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Process Simulation of Two-stage Evaporation and Crystallization Systems for Bis(2-hydroxyethyl) terephthalate Recovery

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Abstract: Bis(2-hydroxyethyl) Terephthalate (BHET) produced from Polyethylene Terephthalate (PET) waste glycolysis process was purified and compared using two stages evaporation or crystallization processes. ASPEN PLUS equipped with vapor-liquid equilibrium databank together with solubility data was used to simulate these operations. Flash column and mixed product removal crystallizer were used to model two stages evaporation and crystallization process, respectively. First stage evaporation process was run at 90-180°C and 130-10,000 Pa while second stage was operated at 120-180°C and 50-250 Pa. The effect of various operating temperatures and pressures on the efficiency of evaporator and product quality were investigated. The optimum conditions for the first and second stage evaporation processes were selected based on the higher Ethylene Glycol (EG) removal with higher BHET recovery and lower heat duty needed. It was found that at higher operating temperature and lower operating pressure the performance of evaporator increased but the heat duty needed also increased which at the same time reduced the BHET recovery. Crystallization operation was simulated at 5-30°C. The BHET recovery in crystallization process decreased as temperature increased. As a conclusion, less heat duty is required as compared to previous works, higher yield and purity of BHET compared to conventional crystallization process, higher EG removal compared to previous works and conventional process and optimum operating temperatures and pressures are obtained for future scaling up process.

Key words: Simulation, bis(2-hydroxyethyl terephthalate) recovery, polyethylene terephthalate waste, 2-stages evaporation, crystallization

INTRODUCTION

The development of industry and the rising of materials consumption by the citizen have caused solid waste generated in Malaysia increasing vigorously. In 2002, 17,000 tonnes per day of solid waste was generated in Peninsular Malaysia and it is expected to reach to 30,000 tonnes per day in 2020 (Yahaya, 2008). Solid waste in Malaysia is usually disposed of to landfill. Currently, plastic waste which is part of the solid waste is the second largest solid waste generated in Malaysia covering 24% of the total solid waste (NSWMD, 2011). Plastic wastes are mostly non-biodegradable and thus, would affect the life span of landfills (Sarker, 2011). Plastic bottles for examples need almost 1000 years to decompose (Lazarevic *et al.*, 2010). Besides, landfilling of plastic wastes will generate the CO₂ emissions by 253 g kg⁻¹ plastics (Eriksson and Finnveden, 2009). Currently, Peninsular Malaysia has 177 landfills but due to limited of land and high rate of waste generation recycling

of plastic waste is an alternative method that can be used to solve the abundant of plastic waste and reduce the plastic waste dispose to landfill. The predicted total revenue from selling recycled plastic obtained from 5% of the total plastic waste in Malaysia is US\$ 1.5 million per annum (Hassan *et al.*, 2000).

Since polyethylene terephthalate (PET) is one type of the plastic wastes, the reduction of PET waste will at the same time decrease the amount of plastic waste in Malaysia. Coelho *et al.* (2011) investigated the opportunities and challenges in recycling PET containers in Brazil and reported that an education is needed to those involved directly and indirectly in the process in reducing consumption of the PET container. This will automatically reduce the amount of waste generated. Another way to reduce PET waste is by chemical recycling of PET waste. Chemical recycling includes chemical glycolysis of PET waste into bis(2-hydroxyethyl terephthalate) (BHET) monomer that needs to be purified before it can be reused for the production of plastics or other advanced materials

(Suh *et al.*, 2000). BHET can be produced by either reacting terephthalic acid or dimethyl terephthalate with Ethylene Glycol (EG) (Scheirs and Long, 2003) or glycolysis of PET wastes using EG (Xi *et al.*, 2005).

