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**DEVELOPMENT OF A REACTIVE DISTILLATION COLUMN
PROTOTYPE TO CONVERT ACRYLIC ACID IN THE PETROCHEMICAL
WASTEWATER TO VALUABLE BUTYL ACRYLATE THROUGH
ESTERIFICATION**

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ABSTRACT

Wastewater containing 2-20wt% of acrylic acid (AA) is currently burned using incinerator which is neither economical feasible nor environmental friendly. Esterification in a reactive distillation column (RDC) is a promising method to recover AA from wastewater. AA could be converted to a valuable ester product while purifying water. A RDC prototype was developed and tested for the recovery of AA from the wastewater. A maximum AA conversion of 99.5% was achieved when the BuOH to AA molar ratio and reflux ratio were 4 and 5 respectively. The data was used to validate the simulation results generated using equilibrium stage model in ASPEN PLUS program. A technically optimized RD process was then proposed.

1. INTRODUCTION

The Oil, Gas and Energy National Key Economic Areas (NKEA) are targeting 5 percent annual growth for the sector (including petrochemical industry) in the decade from 2010 to 2020. This target translates into an increase of RM131.4 billion in the period from 2010 to 2020 (www.miti.gov.my). The petrochemical industry is now an important growth industry for Malaysia amongst other chemical sub-sectors such as petroleum products, inorganic chemicals, oleochemicals and industrial gases. The type of petrochemical products include olefins, polyolefin, aromatics, ethylene oxides, glycols, oxo-alcohols, ethoxylates, phthalic anhydride, acetic acid and acrylic acids (www.mida.gov.my). The effective waste management system of this industry is of crucial to minimise the environmental impact of the petrochemical industries in Malaysia.

In a typical petrochemical industry for acrylic acid (AA) manufacturing, the wastewater has AA concentration in the range of 10–15 wt%. Such wastewaters also consist of high chemical oxygen demand (COD) which renders the direct biological treatment difficult. It is almost always being incinerated in the incinerator which consuming a lot of energy. Several treatment methods, particularly adsorption, biological or a blend of wet oxidation followed by biological treatment, have been explored for the removal of AA from wastewaters (Kumar et al., 2008, 2010; Silva et al., 2004; Oliviero et al., 2000; Mishra et al., 1995). However, these methods are still suffering with the shortcomings of high cost and loss during regeneration.

Recovery of AA from its dilute aqueous solution by using it as a reactant for esterification in a reactive distillation column (RDC) could be a promising approach. This approach has received much attention as the dilute acetic acid, trifluoroacetic acid, lactic acid, adipic acid, myristic acid, succinic acid, chloroacetic acid and glycolic acid, can be recovered to produce a higher valued ester (Kumar and Mahajani, 2007; Mahajan et al., 2008; Sharma and Mahajani, 2003; Talnikar and Mahajan, 2014), which in turn saving raw material cost and solving environment problem. The use of a reactive distillation, a multifunctional reactor combining chemical reaction and distillation in a single column is a promising way for the utilization of the dilute AA to synthesize high valued acrylate esters.

The feasibility of the recovery of acrylic acid through esterification reaction in a RDC has been proven in our previous studies (Ahmad et al., 2014, Chin et al., 2015). The model industrial wastewater with various concentration of AA (10–100wt%) was reacted with 2-ethyl hexanol (2EH) to produce 2-ethyl hexyl acrylate (2EHA) in the setups with total reflux and continuously water removal.

These Amberlyst-15 (ion exchange resin) catalyzed reactions were carried out under the mass transfer resistance free region. The performance of both systems was compared. The yield for the reactions of the AA solutions with the AA concentrations of 30–80wt% was enhanced significantly when the reactions were carried out using the second setup. The findings have shown the potential of recovering AA from the waste water stream via esterification in RDC. It was recommended that the concentrated AA solutions or larger amount of inhibitor should be adopted to prevent the catalyst fouling by the deposition of poly-acrylic acid on the catalyst surface.

