

Process Simulation of Bis (2- hydroxyethyl) terephthalate and Its Recovery Using Two–stage Evaporation Systems

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To preserve the petroleum feedstock and eliminate the environmental problems peculiar to polyethene terephthalate (PET) bottles littering the environment. Chemical recycling method was adopted to convert PET into useful products of prosperous sizeable industrial application. This work employed ASPEN PLUS V8.8 to simulate chemical glycolysis depolymerisation process of PET plastic wastes, using plug flow reactor for commercial production of pure bis (2- hydroxyethyl) terephthalate (BHET). The data for modelling were gotten from the experimental PET glycolysis depolymerisation work. Excess ethylene glycol (EG) was used to degrade PET waste with zinc acetate (Zn(Ac)₂) as the active catalyst. The optimum operating conditions of the reaction were mean particle size PET of 127.5 µm, EG:PET (w/w) ratio of 5:1,469 K temperature, 101325 N/m² pressure and 3 h residence time. Reaction results were 100 % depolymerisation of PET, 85.24 % yield of BHET and 14.76 % Oligomer. Purification of the BHET was done with two stages evaporation processes using flash columns and crystallizer. Higher temperature and lower pressure were observed to increase the efficiency of the evaporators, but the heat duties increased and momentarily reduced the BHET recovery. BHET recovery was observed to decrease with increase in temperature in the case of crystallisation operation. This work achieved a higher yield and purity of BHET, a higher EG removal for re-use and less heat duties demanded in comparison to previous works. The processes with its operating conditions can be used for future scaling up of commercial processes.

1. Introduction

Polyethylene terephthalate plastic (PET) is a versatile polymer that has found many use among the plastics in the world. Its excellent physical and chemical properties makes it attractive and essential to industries for vast applications. Huge amount of PET wastes in the municipal solid waste system has become a serious environmental problems due to high utilization in industrial products such as soft-drink bottles, food containers and others. The non-biodegradable nature of PET plastic wastes is a major problem in disposing it, using conventional methods such as landfilling and incineration (energy recovery) due to the unfavourable environmental, economic and human health impact (Al-Sabagh et al., 2016). PET recycling is presume as the best option in solving the build-up problems of PET wastes considering ecological and economic aspect. Success in solving PET problems in the solid waste stream would be a major breakthrough in waste management (Yoshioka and Grause, 2015). The available PET recycling methods are primary, secondary or mechanical, tertiary or chemical (Raheem and Uyigue, 2010). The most prominent one is chemical recycling with potential of producing PET monomer (BHET) for the production of PET plastic and other high purity demand finished products (Hopewell et al., 2009). Synthesizing of BHET can be done using glycolysis method from depolymerization of PET with ethylene glycol (EG) (Raheem and Uyigue, 2010). A wide range of glycolytic process conditions of 423.15 – 523.15 K temperature and 0.5 – 8 h reaction time (depend on heating medium) were reported (Allen et al., 2015). A conventional means of purifying BHET is reiterated crystallisation process (Goh et al., 2015), drying, distillation (Inada and Sato, 2006), decolorisation,

deionisation and continuous Ion exchange methods. Some of these methods can enhance the quality of BHET, but presence of unhealthy substances (additives and chemicals) cause the high-quality products unattainable (Devraj, 2016). Two stages evaporation process is an advanced method of BHET purification. This is based on the principle of removing contaminants and EG that has a lower boiling point compared to BHET.

However, despite the work done by many researchers there is need for modelling and simulation of BHET process adhering strictly to operating conditions for reaction and products purification to avoid the formation of unwanted contaminants. This work focus on commercial production of BHET that recently emerged as a prominent means of producing high quality PET plastics and other essential products. The research further study the simulation of PET recycling by glycolysis method using “plug flow reactor” that afford large scale production of BHET from PET wastes. The two stages evaporation system was simulated to achieve high products (BHET and EG) recovery at high purity and low energy requirement.

2. PET glycolysis simulation using aspen plus with aspen polymer feature

PFR simulations assume a homogeneous reaction (liquid-liquid) between PET and EG; perfect radial mixing; no axial mixing; steady-state reaction and constant density. PFR was chosen because it is more efficient than batch reactor; short residence time distribution (RTD); simple design and fabrication; good heat transfer and fast reactions. It has advantages of larger pressure drop and more complex process control that does not arise in this work case since our operating pressure is at atmospheric and the process is simple.

