 513.15 K and 32.00 bar pres-

sure. Data and operating parameters for reactor 1's depolymerisation of PET into TPA were already displayed in Table 1 above. As previously noted, a kinetic segment-based power law reaction model was employed, and it was based on Equations 1 and 2 for the power law expression of molarity concentration basis (Ci) displayed in Equations 1 and 2. The findings of reactor 1's [CSTR] degradation of PET bottle trash into TPA are displayed in Table 4 below.

Filter 1 received the reactor 1 product mixture at a higher pressure of 32.00 bar. Filter 1 filtered out 0.0263 kg/sec of solid, unreacted PET as filtrate while operating at 1.01325 bar and 513.15 K. Pump 3 sent it to the purification or treatment area for additional purification before reuse [recycling] or sale while running at 2.0265 bar.

Pump 10, operating at 2.0265 bar through cooler 2, transferred the output of Filter 1's filtration stream of 2.1751 kg/sec of water, 0.0812 kg/sec of EG, and 0.2174 kg/sec of TPA at 513.15 k and 1.01325 bar into Radfrac distillation column 1. Before entering distillation column 1, cooler 2 lowered the temperature to 373.15 K, which is the boiling point of water and the stream's most volatile component. The distillation pressure was 1.01325 bars. Pump 11 delivered the cleaned water into cooler 2, which cooled it to 333.15 K while working at 2.0265 bar. It was sent to be reused or packaged for use in business. Table 2 below contains the information needed to model distillation column 1.

**Table 2: Radfrac distillation column 1 modelling data to recover H<sub>2</sub>O from its mixture with EG and TPA for the neutral hydrolysis method of PET depolymerisation**

Configuration			
<b>Setup options</b>			
Calculation type	Equilibrium		
Number of stages	7		
Condenser	Total		
Reboiler	Kettle		
Valid-phases	Vapour-Liquid		
Convergence	standard		
<b>Operating Specifications</b>			
Distillate rate	Mass	7830.2467	Kg/h
Reflux ratio	Mass	0.7393	
Free water reflux ratio	Mass	0.0000	
<b>Feed Streams</b>			
Name	Stage	Convention	
Feed (Cooler 2 product)	4	Above-stage	
<b>Product streams</b>			
Name	Stage		Phase
Distillation column 1 overhead product	1		Vapour
Distillation column 1 bottom product	7		Liquid
Pressure		1.01325	bar
Parameter			Value

Relative volatility of H <sub>2</sub> O/( EG+TPA) ( $\alpha$ )	96.5824
R <sub>m1</sub> at minimum driving force (DF <sub>min</sub> )	0.1528
R <sub>m2</sub> at maximum driving force (DF <sub>max</sub> )	0.6161
R <sub>o1</sub> at minimum driving force (DF <sub>min</sub> )	0.1833
R <sub>o2</sub> at maximum driving force (DF <sub>max</sub> )	0.7393

Radfrac distillation 1 bottom product was transported by pump 12 operating at 2.0265 bar as a filtered mixture of EG, TPA, and a trace of H<sub>2</sub>O through cooler 4 that cooled it to 373.15 K before entering crystallizer 1. This cooling was to bring the stream temperature within 10 degrees of the crystallizer's operating temperature. Depending on its operating temperature, a crystallizer cooler, chiller, or refrigerator is effective with an input stream and a crystallizer operating temperature difference of no more than 10 degrees. The crystallizer 1 employs a cooler to cool its contents stream to 362.15 K at 1.0133 bar pressure. The following requirements [rules] should be followed while selecting a temperature: (1) Unless it is a trace component that may or may not be soluble in other components with higher freezing points,

its operating temperature must be higher than the freezing points of all other components in the crystallizing stream, excluding the crystallizing component. (2) The operating temperature of the crystallizing stream must be lower than the boiling point of all its constituents. The freezing points of EG, TPA, and trace H<sub>2</sub>O are 260.15 K for EG, 700.15 K [sublimes], and 273.15 K, respectively. The freezing points of EG and H<sub>2</sub>O are higher than 362.15 K, whereas TPA is much lower. H<sub>2</sub>O's [in traces] boiling points are 373.15 K, EG's are 470.45 K, and TPA's are 700.15 K, respectively. The prerequisites were satisfied, which gave us the chance to recover a very high TPA. Table 3 below contains the data for the crystallizer 1 model.