2. RESEARCH METHODOLOGY

The proposed prototype of reactive distillation column (RDC) was designed and fabricated based on the simulation work done by Zeng et al. (2006) and the design guidelines developed by Subawalla and Fair (1999). The RDC consisted of 3 main sections, the one meter each rectifying and stripping sections packed with SULZER EX for separation and the two meter reactive section packed with Amberlyst 15 catalyst in SULZER KATAPAK. The column was equipped with a reboiler at the bottom and a cooling water condenser at the top. Phase separation occurs upon condensation because of the heteroazeotropic behaviour of the test systems. Thus, a decanter was installed after the condenser for splitting the distillate to an organic and aqueous phase. The aqueous distillate was removed while the organic distillate was recycled. The RDC as shown in Figure 2.1 was connected to the SCADA system for data logging purposes. All the sections of the column are provided with a heating blanket, insulation and thermocouple. The operating manual of the RDC prototype is provided in **Appendix A**.

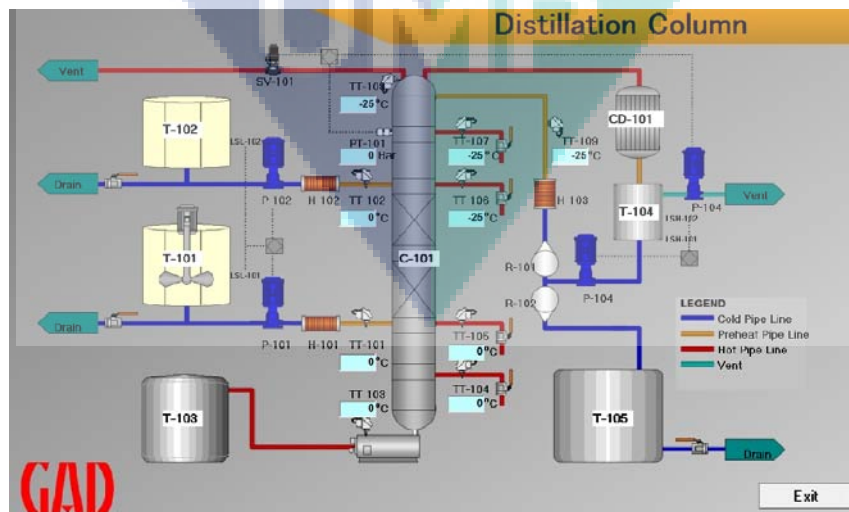


Figure 2.1. RDC linked to the SCADA system.

The reactants, butanol (BuOH) and acrylic acid (AA) were fed to the RDC with controlled flowrate using peristaltic pumps. The feeds were introduced at a temperature of <100 degC. In a typical experiment, BuOH was introduced at the top and AA was fed at the bottom to achieve maximum conversion. After starting the reaction, the temperature in each section of the column was logged. The top product, bottom product and samples along the column were continuously withdrawn at certain time interval, weighed and analysed for their composition until the steady state was achieved (all the sections of columns attained the constant temperatures). The flowrates of the feed, bottom and overhead were measured and a complete material balance was performed. Butyl acrylate, water, BuOH and AA present in the sample was analyzed using gas chromatograph. All the experiments were carried out at atmospheric pressure. Both molar ratio of BuOH to AA and reflux ratio was varied from 1-9. Table 2.1 shows the total number of experiments conducted in the RDC by variation of the process parameters.

Table 2.1. Reactive distillation experiments: variation of operating conditions

Experiment No.	Molar ratio BuOH to AA	Feed flow rate, L/h		Reboiler temperature, °C	Reflux ratio, mol/mol
		BuOH	AA solution		
1	1	1.05	2.7	147	5
2	2	2.1	2.7	147	5
3	4	4.2	2.7	147	5
4	6	6.3	2.7	147	5
5	8	8.4	2.7	147	5
6	4	4.2	2.7	147	3
7	4	4.2	2.7	147	4
8	4	4.2	2.7	147	6
9	4	4.2	2.7	147	7

The modeling and simulation were carried out using (a) Equilibrium Stage Model, RADFRAC available in ASPEN PLUS v9 software package. RADFRAC module in the steady state simulator based upon a rigorous equilibrium stage model for solving the mass balance, phase equilibrium, summation and energy balance (MESH) equations. The equilibrium model assumes vapor liquid equilibrium at each stage. The departure from equilibrium is accounted for by tray efficiency or height equivalent to theoretical plate (HETP). The RDC prototype testing data was used to validate the simulation results. Finally, the process was technically optimized by simulation using the validated Equilibrium Stage Model.