2.1 Simulation for PET glycolysis depolymerisation

Data from the PET glycolysis depolymerisation experimental work were used in the simulation of PET glycolysis recycling using Plug flow reactor (PFR) in the Aspen Plus with polymer feature. It has been used in previous study by Muhammad and Aziz, (2017) to simulate industrial Low Density Polyethylene (LDPE) with tremendous success owing to the efficiency of the software. PET glycolysis depolymerisation experimental and PFR data are shown in Table 1.

Table 1: PET glycolysis depolymerisation operating conditions data

Operating conditions	Values	Units
EG : PET	5:1	
Temperature	469	K
Pressure	10325	N/m ²
Residence time	3	h
Catalyst /PET (w/w) ratio	1 (Zinc acetate)	%
PFR diameter range used	0.15 – 0.90	m
PFR length range used	24.68 - 888.59	m
PFR D/L ratio range used	27.43 – 5923.91	

The simulation was done based on the flow sheet shown in Figure 1 below:

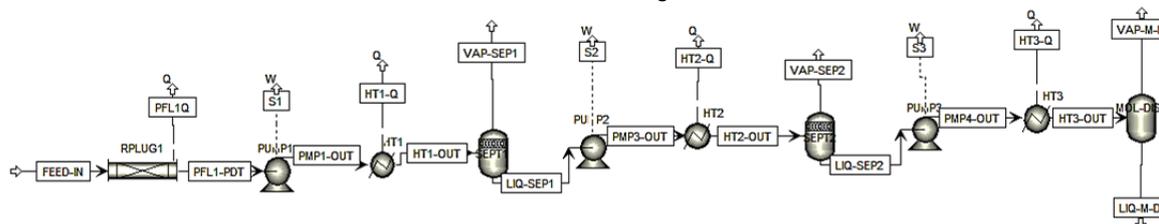


Figure 1: PET glycolysis depolymerisation simulation main flow sheet

2.1.1 PET glycolysis depolymerisation segment-based power law reaction model

A kinetic Segment-based power law reaction model was used in the simulation of PET glycolysis recycling, which conforms with the study of Amran et al., (2017) that simulated methane steam reforming (MSR) from natural gas shift (WGS) for hydrogen production using RPLUG reactor in Aspen Plus software. Power law expression of molarity concentration basis (C_i) was used as given in the Eq(1) below.

$$r = kT^n e^{-E_a/RT} \prod (C_i)^{\alpha_i}$$

Eq(1) above is applicable if reference temperature T_0 is not specified. Else, the Eq(2) below is applicable if reference temperature T_0 is specified.

$$r = k \left(\frac{T}{T_0} \right)^n e^{\left(\frac{-E_a/R}{1/T - 1/T_0} \right)} \prod (C_i)^{\alpha_i} \quad (2)$$

Where r is rate of reaction, k is pre-exponential factor, T is temperature in degrees K, T_0 is reference temperature in degree K, n is temperature exponent, E_a is activation energy, R is universal gas law constant, C is Molarity (kgmole/m^3), Π is the product operator, and i is component index. Relevant and suitable models can also be developed for the work as it was done by (Rossia et al., 2015) that developed a general dynamic model for pseudo-homogeneous catalytic plug flow reactor. It should be noted that depolymerization of PET using EG to produce BHET is a first order reaction concerning digestion of PET. Second order reaction for the digestion of BHET to produce BHET dimer and EG and first-order reaction for the reaction of EG with BHET dimer to produce BHET (0.5 reaction order for EG and 0.5 reaction order for BHET dimer). The conversion of PET, BHET (monomer) and Oligomers (BHET dimer) yields are 100 %, 85.24 % and 14.76 %. The reaction pathway is shown in Figure 2.