**Table 3: Crystallizer 1 solid component and its solubility, solvent composition, phases, and property method, manipulated and parametric variables for the neutral hydrolysis method of PET depolymerisation at 363.15 K temperature and 1.0133 bar pressure**

Solid component						
Component	Mass	Unit				
TPA	782.72	Kg/h				
<b>TPA solubility</b>	0.0001	g of solute per 100 g of solvents mixture	0.0001 g / 0.0899 L of solvents mixture			0.0012 g / L
Solvents composition						
Basis	mass	Kg/h				
Component	Flow (kg/h)	Fraction	100 g of solvent	Density (g/cm <sup>3</sup> )	Solvent vol. (cm <sup>3</sup> )	Solvent vol. (L)
EG	292.25	0.9994	99.94	1.1130	89.793	0.089793
H <sub>2</sub> O	0.18	0.0006	0.06	1.0000	0.062	0.000062
<b>Total</b>	<b>292.43</b>	<b>1.0000</b>	<b>100.00</b>		<b>89.855</b>	<b>0.089855</b>
Phases and property method						
Valid phases	Solubility phase	Property method				
Vapour - Liquid	Liquid	POLYNRTL				
Manipulated and parametric variables						
Parametric variable						
Variable	Value	Unit				
Pressure	1.01325	bar				
Manipulated variable (Equidistant)						
Variable - Temperature	Value	Unit				
Start point	273.15	K				
Manipulated variable (Equidistant)						
End point	373.15	K				
Number of intervals	20					
Increment	5					

The filtration composition of filter 3 was a mass fraction mixture of 0.9994 (0.0812 kg/sec) of EG, 0.0006 (5.0443E-05 kg/sec) of water, and 9.7028E-07 [7.8816E-08 kg/sec] of aqueous TPA. It is a waste designated as EG-W-1 at 362.31 K and 1.0133 bar pressure. It was transported by pump 14 operating at 2.0265 bar pressure through refrigerator 3 that refrigerated it to a room temperature of 298.15 K. The waste effluent from EG-W-1 was discharged into the waste pond or treated to recover its components. While the filtrate of filter 3 consisted of 0.2174 kg/sec TPA crystal, it was sent by pump 15 operating at 2.0265 bar for further purification.

### Results and Discussion for the Neutral Hydrolysis Method of PET Depolymerization into TPA

The overall material and energy balances for the chemical recycling of a 1000 kg/h flow rate of PET bottle waste into TPA using the neutral hydrolysis method were obtained using intermediate products and recovered materials. The reaction and separation of the recovered and product materials were covered under the in-line processing scope of this work. The outcomes are displayed below.

**Table 4: Validation of this work of neutral hydrolysis depolymerisation of PET bottle waste into TPA (reactor 1 products) with that of [19]**

Reactor 1 output						
Component	Quantity (kg)	%	Mass fraction	Mole fraction	% yield	selectivity
PET conversion	905.39	90.54				
Unreacted PET	94.61	9.46	0.0105	0.0011		
Water conversion	169.75	2.12				
Unreacted + excess water	7830.25	97.88	0.8700	0.9777		
Expected TPA	864.51					
Produced TPA	782.72		0.0870	0.0106	90.54	0.7280
Expected EG	322.99					
Produced EG	292.43		0.0325	0.0106	90.54	0.2720
Property	This work		(Liu et al., 2012)		Difference	
	Value	Unit	Value	Unit	Value (Unit)	
Temperature	513.5	K	513.15	K		
Pressure	32.00	bar	32.00	bar		
Residence time	0.5	h	0.5	h		
(Mass ratio) H <sub>2</sub> O:PET	8:1		8:1			
yield of TPA	90.54	%	90.50	%	0.05 (%)	
yield of EG	90.54	%	90.50	%	0.05 (%)	
Selectivity of TPA	0.7280		0.7280		Nil	
Selectivity of EG	0.2720		0.2720		Nil	