3. LITERATURE REVIEW

3.1 Introduction

Acrylic Acid (AA) is very toxic to living species and it appears as an unsaturated organic acid. During the manufacture of acrylic esters, acrylic acid is being released to the environment. It has been reported that in a typical AA plant, the concentration of AA ranges from 10-20 g/l in the wastewater stream (Kumar et al., 2008). Thus, the recovery of dilute acrylic acid from the wastewater stream has become very important due to its economic and environmental awareness.

3.2 Wastewater treatment technology for carboxylic acid recovery

According to Cheremisinoff (2002, p.1), wastewater treatment technology can be divided into three areas: Physical Methods, Chemical Methods and Energy Intensive Methods. Physical methods for wastewater treatment are mainly represented by solid-liquid separation techniques. Filtration plays an important role in solid-liquid separation techniques as it is an integral component of wastewater treatment application. In understanding the role of filtration, it is important to make distinctions not only with other technologies applied in the purification of industrial water, but also includes the objectives of different unit processes.

Besides that, chemical methods for wastewater treatment depend upon the chemical reaction of the contaminants to be recovered from the water. It is applied as a stand-alone technology as well as an integral part of the treatment process with physical methods.

Moreover, as for energy intensive technologies, the thermal methods have gained much attention due to its dual role in wastewater treatment applications. They can be utilized as a mean of sterilization or utilized to the processing of solid wastes or sludge. In the latter cases, thermal methods can also be applied to sterilize sludge contaminated with organic contaminants.

Several methods have been explored in recovering carboxylic acids from wastewater. In the past, the conventional method includes adsorption through activated carbon (Kumar et al., 2010) and distillation and extraction (Arpornwichanop et al., 2008). However, distillation approach requires high energy usage in vaporizing the water present whereas, extraction is limited by the phase separation and distribution of the component (Saha et al., 2000). As for adsorption through activated carbon, it only deals with chemical wastewater with a low concentration of organic compounds (Kumar et al., 2010). Wet air oxidation (WAO) treatment has also been explored as an alternative method. Due to the high energy consumption which leads to high operation cost, this method is not being favoured (Lin et al., 1996).

Thus, reactive distillation has been introduced as a method in recovering acrylic acid from its dilute aqueous solution. It applies the concept of using the recovered acrylic acid as the reactant for esterification. According to Arpornwichanop et al. (2008), this approach is able to produce a higher valued ester, which could save raw

material cost and environment issues. Table 3.1 shows the several methods for the recovery of carboxylic acids that have been investigated by past investigators.

Table 3.1 Methods which have been applied for the recovery of carboxylic acids.

Method	Reference	Remarks
Adsorption through activated carbon	Kumar <i>et al.</i> (2010)	Deals only with low concentration of organic compounds (50-500 mg/l) due to long residence time.
Distillation	Saha <i>et al.</i> (2000); Arpornwichanop <i>et al.</i> (2008)	Unable to achieve high conversion due to esterification process is reactive equilibrium limited.
Extraction	Saha <i>et al.</i> (2000); Arpornwichanop <i>et al.</i> (2008)	Unable to achieve high conversion due to esterification process is reactive equilibrium limited.
Wet air oxidation (WAO)	Lin <i>et al.</i> (1996)	High temperature of 250 °C to maintain the pressure inside the reactor. This will cause high energy consumption to occur.
Esterification process by RDC	Arpornwichanop <i>et al.</i> (2008)	Able to achieve a conversion of around 95% with 35 % w/w acetic acid.

3.3 Esterification reaction to recover carboxylic acid from wastewater

According to Arpornwichanop *et al.* (2008), esterification reaction can be applied to recover carboxylic acid from wastewater by in cooperating with RDC. Through RD, the recovered carboxylic acid will be used as a reactant for the esterification process which in turn will produce a higher valued ester, save raw material cost and environmental issues concerning with the present of carboxylic acid in wastewater can be overcome. Some esterification reaction which has been applied for the recovery of carboxylic acid is shown in Table 3.2 below. Based on the table below, it can be seen that only the recovery of acetic acid through RDC has been studied by past researches up till now. Generally, it can be summarized that the overall

conversion of acetic acid with different degree of dilution into acetate esters range from 67- 95 %.

Table 3.2 Summary of esterification reaction which have been applied in recovery of carboxylic acid through RDC.