In the production of polymer, polymer additives such as plasticizers, thermal stabilizers, slip additives, light stabilizers and antioxidants are added to polymer to improve their performance (Lau and Wong, 2000). Besides, some compounds such as benzaldehyde, butoxybenzene and many others are identified in virgin PET (Gramshaw *et al.*, 1995). During recycling of PET wastes, these foreign materials will cause a reduction in the production efficiency of manufacturing recycled PET product and a decrease in the product quality (Shuji and Kikuchi, 2007). Therefore, purification of BHET which is the monomer of the PET prior to polymerization process in manufacturing the PET products from recycled PET waste is obligatory.

A conventional method used in purification of BHET is repeated crystallization process. Although this method can improve the quality of BHET, harmful materials such as polymer additives practically still exist and cause the production of high quality PET become difficult (Shuji and Kikuchi, 2003a). Meanwhile, the glycolysed product which is the contaminated BHET can also be purified by other methods such as decolorization, deionization, evaporation and distillation to obtain a higher purity of BHET (Shuji and Kikuchi, 2007).

An advanced BHET purification method is two stages evaporation process. This method is used to remove the impurities having boiling point lower than BHET including EG solvent. The evaporation process is operated in two stages rather than single stage to prevent the feed stream directly expose to very low pressure and high temperature. At this condition i.e. very low pressure and high temperature, large amount of EG and BHET will react to form by-product such as diethylene glycol (DEG) and DEG ester. Besides that, the BHET may react with each other to form oligomers (Shuji and Kikuchi, 2007). This may cause the amount of by-product and by-produced oligomers become larger compares to by-products produced from two stages evaporation process.

In two stages evaporation process, the glycolysed product is first subjected to preliminary evaporation follows by second stage where the residue is further evaporated under reduced pressure to obtain purified BHET. At both stages, a particular temperature and pressure are selected to ensure that EG and any compounds having a boiling point lower than BHET are distilled off (Shuji and Kikuchi, 2003b).

This study presents the effect of changing operating temperatures and pressures toward the efficiency of two stages evaporation in terms of EG removal and the quality of final product obtained in terms of purity, viscosity and density. Besides that, this paper also shows the comparison between crystallization and two stages evaporation processes in terms of BHET recovery.

SIMULATION PROCEDURE

Two stages evaporation: In order to model the two stages evaporation process using ASPEN PLUS, a few assumptions need to be made as follow:

- Both evaporation processes are in steady state
- Glycolysed product (Stream 2 in Fig. 1) consists of 19% BHET, 4% oligomer and 77% EG only
- Glycolysed product enters the evaporator in liquid form
- Polymerization reaction does not occur in the two stages evaporator.

The ASPEN PLUS flash column was used to simulate two stages evaporation. This model was selected because it can separate the inlet into two outlet streams by using rigorous vapor-liquid equilibrium (ASPEN PLUS, 2006). Figure 1 shows the process flow diagram for the purification of glycolysed product using two stages evaporation process. Flash columns were used in modeling both the evaporators.

In equilibrium system, the Gibbs phase rule demonstrates that a mixture of three components that forms two phases have three degrees of freedom. If the pressure and temperature are fixed for the process, one degree of freedom remains (Felder and Rousseau, 2005) which is the concentration of each outlet streams.

In this method, for the calculations of the equilibrium composition, the operating temperature and pressure were specified. After defining the operating temperature and pressure, the equilibrium composition for each outlet streams was calculated by using Raoult's law (ASPEN PLUS, 2006):

$$y_i P = x_i p_i \quad (1)$$

where, y_i , P , x_i and p_i are mole fraction of component in the vapor phase, total pressure in Pa, mole fraction of component in the liquid phase and vapor pressure of pure component in Pa, respectively.