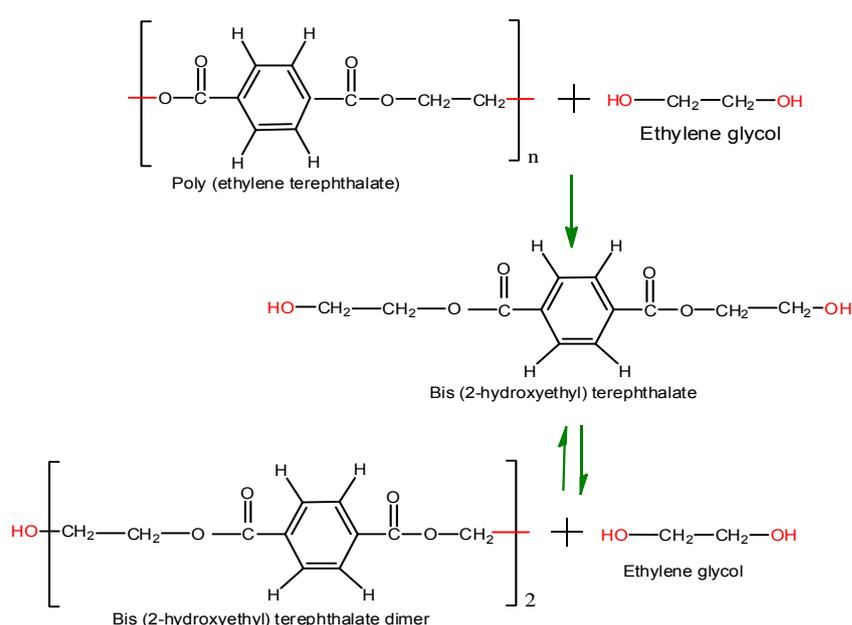


Figure 2: PET glycolysis depolymerisation reaction

2.2 Two – stages evaporation simulation procedure

The following assumptions were made to simulate two – stages evaporation:

Steady state in the two evaporation processes:

The glycolysis product mixture (PFL1-PDT) consist of 78.35 % EG, 18.80 % BHET, 2.85 % Oligomers (Tilmatine et al., 2009). Filter removed catalyst, unreacted PET and contaminants particles. The outlet products from PFL1-PDT consist of EG, BHET and Oligomers.

Glycolyzed products entered the evaporators in liquid form. Polymerization reaction does not occur in the evaporators.

Two – stages evaporation system was simulated using ASPEN PLUS V8.8 flash columns and separate inlet into two outlet streams using rigorous vapor-liquid equilibrium. The flash operation to separate BHET and EG is multicomponent and the flash vapor is richer in more volatile component of EG (melting point: 260.25 K, flash point: 289.15 K and 470.45 K boiling point) than the remaining liquid of BHET (melting point of 379.15 K, flash point of 445.15 ± 292.55 K). This research work presents the optimum conditions for glycolytic depolymerisation of PET to obtain a higher yield of BHET. It also considered the results of changing pressures and temperatures to enhance the efficiency or performance of two-stage evaporation regarding separating EG and BHET. It improves the quality of final BHET product acquired in term of purity. The operating conditions in Table 1 were used for glycolysis depolymerization of PET with EG as the reacting agent. The products mixture in the product stream after filtration (removal of catalyst) consist of 78.35 % EG, 18.80 % BHET and 2.85 % Oligomers were used as the feedstock for the first stages evaporation.

3. Results and discussion

The first stage operating temperature and pressure were 353.15 to 463.15 K and 120 to 11000 N/m². The results observed were 24.19 to 100 % BHET recovered, 36.95 to 99.98 % EG removed and the heat duty of 166.3 to 1251.3 kW for 6000 kg/h feed stock. The first stage evaporator effective operating conditions range were 403.15 to 443.15 K and 300 to 1000 N/m². A temperature lower than 573.15 K will take a longer residence time to evaporate low-boiling-point components (EG) to the expected concentration. Longer residence time will produce unwanted oligomer from BHET. A higher temperature than 443.15 K produces diethylene glycol (DEG) from EG by thermal history due to high temperature. The DEG produced will further react with BHET to produce 2-hydroxyethyl (2- (2- hydroxyethoxy) ethyl) terephthalate called DEG ester. A first evaporator operating at a lower pressure than 300 N/m² will have solute BHET entrain evaporating low-boiling-point components such as EG. A first evaporator operating at a higher pressure than 1000 N/m² will take a longer time to evaporate low-boiling-point components to the desired concentration, and oligomer production from BHET proceeds slowly. Lower temperature below 403.15 K and lower pressure below 300 N/m² will take a longer time to achieve the desired product concentration, produces oligomer from BHET, and the BHET entrains EG. Higher temperature more than 443.15 K and higher pressure than 1000 N/m² will produce DEG from EG, transform DEG to DEG ester, longer time to reach the desired concentration, and eventually produces oligomer. If one of the temperature or pressure is out of the above ranges of 403.15 to 443.15 K and 300 to 1000 N/m², the unwanted result is produced (Inada and Sato, 2007).