Reactants	Products	Type of catalyst used	Remarks	Reference
Acetic acid + n-butanol	n-butyl acetate + Water	Amberlyst-15 (Heterogeneous catalyst)	35 % w/w Acetic acid	Arpornwichanop <i>et al.</i> (2008)
		-	30 % w/w Acetic acid	Gangadwala <i>et al.</i> (2007)
Acetic acid + 2-ethyl-1-hexanol	2-ethylhexyl acetate + Water	Amberlyst-15 (Heterogeneous catalyst)	6-15 % w/w Acetic acid	Ragaini <i>et al.</i> (2007)
Trifluoroacetic acid + 2-propanol	2-propyl trifluoroacetate + Water	Ion exchange resin, T-63 (Heterogeneous catalyst)	10 % w/w Trifluoroacetic acid	Mahajan <i>et al.</i> (2008)
Acetic acid + ethanol	Ethyl acetate + Water	Polystyrene-supported sulfonic acid (Heterogeneous acid)	50 % w/w Acetic acid	Yagyū <i>et al.</i> (2013)

3.4 Catalyst in esterification

3.4.1 Introduction

Basically, catalyst can be divided into homogeneous or heterogeneous. This is also applicable for reactive distillation column.

In the term of chemistry, homogeneous catalysis occurs when the catalyst is in the same phase (solid, liquid or gas) as the reactants. Homogeneous catalysis on the other hand is likely to be influenced by the changing of concentration to enhance or lower the reaction velocity (Sundmacher and Kienle, 2003, p.48). Enzymes are homogeneous catalysts which are also known as biocatalysts.

Meanwhile, heterogeneous catalysts which are practically used in the industry are in the form of solids. According to Altiokka and Çitak (2003), heterogeneous catalyst is more advantages compare to homogeneous catalyst. Heterogeneous catalyst is able to eliminate corrosive environment, can be easily remove from the reaction mixture by decantation or filtration and lastly, the purity of the products is higher compare to homogeneous catalyst since the side reactions can be completely eliminated or are less significant. Examples of heterogeneous catalysts used for esterification reaction in the recovery of carboxylic acid from wastewater are Amberlyst-15 (Arpornwichanop et al., 2008; Ragaini et al., 2007) and Indion 130 (Saha et al., 2000).

3.4.2 Homogeneous

Strong mineral acids, such as H_2SO_4 , HCl and HI , and also strong organic acids, such as $HCOOH$ are some types of homogeneous catalysts which are being applied for the esterification of carboxylic acid (Lilja et al., 2002). During the esterification reaction involving homogeneous catalyst, the slow step of the reaction involves the nucleophilic attack of the alcohol on the protonated carbonyl group of carboxylic group. According to Liu et al. (2006), the mechanisms route can be describe as follows:

- Firstly, protonation of the carboxylic acid takes place.
- Then, reaction with nonprotonated alcohol to yield a tetrahedral intermediate is activated.
- Finally, by decomposition, it produces the products of reaction which are ester and water.

However, there are some drawbacks towards homogeneous catalyst. According to Lilja et al. (2002), the miscibility of homogeneous catalyst with the reaction medium will cause difficulty in the separation between the products and reactants. Furthermore, the present of higher catalyst concentration will cause corrosion of the equipment to occur.

Even though due to the disadvantages of homogeneous catalyst which have been stated above, there are still studies being carried out by researchers on the esterification process by applying homogeneous catalyst. Lilja et al. (2002) have studied the esterification of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol in the present of liquid HCl whereas Liu et al. (2006) have studied the esterification of acetic acid with methanol in the present of H_2SO_4 .

3.4.3 Heterogeneous

Heterogeneous catalyst can be divided into three categories: solid ion exchange resins, zeolite and enzymes. According to Komoń et al. (2013), there are two main classes of sulfonated ion exchange resins which are popular in the industry: one is based on polystyrene/divinylbenzene matrix which includes Amberlyst and Dowex type resins and the other is based on perfluorinated sulfonic acid resins like Nafion and Aciplex.

On the other hand, as for zeolite type heterogeneous catalyst, H-ZSM-5 and NaY and VOx over USY have been stated in past literatures (Okuhara et al., 1998; Marchetti and Errazu, 2008). The NaY over USY is a base catalyst whereas the VOx over USY is an acid catalyst. Lipozyme CALB and Lipozyme T.L 100L from Novozymes are some example of enzyme based heterogeneous catalysts which have been studied by Marchetti and Errazu (2008).