The components in the feed stream were extracted from "Polymer" and "Pure 20" databank in ASPEN PLUS which both databanks contain the parameter of extended

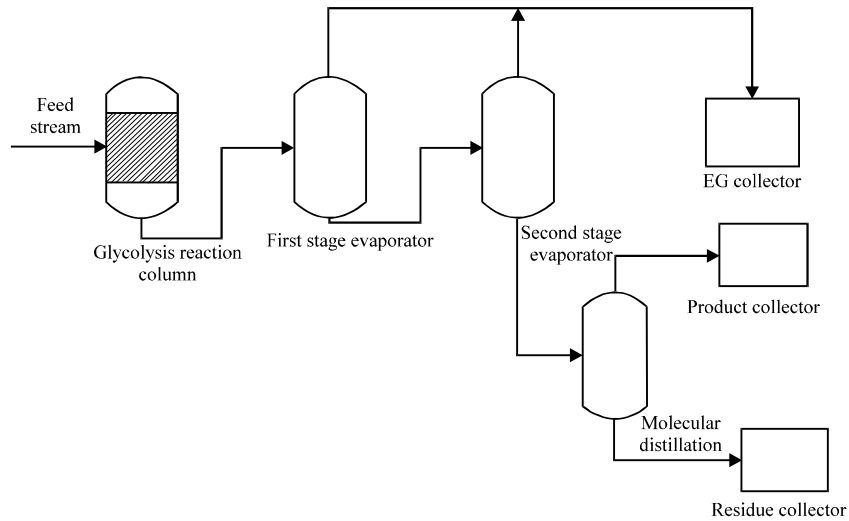


Fig. 1: Flow diagram of purification process using two stages evaporation process

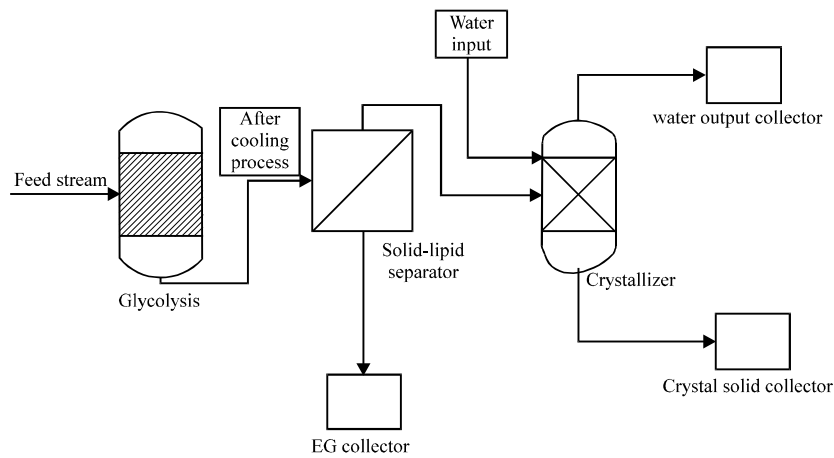


Fig. 2: Flow diagram of purification process using crystallization process

Antoine equation. The vapor pressure in Raoult's law was calculated using extended Antoine equation (ASPEN PLUS, 2006):

$$\ln p_i = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i} \ln T + C_{6i}T^{C_{7i}} \quad (2)$$

where, p_i is pure component vapor pressure at system temperature in Pa, C_{1i} is coefficients in Kelvin and T is system temperature in Kelvin.

The feedstock used for two stages evaporation was glycolysed product obtained from depolymerisation of PET flakes using EG as a solvent. Table 1 shows the operating condition of glycolysis process. The glycolysed product obtained was 77 wt.% EG, 19 wt.% BHET and 4 wt.% oligomer.

Crystallization: In order to model the crystallization process using ASPEN PLUS, a few assumptions need to be made as follow:

- The crystallization process operates in steady state
- Input (Stream 3 in Fig. 2) contains 83 wt.% BHET and 17 wt.% oligomer
- Input enters the crystallizer in solid form
- The ratio of water stream to input stream is 7:1 (Pilati *et al.*, 1996)

The ASPEN PLUS crystallizer was used to simulate crystallization process. The process flow diagram of purification of glycolysed product using crystallization process is shown in Fig. 2. The final product obtained from crystallization process was

Table 1: Operating conditions of glycolysis process

Glycolysis conditions	Values
Catalyst	Zinc acetate (1.5 % of PET flake used)
PET: EG	1:5
Temperature	196°C
Time	8 h