The data and findings of this study were also validated by comparison with the earlier research of the writers listed below. When employing the neutral hydrolysis process to turn PET bottle trash into TPA, there are several variations in the operating parameters. The study by that used supercritical water conditions and had a 90.50% yield of TPA was 99.96% accurate in

### Reactor

Equation 3 above displays the reaction's stoichiometry equation. For reactor 1, the activation energy,  $E_a$ , is 80.940406817 kJ/mol and the reaction rate constant,  $k$ , is 23.02585093. Equation (3) states that a reaction between one mole of PET and two moles of water results in one mole of TPA and one mole of EG. The depolymerization of PET bottle trash at a rate of 1000 kg/h using neutral hydrolysis served as the foundation for this work, and the projected outcome was based on the reaction equation [4.88]. Results from this study and those from are displayed in Table 4. It is evident that the yields of 90.54% for TPA and EG, as well as their corresponding selectivities, were in line with the results obtained by Liu and colleagues in 2012. At the identical optimal operating conditions of 513.15 K, 32.00 bar pressure, and 0.5 h residence time, they barely differ from one another. Additionally, the process's selectivity of 0.7280 for TPA and 0.2720 for EG demonstrated its viability and demonstrated that it favors the manufacture of TPA rather than EG [19].

comparison to this study's 90.54% yield of TPA. For both the green-coloured PET bottle trash with an 85.00% yield of TPA and the colorless PET bottle waste with a 90.00% yield of TPA supercritical water conditions were utilized [12,19]. The two outcomes are not far from the outcomes of this investigation.

## Distillation column

Evaluations were made of the reflux ratio, overall stage count, feed entering stage, overhead product stage, and bottom product stage. They were determined using Raoult's law and the vapor-liquid equilibrium [VLE] relations of the mixture's constituent parts. The vapor pressures of the components were determined using the extended Antoine equation (4), a vapor pressure model. Equation 5 was used to calculate relative volatility.

$$\ln P_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{C_{7i}} \quad \text{for } C_{8i} \leq T \leq C_{9i} \dots \dots (4)$$

The pure component properties parameters of Aspen plus at PLXANT contain the expanded Antoine equation presented in Equation (4) above. Since the DIPPR equation does not include

The mole fraction of the light key (water) in the saturated liquid phase as well as the mole fraction in the saturated vapor phase were derived using the predicted vapor pressures and mole fractions of the mix components, with TPA and EG as the heavy keys. Calculations were made for the light key's [water] distillation driving force as well as the light key's relative volatility to the heavy key [TPA + EG].

those parameters, it is also utilized for DIPPR vapor pressure data based on the equation above with two zeros (0's) [for C3i and C4i] placed into the parameter list.

$$\text{Relative volatility, } \alpha = \frac{\text{vapour pressure of air} / \text{mole fraction of air component in liquid phase}}{\text{vapour pressure of water} / \text{mole fraction of water in liquid phase}} \dots \dots (5)$$

The fraction of the light key (water) component in the saturated liquid phase was obtained from the distillation column feed stream and is denoted by x. The relative volatility of water with respect to TPA and EG must be greater than one for distillation to separate water [lighter key] from TPA and EG (the heavier key). While Equation (6) was used to calculate the mole fraction of the light key (water) component in the saturated vapour phase, which is represented by the letter y. Using Equation (7), the driving force to distill the light key component [water] was

assessed. The driving force for light key distillation is plotted against the mole fraction of light key [water] in the saturated liquid phase in Figure 2. For evaluating bubbles and dew points, respectively, use equations (8) and (9), correspondingly. A saturated liquid will generate a bubble of vapor at a bubble point when the temperature rises by a certain amount. The dew point is the temperature at which, after a one-degree drop in temperature, a drop of liquid emerges from a saturated vapor.