Examples of heterogeneous catalysts which have been used for esterification reaction are as follows:

- Esterification of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol in the present of fibrous polymer-supported sulphonic acid catalyst, Smopex-101 (Lilja et al., 2002).
- Esterification of acetic acid with methanol on the present of Nafion/silica nanocomposite catalyst (SAC-13) (Liu et al., 2006).
- Esterification of propanoic acid with n-butanol in the present of solid acid $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ in the present of excess water (Okuhara et al., 1998).

3.5 Reactive distillation technology

Instead of carrying out the reaction and separation process separately, it is possible to combine these operations into a single unit operation. This is called reactive distillation or catalytic distillation (Luyben and Yu, 2008, p. xvii). Reactive distillation is an excellent example of process intensification which is able to provide an economically and environmentally attractive alternative to conventional multiunit flow sheets in some systems. RDC consists of a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom of the RDC. In the reactive column, the products are separated in situ, which drives the equilibrium to the product side and thus, preventing any undesired side reactions between the reactants and product which could hinder the achievements of a high conversion (Taylor and Krishna, 2000; Luyben and Yu, 2008, p.2).

For many decades, a small number of industrial applications of reactive distillation have been seen. The most important industrial application which has gained much attention was the production of methyl tertiary butyl ether (MTBE). Moreover, about two decades ago, engineers at Eastman Chemical published a very inspiring paper which has cause reactive distillation to gain so much interest in both industry and academia (Agreda et al., 1990). The Eastman single RD column managed to keep the concentration of methyl acetate low in liquid form where reversible reaction is occurring. Therefore, the reaction is driven to the product side where high conversion can be achieved. Table 3.3 gives a comprehensive insight of different types of reactions which has been investigated as candidates for RD column.

On the other hand, besides its role as a reactor and distillation, RDC can function as an efficient separator to enhance the recovery rate and further purify the chemicals. Reaction such as etherification and esterification are suitable to be used in the RDC. Theoretically, the recovery of acrylic acid through esterification process by RDC as proposed in this study can be fully understood. Furthermore, due to the in situ separation of products, the component to be removed is allowed to react in the RDC and the resultant product can be separated simultaneously which in turn will decrease the operational cost and also overcome environmental issues.

Table 3.3 Important industrial processes investigated in RDC.

Reactants	Products	Catalyst used	Reference
Acetalization			
Methanol + Aqueous formaldehyde	Methylal + Water	Ion exchange resin, Indion 130	Kolah <i>et al.</i> (1996)
Ethanol + Aqueous formaldehyde	Ethylal + Water	Ion exchange resin, Indion 130	Chopade and Sharma (1997)
Propylene glycol + acetaldehyde	Acetal + Water	Amberlyst-15	Dhale <i>et al.</i> (2004)
Hydration			
Cyclohexane + Water	Cyclohexanol	SiO ₂ /Ga ₂ O ₃	Khaledi and Bishnoi (2006)
Ethylene oxide + Water	Ethylene glycol	Cationic/anionic exchange resins	Liu <i>et al.</i> (2002)
Isoamylene + Water	<i>Tert</i> -amyl alcohol	Amberlyst-15	Gonzalez <i>et al.</i> (1997)
Isobutene + Water	<i>Tert</i> -butanol	Cationic exchange resin	Reusch <i>et al.</i> (2006)
Propylene + Water	Isopropanol	Cationic exchange resin	Sakuth and Peters (1998)
Alkylation			
Benzene + Ethylene	Ethyl benzene	Zeolite- β	Pohl (2006)
Benzene + Propylene	Cumene	Union Carbide-LZY- 82	Pohl (2006)
Isobutane + Propylene/Butylene	Highly branched paraffins	Lewis acid promoted inorganic oxide catalyst	Huss and Kennedy (1990)
Hydrogenation/Dehydrogenation			
α -methyl styrene + Hydrogen	Cumene	Palladium oxide supported on alumina, carbon or silica	Hildreth and Wyckoff (1999)

Table 3.3 Continued.