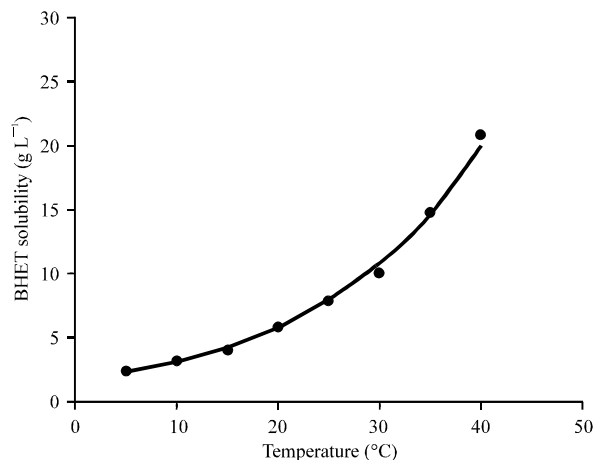


Fig. 3: Solubility of BHET in water (Pilati *et al.*, 1996)

calculated based on the solubility of BHET in water (Pilati *et al.*, 1996) as shown in Fig. 3.

RESULTS AND DISCUSSIONS

First stage evaporation: Figure 4 shows the simulation results for first stage evaporation process. At the first stage of evaporation, the operating temperature and pressure were set at 90-180°C and 130-10,000 Pa. The percentage of EG removed in the first stage evaporator was more than 25% as shown in Fig. 4a. The range of heat duty required (Fig. 4b) for purifying 10,000 kg h⁻¹ feedstock and the percentage of BHET recovered (Fig. 4c) in the first stage evaporation were 881-2658 kW and 70-100%, respectively. The amount of EG evaporated increased as the operating temperature increased and operating pressure decreased. The required heat duty showed the same trend as the percentage of EG removal. This is because of more energy was required to heat the feed stream to higher temperature and also to evaporate the EG. The amount of BHET obtained in the first stage evaporation product stream decreased as temperature increased and pressure decreased. This is due to the lower pressure would lessen the boiling point of the BHET and thus the BHET would easily vaporize.

The density and viscosity of the first stage evaporation product are shown in Fig. 4d-e, respectively. The product density decreased as the operating pressure increased. The density would increase when the temperature increased but when the percentage of EG

Table 2: Performance of selected four operating conditions which can remove 95% EG at first stage evaporation process

Operating	EG removed (%)	BHET recovered (%)	Heat duty (kW)
105	95.5216	99.9984	2162.65
120	95.7909	99.9947	2230.57
140	95.5265	99.9837	2311.01
150	95.4932	99.9726	2354.44

removal became almost constant, the density was slightly decreased as temperature increased. Since density was affected by the mass and volume and EG represented large volume of the feed stream (77 wt.%), at lower temperature as temperature increased the amount of EG decreased significantly, thus indirectly reduced the volume of product stream and increased the density. At higher temperature on the other hand, the amount of EG removed became almost constant but the amount of BHET removed increased significantly. Thus, the mass of product diminished as the operating temperature increased. As a result, the product's density as a function of mass of the product decreased as temperature increased.

Viscosity decreased when the temperature increased. At lower temperature, the viscosity decreased as the operating pressure increased. The quantity of EG removed decreased as pressure increased, led to the proportion of EG in the product increased and thus decreased the viscosity of the product. At higher temperature on the other hand, operating pressures did not give any significant effect to the process leading to constant viscosity of the product. This is because, at higher operating temperature the amount of EG and BHET removed increased, thus the composition of the product became similar. Since the viscosity was calculated based on the viscosity of pure component and the ratio of the components in the mixture, the viscosity of the purified product tended to be constant at higher temperature.