$$\text{Mole fraction of light key in saturated vapour phase, } y = \frac{\alpha x}{(1+(\alpha-1)x)} \dots (6)$$

$$\text{Light key distillation driving force, } DF = \frac{\alpha x}{(1+(\alpha-1)x)} - x \dots \dots (7)$$

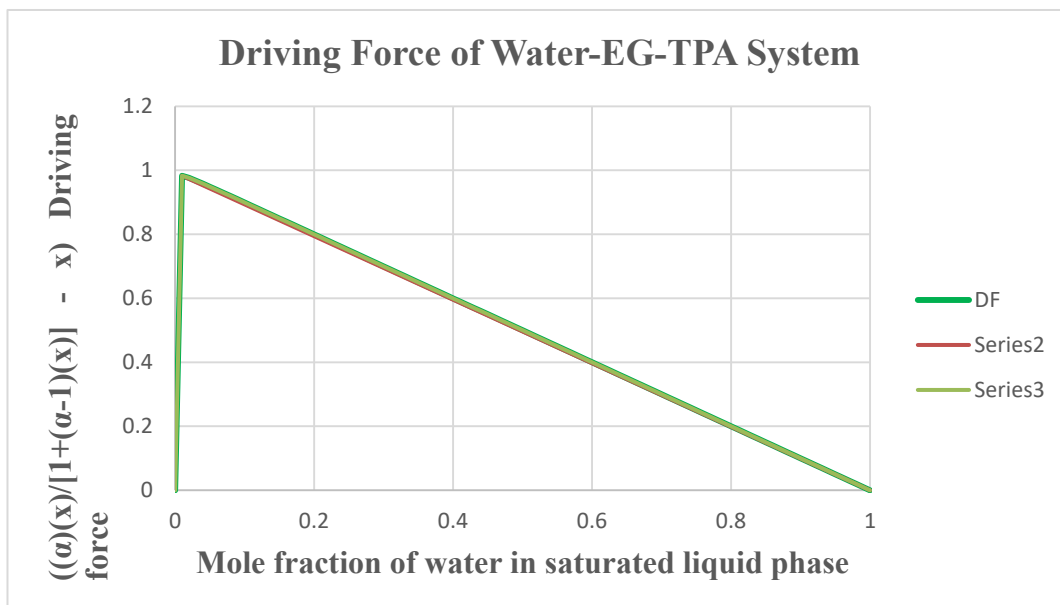
$$\text{Bubble point: } \sum y_i = \sum k_i x_i = 1. \dots \dots (8)$$

Where  $k_i$  is the physical equilibrium constant,  $x_i$  is the mole fraction of light key component specie  $i$  in the saturated liquid phase, and  $y_i$  is the mole fraction of light key component specie  $i$  in the saturated vapor phase.

[water's] maximum driving force for distillation was 0.8152. This matched the highest stage [stage 1] in the column, where tray number 1 was located, the point at which overhead product was withdrawn, and the point at which the reflux ratio was computed. It also matched the point at which the maximum light key (water) component was achieved.

Figure 2 demonstrates that the mole fraction of the light key [water] in the saturated liquid phase was 0.09, and the light key's





**Figure 2:** Graph plot of the neutral hydrolysis method of PET depolymerisation Radfac distillation column 1: light key [water] distillation driving force versus mole fraction of light key [water] in saturated liquid phase

The steps necessary for distillation column separation—feed entering, overhead product collection, and bottom product collection—depend on the reflux ratio [R] that is applied. The distillation column with optimal R (Ro) has the lowest annual operating

cost. The ideal reflux ratio (R) is always in the range of 1.2 to 1.5 times the minimal reflux ratio [Rm]. To evaluate Ro, this work multiplied Rm by 1.2. The amount of phases [Nm] was calculated using equation 10 below.