The products obtained from first stage evaporator were 96.84 to 99.76 % EG removed, 92.18 to 99.98 % BHET recovered, and 913.74 to 1081.80 kW heat duty for purifying 6000 kg/h feed stock. Increase in temperature and decrease in pressure favors the removal of EG. Higher heat duty was required to remove higher EG, since more energy was required to heat the feed stream to the higher temperature required to evaporate EG. BHET obtained in the first stage evaporator decrease with increase in temperature and decrease in pressure because lower pressure reduces the BHET boiling point and favor vaporization.

Table 2 shows the operating conditions and the corresponding results for BHET recovery and EG removal. The optimum operating condition 403.15 K and 1000 N/m² were chosen for removing 96.84 % EG and recovered highest BHET with a value of 99.98 % at the lowest heat duty of 913.74 kW.

Table 2 . Results for Comparison of performances of the First Stage Evaporation Process at Effective Temperature and Pressure.

Pressure (N/m ²)	Temperature (K)	BHET recovered (%)	EG removed (%)	Heat duty (kW)
300	403.15	99.90	98.35	935.50
400	403.15	99.91	98.08	931.36
500	403.15	99.93	97.84	927.81
600	403.15	99.95	97.62	924.62
700	403.15	99.96	97.41	921.68
800	403.15	99.96	97.21	918.92
900	403.15	99.97	97.02	916.28
1000	403.15	99.98	96.84	913.74

The composition of the product from the optimum operating conditions of 413.15 K and 1000 N/m² of the first stage evaporation was 77.89 % BHET, 11.84 % Oligomer, and 10.27 % EG. The quantity of the EG in the first stage evaporation product stream represents 3.16 % of the total EG produced by the reactor. At the operating condition range of 413.15 K to 443.15 K and 300 to 1000 N/m², the first stage evaporation product contained 3.16 % EG which is in agreement with the range 3 to 10 % reported by (Inada and Sato, 2007). Although much EG has been removed, and higher BHET recovered at the first stage evaporator. It is still necessary to carryout second stage evaporation to attain higher purity of BHET and remove EG to the bearest minimum.

The product stream from first stage evaporation process contains 77.89 % BHET, 11.84 % Oligomer, and 10.27 % EG served as feed stock for the second stage evaporation process. The desire of the second stage evaporation was to remove at least 96 % of EG from first stage evaporation and overall EG removed at 99 % of the total EG produced by the reactor. The effective operating conditions for the second stage evaporation process are 413.15 K to 443.15 K and 50 to 250 N/m². Also a temperature lower than 413.15 K takes a long time to evaporate low-boiling-point component (EG) and eventually produced oligomer from BHET. Temperature higher than 443.15 K produced DEG by high temperature which reacted with BHET to produce DEG ester. A small quantity of EG in the feed stream afford the pressure to be reduced as low as 50 N/m² and below the EG entrainment by the BHET occur. Pressure greater than 250 N/m² will take a longer time to evaporate low-boiling-point component (EG) to the required concentration, and will result in undesired

oligomer from BHET. This second evaporation process reduced EG to 0.10 weight percentage of its total content produced by the reactor and agrees with no more than 0.45 weight percent reported by (Inada and Sato, 2007). Higher EG content in the second stage evaporation product stream than 0.45 weight percent may result in side reactions that produce DEG and DEG ester in the molecular distillation step (Inada and Sato, 2007). If a single step evaporation process is subjected to reduction of EG concentration to the required 0.45 in the crude BHET, there will be disadvantages of exposing it to severe condition of temperature higher than 443.15 K. This will give rise to the production of higher concentrations of DEG, DEG ester, and oligomers. Also, the required separator size needed will be too large making the industrial productivity of BHET costly. Table 3, shows 98.49 to 99.74 % of purified BHET was obtained with 96.44 to 99.24 % of EG removed from the heat duty range of 63.50 to 81.83 kW. 423.15 K and 50 N/m² were chosen as the optimum condition simply because it removed 96.80 % EG, and recovered highest BHET with a value of 99.74 % at the lowest heat duty of 63.50 kW. The total reactor products recovered at this optimum condition of 423.15 K and 50 N/m² of the second stage evaporation process were 99.72 % BHET, and 99.90 % EG respectively as shown in Table 3. The second stage evaporation process product stream consists of 86.46 % of BHET, 13.18 % Oligomer, and 0.37 % EG that served as the feed stock for the molecular distillation.