The target of the first stage evaporation was to remove 95% of the EG in the inlet solution with lower heat duty and higher BHET recovery. 105°C and 1000 Pa, 120°C and 2000 Pa, 140°C and 5000 Pa and 150°C and 7500 Pa were the operating temperatures and pressures that could remove 95% EG in the feed stream. Table 2 shows the performance comparison between these four selected operating conditions. Among the four selected conditions, 105°C and 1000 Pa was chosen as the optimum condition for the first stage evaporation process. As compared to the other three selected conditions, 105°C and 1000 Pa had the lowest heat duty (2162.65 kW) and highest percentage of BHET recovery (99.9984%). Even though higher BHET recovery was obtained after the first stage evaporation process, the second stage evaporation is still necessary to remove the remaining EG that exist in the mixture.

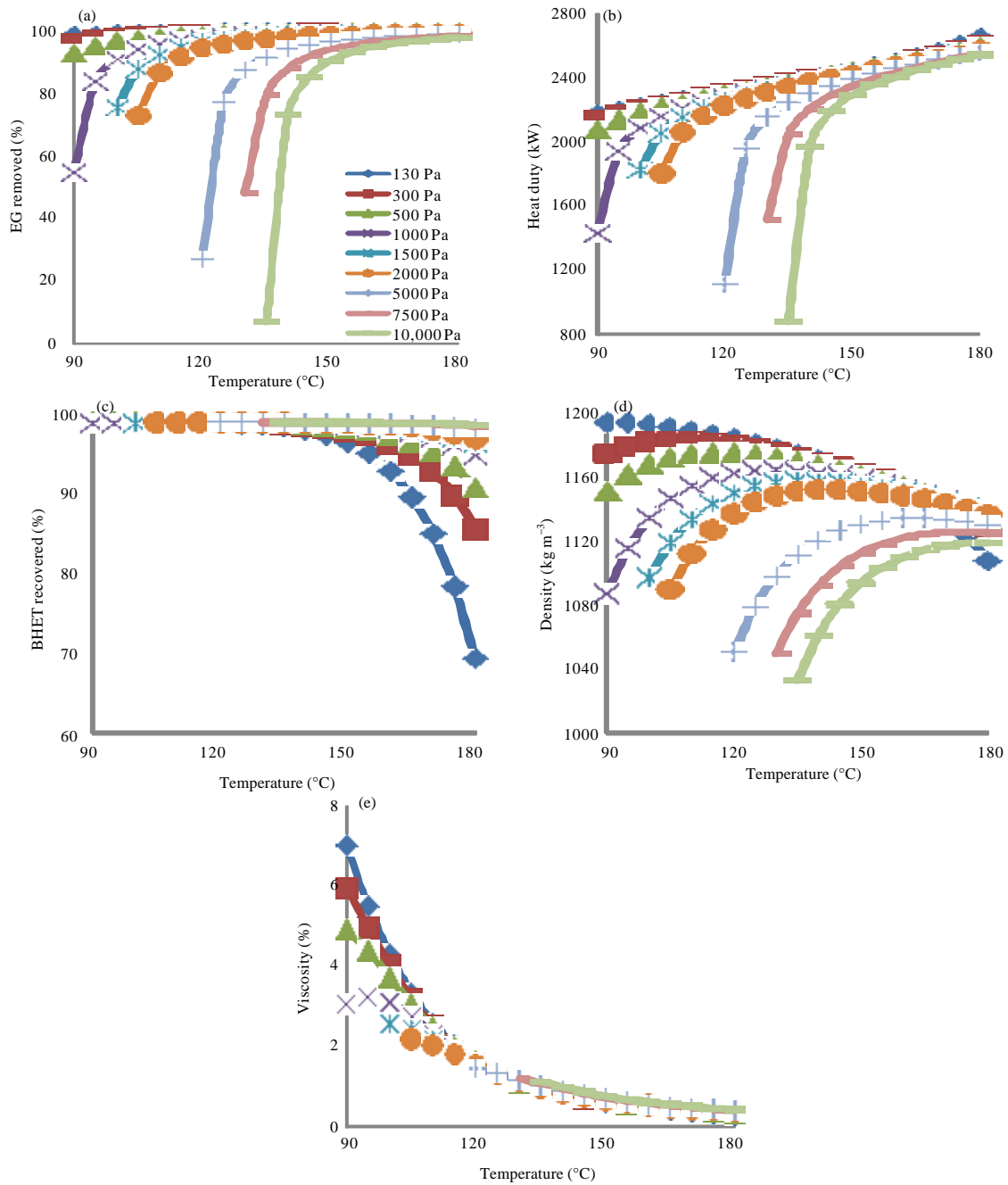


Fig. 4(a-e): Simulation result for first stage evaporation process, (a) Percentage of EG removed, (b) Heat duty, (c) Percentage of BHET recovered, (d) Density and (e) Viscosity