$$N_m = \frac{\text{Log} \left[ \frac{x_{Lk}}{x_{Hk}} \right]_d \left[ \frac{x_{Hk}}{x_{Lk}} \right]_b}{\text{Log} \alpha_{Lk}} \dots \dots \dots (10)$$

Where  $\alpha_{Lk}$  is the light key average relative volatility in respect to the heavy key.  $N_m$  is the minimum number of distillation column required plate. Whereas  $x_{Lk}$  and  $x_{Hk}$  are Where  $\alpha_{Lk}$  is the light key's average relative volatility with respect to the heavy key.  $N_m$  is the minimum number of distillation columns required per plate. Whereas  $x_{Lk}$  and  $x_{Hk}$  represent the mole fractions of light

and heavy key components in the saturated liquid phase, with d and b representing distil (overhead) and bottom products, respectively. Equations (11), (12) and (13) were used to calculate  $R_m$  and Ro, respectively, and to show the overhead product, feed stream, and bottom product stage numbers. They were shown in Table 2 above.

$$\text{Reflux ratio, } R = \frac{\text{flow returned as reflux}}{\text{flow of top product taken off}} \dots \dots \dots (11)$$

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1 \dots \dots \dots (12)$$

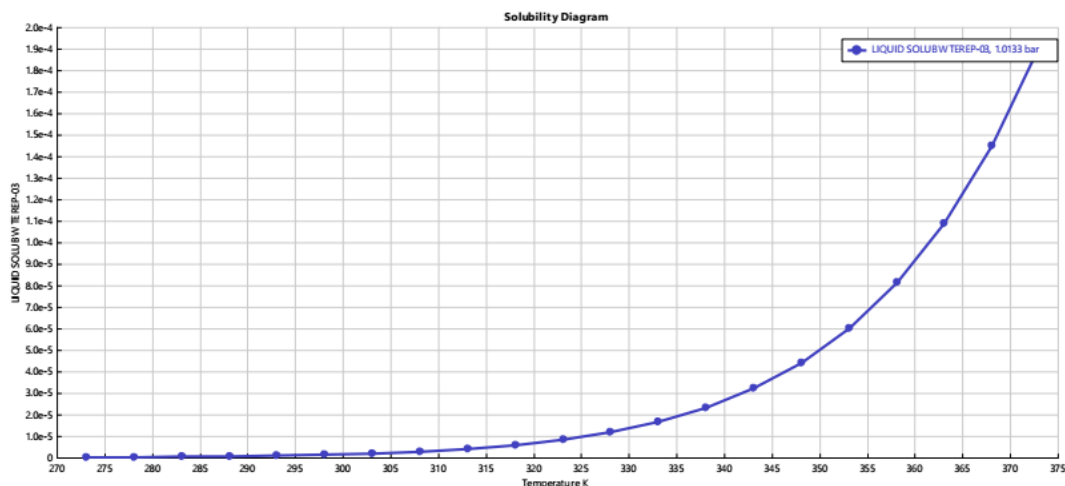
Where  $\theta$  represents the root of the equation,  $x_{i,d}$  is the concentration of component  $i$  in the distillation column top at minimum reflux, and other parameters are as defined earlier.

$$R_o = 1.2R_m \dots \dots \dots (13)$$

7830.07 kg/h (99.9977 mass percent) H2O was recovered with very minor contaminants of 0.18 kg/h (0.0023 mass percent) EG and 4.09E-11 kg/h [0.0000 mass percent] TPA. The recovered water purity was 100.00% and is highly recommended for consumption and all other uses. Recovered water, designated as W-R-1, was transported, with the aid of pump 11, operating at 2.0265 bar, into Cooler 2, which cooled it to 333.15 K and sent for re-use or packaging for commercial purposes.