Table 3. Results for Comparison of performances of the Second Stage Evaporation Process at Effective Temperature and Pressure

Pressure (N/m ²)	Temperature (K)	BHET recovered (%)	EG removed (%)	Heat duty (kW)
50	423.15	99.74	96.80	63.50
50	433.15	99.36	98.53	72.56
50	443.15	98.49	99.24	81.83
100	433.15	99.69	96.44	70.74
100	443.15	99.26	98.31	80.01
150	443.15	99.51	97.17	78.91

The product stream from second stage evaporation process served as the feed stock for molecular distillation (86.46 % of BHET, 13.18 % Oligomer, and 0.37 % EG) with the total products recovered the level of 99.72 % BHET, 99.99 % Oligomer, and 99.90 % EG. The aim of the molecular distillation stage was to remove approximately 100 % EG from the BHET final product stream and recovered at least 99 % BHET. The optimum operating conditions for molecular distillation was 453.15 K at 25 N/m² with final products of 99.49 % BHET recovered and approximately 100 % EG removed using 22.49 kW heat duty as presented in Table 4.

Table 4: Results of the final products after molecular distillation at effective operating conditions.

Pressure (N/m ²)	Temperature (K)	Total BHET recovered (%)	Total EG removed (%)	Molecular distillation heat duty (kW)
15	453.15	99.30	99.99	22.86
20	453.15	99.43	99.99	22.63
25	453.15	99.49	99.99	22.49
25	458.15	99.36	99.99	26.16
25	463.15	99.16	99.99	29.98

The current work was compared to the work of Inada and Sato (2007) and Goh et al. (2012). The first stage evaporation process BHET recovered was higher while both EG removed and heat duty was lower in comparison with the previous work reported by Inada and Sato (2007) at the same operating conditions. This is due to lower feed stock of the current work, as well improve the accuracy of ASPEN PLUS V8.8 used for simulation. The lower EG removed in the current work might have resulted in its lower heat duty, because lower energy (heat duty) was required to remove lower EG and vice versa. Higher EG removed, and relatively same BHET recovered with lower heat duty was observed when compared to the one reported by Goh et al. (2012). This might be due to their different in operating conditions, and lower feed stock or improvement on the previous work. Second evaporation process removed higher EG and lower BHET recovered with lower heat duty than the two previous works. The final products after the molecular distillation show approximately 100 % of the total EG was removed in all the operating conditions of the current work compared to previous works with EG in the final product. The total BHET recovered agrees with the previous works with very small (about 0.51 %) of the total BHET produced in the EG sent for further purification before recycling for reuse in PET depolymerization process. This small BHET could aid in the PET depolymerization in the reactor. The lower heat duty obtained in this work saves both energy and cost. It also helps in reducing both environmental and economic impacts of the process that is the innovation trend in achieving an eco-process-system.

4. Conclusions

PET waste glycolytic depolymerization process requirements to obtain higher yields of BHET (monomer) were explored experimentally and the data used for modelling in ASPEN PLUS V8.8 simulator using plug flow reactor to target commercial production. Increase in residence time, reactants ratio of EG:PET, and catalyst:PET ratio increases the BHET yield till the attainment of reaction equilibrium. The optimum operating conditions for this process were residence time of 3 h, 5:1 weight ratio of EG:PET, and 0.01:1 ratio of Zn(Ac)₂:PET. 100 % conversion of PET was achieved with 85.24 % yield of BHET (monomer), 14.76 % oligomer (mainly dimer) and excess EG as product mixture. BHET selectivity was 86.80 %, and that of oligomer was 13.20 %. Two stages evaporator and crystallizer were modelled using ASPEN PLUS V8.8 software to purify the BHET product and recovered the excess EG in the system. The sensitivity of the methods at different operating conditions was investigated. For the first separator, 99.99 % BHET recovery and 97.08 % EG removal were achieved from the main reactor product stream. While the second separator also recovered 99.99 % of BHET and 99.09 % of EG from the separator 1 product stream. The crystallizer has the final product of 99.96 % BHET recovered and 99.96 % EG removed. It was observed that lower temperature and higher pressure favours the recovery of higher BHET yield. However, higher temperature and lower pressure enhanced the EG removal. This work achieved a higher yield and purity of BHET, a higher EG removal for re-use and fewer heat duties demanded in comparison to previous works. The two stages evaporator provide us with different pairs of temperatures and pressures with their respective percentages of BHET recovery and EG removal as a guide to the optimal production of our products of interest. It provides guide for easier and saves operation. It can serve as good replacement for conventional crystallisation of BHET purification and EG recovery for industrial applications.

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