The composition of the product obtained from optimum condition of the first stage evaporation process was 71.84% BHET, 13.04% EG and 15.12% oligomer. Previous research reported that at the first stage evaporation process carried out at temperature range of

130-170°C and pressure range of 300-1000 Pa, the obtained product contained 3-10% EG (Shuji and Kikuchi, 2007). Although the result shows that the product obtained from the first stage evaporation process carried out at 105°C and 1000 Pa contained slightly higher EG (13.04%

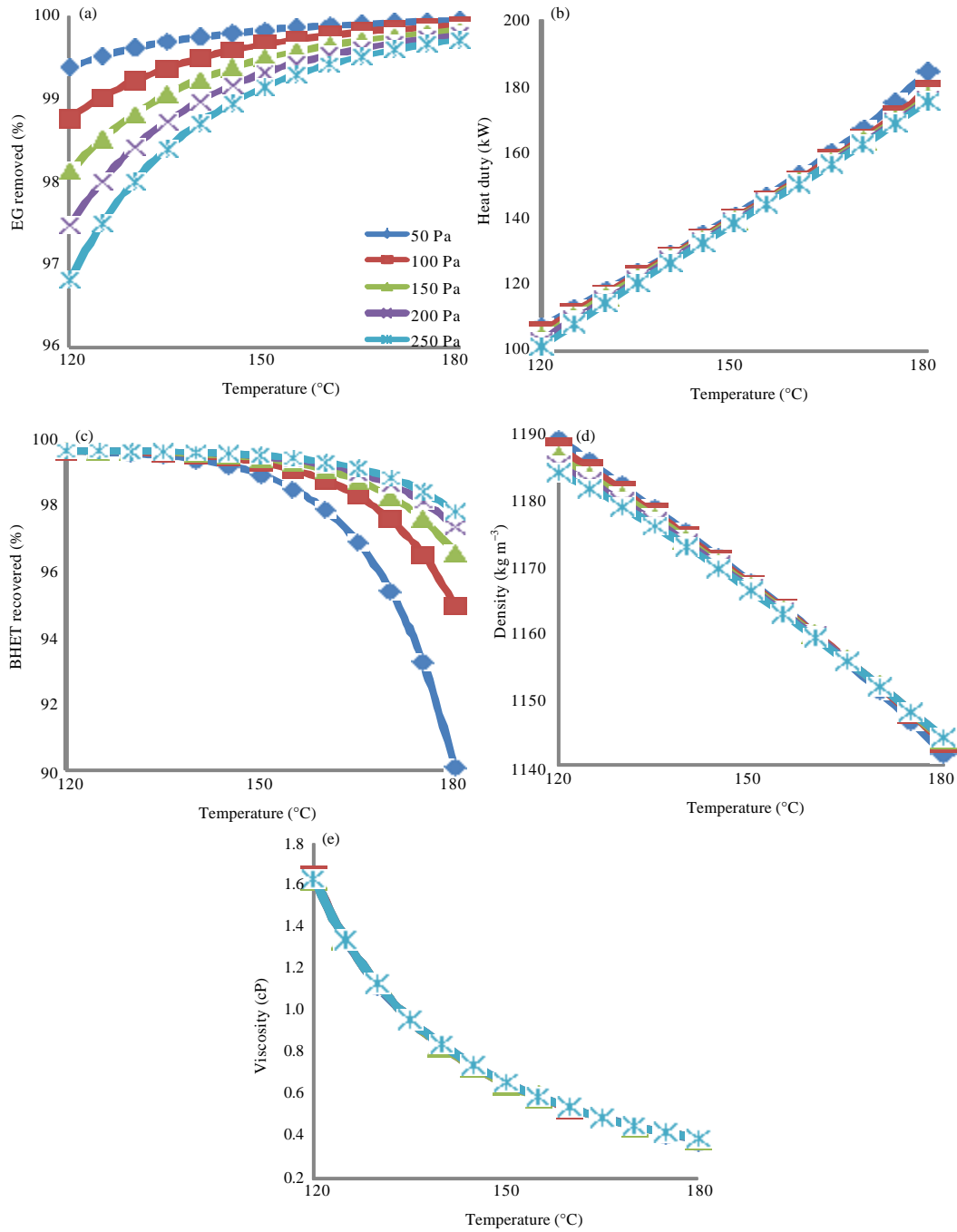


Fig. 5(a-e): Simulation result of second stage evaporation process, (a) Percentage of EG removed, (b) Heat duty, (c) Percentage of BHET recovered, (d) Density and (e) Viscosity

EG) as compared to the reported work (Shuji and Kikuchi, 2007) as that was operated at higher temperature and higher vacuum pressure which required higher capital cost to conduct the process.

Second stage evaporation: Figure 5 shows the simulation results for the second stage evaporation process operated at temperature range of 120-180°C and pressure range of 50-250 Pa. From the result shown in Fig. 5a, the second

stage evaporation process could remove at least 92% of the remaining EG resulted from the first stage evaporation process. The range of required heat duty (Fig. 5b) and the remained BHET (Fig. 5c) in the final product were 102-184 kW and more than 96%, respectively.

The density and viscosity of the final product decreased when the temperatures increased as portrayed in Fig. 5d-e. As pressure decreased, the amount of EG and BHET evaporated became larger. The composition of the product became constant since both properties did not demonstrate any significant different as the pressure varied.