### Crystallizer

TPA was only 0.0001 percent soluble in the solvents and working conditions of the crystallizer. As indicated in Table 3 and depicted in Figure 3, it means 0.0001 g of TPA in 100 g of the solvent mixture, or 0.0012 g of TPA/L of solvent mixture.



**Figure 3:** Graph plot of solubility of solute [TPA] in 0.9994 mass of EG and 0.0006 mass fraction of water at 363.15K temperature and 1.0133 bar pressure for neutral hydrolysis method of PET depolymerisation of crystallizer 1

At 362.15 K temperature and 1.0133 bar pressure, the product stream from Crystallizer 1 contained 0.7280 [0.2174 kg/sec] mass fraction of TPA crystal, 2.6391 E-07 [7.8816E-08 kg/sec] mass fraction of aqueous TPA, 0.2718 [0.0812 kg/sec] mass fraction of EG, and 0.0002 [5.0443E-05 kg/sec] mass fraction of

water. Pump 13 pushed the product stream from the crystallizer 1 into filter 3 at a pressure of 2.0265 bar. The filter 3 defines phase separation of fraction of liquid from fraction of solid and operates at 1.0133 bar pressure.

**Overall material balance of the neutral hydrolysis method of chemical recycling of PET bottle waste.**

**Table 5:** Summary of the overall material balance of the waste system boundary of the neutral hydrolysis method of chemical recycling of PET bottles in terms of feeds, wastes generated, and products [recovered materials and purified products].

<i>Operation/Component</i>	PET	Water	Zn(Ac) <sub>2</sub>	
Feed 1	1000.00	1000.00		
Feed 2		7000.00	15.00	
<b>Total (kg/h)</b>	<b>1000.00</b>	<b>8000.00</b>	<b>15.00</b>	
<b>Feeds grand total (kg/h)</b>	<b>9015.00</b>			
<i>Operation/Component</i>	PET	Water	TPA	EG
Product 1 (PET-R-1)	94.61			
Product 4 (W-R-2)		7830.07		0.18
Product 5 (TPA-PD-1)			782.72	
<b>Products Total (kg/h)</b>	<b>94.61</b>	<b>7830.07</b>	<b>782.72</b>	<b>0.18</b>
<i>Operation/Component</i>	PET	Water	Water	Air
<b>Products grand total (kg/h)</b>	<b>8707.58</b>			
<i>Operation/Component</i>	EG	Water	Zn(Ac) <sub>2</sub>	
Waste 3 (EG-W-1)	292.25	0.18	15.00	
<b>Wastes total (kg/h)</b>	<b>292.25</b>	<b>0.18</b>	<b>15.00</b>	
<b>Wastes grand total (kg/h)</b>	<b>307.43</b>			

## Energy balance for cooling and refrigeration for the neutral hydrolysis method of chemical recycling of PET into TPA

**Table 6: Energy Balances for Cooling for the Neutral Hydrolysis Method of Chemical Recycling of PET into TPA**

Cooling Medium	Cooling water	Cooling water
Unit	Cooling water ( $T_{in} = 293.15 \text{ K}$ ; $T_o = 298.15 \text{ K}$ ; $\Delta T = 5$ ) (kJ/h)	$C_{p1}=4.182, T_1=20 \text{ }^\circ\text{C}$ ; $C_{p2}=4.180, T_2=25 \text{ }^\circ\text{C}$ . $C_{p(avg.)}$ $dT = (4.180+4.182)/2*(25-20) = 4.181*5 = 20.905$ kJ/kg Mass flow (kg/h)
Cooler 1	5788198.6796	276881.0658
Cooler 2	1363157.8705	65207.2648
Cooler 3	282705.4471	13523.3412
Crystallizer 1	145905.4728	6979.4534
RDC1 condenser	30763575.3963	1471589.3517
<b>Total</b>	<b>38343542.8663</b>	<b>1834180.4769</b>