The aim of the second stage evaporation process was to remove 99% EG that remained in the first stage evaporation product. There are five operating temperatures and pressures that could achieve 99% EG removal namely 130°C and 50 Pa, 150°C and 100 Pa, 160°C and 150 Pa, 165°C and 200 Pa and 175°C and 250 Pa. Table 3 displays the performance comparison between these five selected conditions. Pressure 50 Pa and temperature 130°C was chosen as the optimum condition for the second stage evaporation process due to the ability to evaporate 99% remaining EG with the lowest heat duty (118.43 kW) and highest BHET remained (99.9568%) in the final product as compared to other selected operating temperatures and pressures.

According to Shuji and Kikuchi (2007), the product of the second stage evaporation process operated at temperature range of 130-170°C and pressure range of 50-250 Pa contained less than 0.45 % EG. The composition of the product yielded from this second stage evaporation process conducted at optimum condition of 50 Pa and 130°C was 82.48% BHET, 0.15% EG and 17.37% oligomer. This indicated that the selected optimum condition could accomplish similar result as previous reported work.

Table 4 shows the comparison between previous and current research according to ASPEN PLUS simulation result. The first stage evaporation process carried out at optimum condition could remove 95.52% EG which was lower than the previous research but the percentage of BHET recovery was higher and the heat duty required was lower. The optimum condition of the second stage evaporation was within the range of previous research therefore the percentage of EG removal, percentage of BHET recovery and heat duty should be in the range of previous research's output.

Two stages evaporation that operated at optimum condition selected was able to remove 99.03% EG with 99.96% BHET recovered. Both were within the range as the previous research but the total heat duty needed was much lower than the previous research which was 2281.08 kW as compared to previous research (2354.01-2548.26 kW).

Table 3: Performance of selected five operating conditions which can remove 99% EG at second stage evaporation process

Operating		EG removed (%)	BHET recovered (%)	Heat duty (kW)
Temperature (°C)	Pressure (Pa)			
130	50	99.0285	99.9568	118.43
150	100	99.1532	99.8479	140.08
160	150	99.1300	99.7537	151.24
165	200	99.0314	99.7174	156.79
175	250	99.1503	99.4874	168.74

Table 4: Comparison between previous and current research based on ASPEN PLUS simulation result

	Previous Work (Shuji and Kikuchi, 2007)	Current research
First stage		
Operating temperature (°C)	130-170	105.00
Operating pressure (Pa)	300-1000	1000.00
EG removed (%)	99.02-99.95*	95.52
BHET recovered (%)	93.68-99.96*	99.99
Heat duty (kW)	2338.74-2547.38*	2162.65
Second stage		
Operating temperature (°C)	130-170	130.00
Operating pressure (Pa)	50-250	50.00
EG removed (%)	77.17-99.09*	99.03
BHET recovered (%)	99.62-99.99*	99.96
Heat duty (kW)	0.88-59.14*	118.43
Total EG removed (%)	99.78-99.99*	99.96
Total BHET recovery (%)	93.67-99.96*	99.96
Total heat duty (kW)	2354.01-2548.26*	2281.08

*(% EG removed, (% BHET recovered and heat duty were obtained using operating conditions given by Shuji and Kikuchi (2007) simulated in the ASPEN Plus simulation

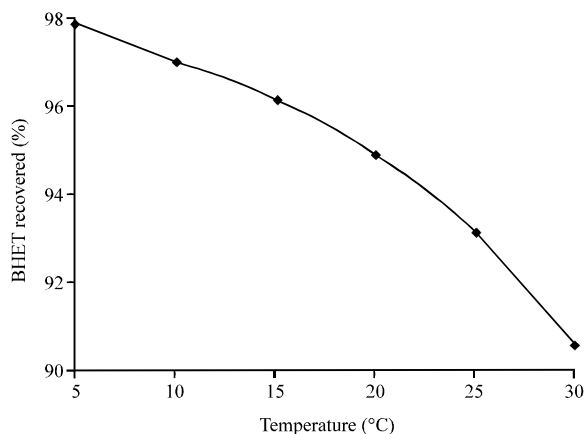


Fig. 6: Percentage of BHET obtained from crystallization process at various temperatures

Comparison between crystallization and evaporation: A simulation for crystallization process was carried out to compare the effectiveness between two stages evaporation and crystallization processes in term of BHET recovery at the final stage. Figure 6 shows the percentage of BHET obtained as crystal solid decreased as the operating temperature increased. This is due to the solubility of BHET in water increased as the temperature increased.

By assuming the crystallization process was operated at 5°C, the BHET recovered was 98% while two stage evaporation process conducted at the chosen optimum condition was able to recover almost 100% of the BHET from the feed stream. Although the percentage of BHET recovered by both methods was only 2% different, the two stage evaporation was preferred to purify glycolysis product rather than crystallization process. This is because of the purified BHET obtained from crystallization process still contains harmful impurities which become a barrier when the BHET is used to produce recycled PET (Shuji and Kikuchi, 2003a). Furthermore, crystallization process will generate large volume of wastewater from filtration and washing that may contain impurities, oligomer and BHET. This wastewater needs to be treated prior to discharge to water body.

CONCLUSION

Two stages evaporator and crystallizer were modeled using ASPEN PLUS simulator. The models were used to examine the performance of both methods at various conditions. The first stage evaporation was able to operate at temperature range of 90-180°C and pressure range of 130-10,000 Pa while the second stage evaporation was able to function at temperature range of 120-180°C and pressure range of 50-250 Pa. Higher temperature and lower pressure increased the EG removal leading to a reduction in the BHET recovery. However, the heat duty needed was also increased. The optimum condition of two stages evaporation was chosen based on the higher EG removal with lower heat duty and lower BHET removal. To validate the product purification, the purity as well as density and viscosity of the product were analyzed. The simulation also found that repeated crystallization process was able to perform at temperature range of 5-30°C with the BHET recovery reduced as temperature increased. As a conclusion, two stages evaporation could be used as an alternative technique to replace a conventional repeated crystallization in the purification of BHET for future applications.

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