**Table 7: Refrigeration energy balances for Neutral hydrolysis method of chemical recycling of PET into TPA continues**

Refrigeration Medium	Refrigerant 1 Cooling - Propane	Refrigerant 1 Cooling - Propane
Unit	Refrigerant 1 ( $T_i = 248.15 \text{ K}$ ; $T_o = 249.15 \text{ K}$ ; $\Delta T = 1$ ) (kJ/h)	Refrigerant 1: $T = 248.15 \text{ K}$ (-25 $^\circ\text{C}$ ): Sensible heat = $C_p(av.)dT = 4.00 \text{ kJ/kg}$ . Mass flow (kg/h)
Refrigerator 1	45493.4298	11373.3449
<b>Total</b>	<b>45493.4298</b>	<b>11373.3449</b>

## Heating energy balances for the neutral hydrolysis method of chemical recycling of PET into TPA

**Table 8: Heating energy balances for the neutral hydrolysis method of chemical recycling of PET into TPA continues**

Heating medium	High Pressure Steam (HPS)	High Pressure Steam (HPS)
Unit	HPS ( $T_i = 523.15 \text{ K}$ ; $T_o = 522.15 \text{ K}$ ; $\Delta T = 1$ ) (kJ/h)	$P = 40.0 \text{ bar}$ , $T_i = 523.15 \text{ K}$ and $L_v = 1705.62 \text{ kJ/kg}$ (kg/h)
Heater 1	2819906.1870	1653.3027
Heater 2	19406523.2160	11377.9876
Reactor 1	17069750.7932	10007.9448
RDC1 reboiler	31046034.0463	18202.1986
<b>Total</b>	<b>70342214.2425</b>	<b>41241.4337</b>

## Energy balances for pumps and compressors used in the neutral hydrolysis method of chemical recycling of PET into TPA

**Table 9: Energy balances for pumps and compressors used in the neutral hydrolysis method of chemical recycling of PET into TPA.**

Unit	Electricity (kWh)	Unit	Electricity (kWh)
Pump 1	7.46	Pump 6	0.19
Pump 2	22.38	Pump 7	0.09
Pump 3	0.09	Pump 8	0.09
Pump 4	0.75	Pump 9	0.09
Pump 5	0.75	Dist 1 reflux pump	5.59
<b>Total Pump energy (kWh)</b>	<b>37.48</b>	<b>Total electricity used (kWh)</b>	<b>37.48</b>

The neutral hydrolysis approach needed 8000 kg/h and 15.00 kg/h flow rates of process water and zinc acetate (catalyst), respectively, to depolymerize a 1000 kg/h flow rate of PET into TPA. The raw materials utilized in it flowed at a total rate of 9015 kg/h. The flow rates of TPA (the major product), PET, and water with minimal EG contamination [0.18 kg/h] were 782.72 kg/h, 94.61 kg/h, and 7830.25 kg/h, respectively, for the main

products, recovered materials, and by-products. The overall flow rate of the products was 8707.58 kg/h; EG-W-1, which stood for ethylene glycol effluent waste, had a flow rate of 292.25 kg/h; and Zn(Ac)2-W-1, which stood for spent catalyst waste of zinc acetate, had a flow rate of 15.00 kg/h. According to Table 5, the total weight of the wastes for the neutral hydrolysis system was 307.43 kg/h. There was no difference between the 9015.00 kg/h

of feeds and the 9015 kg/h of products [totalled 8707.58 kg/h + wastes totalled 307.43 kg/h].

The utilities used for the 1000 kg/h depolymerisation of PET using the neutral hydrolysis method were cooling water and propane. As earlier described, the cooling water has an inlet temperature ( $T_i$ ) of 293.15 K [20 °C] and an outlet temperature ( $T_o$ ) of 298.15 K [25 °C]. It has specific heat capacities ( $C_p$ ) of 4.183, 4.182, and 4.180 at pressures of 1, 5, and 10 bars, respectively, with an average of 4.182 kJ/kg-K used for the computation, and is operational at the aforementioned pressure range of 1 to 10 bar. The total mass flow rate of cooling water used was 1834180.4769 kg/h. In this case, propane refrigerant was used under one (1) condition designated by Aspen plus V10 as refrigerant 1, with a  $T_i$  of 248.15 K [-25 °C],  $T_o$  of 249.15 K (-24 °C), sensible heat  $C_p$ [avg.]  $dT$  of 4.00 kJ/kg, and a flow rate of 11373.3449 kg/h of propane refrigerant. It should be recalled that sensible heat was used because propane was used as a secondary working fluid that transmitted refrigeration from the utilities-supplying industry over the window into other manufacturing industries. The energy required for the system cooling [exothermic energy] from cooling water for the neutral hydrolysis method was 38343542.8663 kJ/h [38343.5429 MJ/h]. While the refrigeration energy requirement was 45493.4298 kJ/h [45.4934 MJ/h]. The cooling and refrigeration energy totalled 38389036.2961 kJ/h [38389.0363 MJ/h].

Aspen Plus v10 heating formats and their operating conditions were used for this work, and they were designated as LPS, MPS, HPS, HO, FH1, and FH2, respectively. This work spanned just one (1) category of HPS that has a steam flow rate of 41241.4337 kg/h when operating at  $T_i$  of 523.15 K,  $T_o$  of 522.15 K, and  $P$  of 40.0 bar, with a latent heat of vaporization  $L_v$  of 1705.62 kJ/kg. The energy required for high heating of the system for the neutral hydrolysis method was 70342214.2425 kJ/h [70342.2142 MJ/h].

The total electricity consumed by the centrifugal pumps used in this work was 37.48 kWh [134.928 MJ]. Tables 6, 7, 8, and 9 showed results for cooling, refrigeration, heating, and electricity utility use, respectively.

## Conclusions

Experimental PET depolymerisation into TPA was accomplished using the neutral hydrolysis approach to chemical recycling. With the help of CSTR, the data was used for design, modeling, and simulation in the Aspen plus V10 simulator to address the issues with product mix separation specific to PET bottle trash. The commercial manufacturing of TPA using PET bottle trash is another goal. Increases in residence time, the H<sub>2</sub>O:PET reactant ratio, and the catalyst:PET ratio increase TPA and EG yields until reaction equilibrium is reached. The ideal working parameters for this procedure were a 0.5-hour residence period, an H<sub>2</sub>O:PET weight ratio of 8, and a Zn(Ac)<sub>2</sub>:PET ratio of 0.015. TPA and EG yields of 90.54 percent and 90.54 percent, respectively, were achieved, with selectivity of 0.7280 for TPA and 0.2720 for EG. In order to separate the combination of products, Aspen plus V10 software was used to simulate nine pumps:

a reflux pump, a reboiler, a condenser, two filters, a distillation column, a crystallizer, two heaters, coolers, and a refrigerator. H<sub>2</sub>O [7830.2520 kg/h], EG [292.4273 kg/h], unreacted PET [94.6109 kg/h], and TPA [782.7156 kg/h] were the reactor's outputs. Filter 1 completely eliminated unreacted PET. 100% pure water was distilled in a distillation column. TPA was crystallized from EG, and filter 2 separated the filtrate into 100% pure TPA and 99.94% pure EG. A total of 1834180.4769 kg/h of cooling water was used to produce 38343542.8663 kJ/h of cooling energy for the entire system. The energy required for refrigeration, using 11373.3449 kg/h of propane, was 45493.4298 kJ/h. Running 41241.4337 kg/h of high-pressure steam provided the system with the 70342214.2425 kJ/h of total heating energy needed. A total of 37.48 kWh of power were consumed for pumping. Higher yields, purer products, and recovered materials were produced as a result of this work. The necessary heating, cooling, refrigeration, and power were realistic requirements. It serves as a guide for the most effective creation of the desired items. It offers guidance for simpler and more economical operations. For actual industrial applications, it can be a useful processing guide.

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