Reactants	Products	Catalyst used	Reference
Benzene + Hydrogen	Cyclohexane	Alumina supported Ni catalyst	Gildert (2001)
Isophorone + Hydrogen	Trimethylcyclohexanol	-	Schmitt (1996)
Mesityl oxide + Hydrogen	Methyl isobutyl ketone (MIBK)	Bifunctional catalyst: cation exchange resin with palladium/nickel	Vandersall and Weimand (2005)
Isopropanol	Acetone + Hydrogen	-	Chung <i>et al.</i> (1997)
Etherification			
Methanol + Isobutene	Methyl <i>tert</i> butyl ether	Amberlyst-15	Ryu and Gelbein (2002)
Methanol + Isoamylene	<i>Tert</i> -amyl methyl ether	Ion exchange resin	Kolodziej <i>et al.</i> (2004)
Esterification			
30 % w/w Acetic acid + n-Butanol	n-Butyl acetate + Water	Indion 130	Saha <i>et al.</i> (2000)
10 % w/w Trifluoroacetic acid + 2-propanol	2-propyl trifluoroacetate + Water	Ion exchange resin, T-63	Mahajan <i>et al.</i> (2008)
Palmitic acid + Isopropanol	Isopropyl palmitate + Water	Zinc acetate supported silica gel catalyst	Bhatia <i>et al.</i> (2007)

3.6 Reactive distillation with structured packings

Sulzer Chemtech has been one of the leading provider of structured packings to the chemical industry up till today. Through the discovery of structured packings, reactive distillation technology has been made possible. As reactive distillation consists of reactive and non reactive section, KATAPAK-SP and Sulzer-BX is mostly being applied in the reactive and non reactive section respectively. Pöpken *et al.* (2001), Bhatia *et al.* (2007) and Niesbach *et al.* (2012) have used KATAPAK-SP and Sulzer-BX in their simulation studies on esterification process through RDC in their past research respectively. Table 3.4 below shows the different types of structured packings from Sulzer Chemtech.

Table 3.4 Summary of different types of structured packings available (Sulzer Chemtech, n.d).

Types of packing	Material used	Applications	Size and operating conditions	Characteristics
Mellapak 64.X/64.Y Mellapak 125.X/125.Y Mellapak 170.X/170.Y Mellapak 2 X/2 Y Mellapak 250.X/250.Y	Stainless steels Carbon steel Hastelloy, monel, aluminium, copper-bronze, brass, titanium, nickel	Basic chemicals and petrochemicals, ethylbenzene/styrene, fatty acids, refinery operations, absorption/desorption columns	From 80 mm up to 17 m Vacuum to high pressure Liquid load 0.2 to more than 200 m ³ /m ² h	Universal packing type, suitable for wide range of applications Low to very high liquid loads
BX gauze packing BXPlus gauze packing CY gauze packing	Stainless steels Copper-bronze, monel, hastelloy, nickel, titanium	Fine chemicals Isomers Fragrances Flavours Low liquid loads with aqueous solutions	40 mm to 6 m 1 mbar to atmospheric pressure, optimum: 1-100 mbar 100 mm to 4m 1 mbar to moderate pressure 80 °C (max. temp.)	High separation efficiency, even at small liquids loads Low pressure drop, small hold-up BXPlus: same efficiency as BX, lower pressure drop, self wetting, even with aqueous solutions Large number of transfer units per meter, even with small liquid loads
Katapak-SP 11 Katapak-SP 12 Katapak-SP 13	Stainless steels	Acetates, methyl acetate hydrolysis, fatty acid esters Acetals MTBE, ETBE, TAME	From 50 mm Vacuum to moderate pressure	Packing for reactive distillation and trickle-bed reactors High separation efficiency and high reaction capacity Modular concept

3.7 RDC modelling and simulation

Modelling and simulation for a RDC involves the proper selection of the RD model, kinetic model and thermodynamic model for the production of acrylic ester. RADFRAC model is being chosen due to the lack of data on the physical properties such as surface tension, diffusion coefficients and viscosities which are needed for the calculation of mass and heat transfer coefficients and interfacial areas for the synthesis of n-butyl acrylate via esterification process. This is because there is only a few investigation on reactive distillation for the production of n-butyl acrylate up till now, which is summarized in the previous research (Niesbach et al., 2012). Besides that, according to Peng et al. (2002), RATEFRAC (rate-based model) is more complicated compare to RADFRAC (equilibrium-based model) and it is also more difficult to converge. Generally, the results obtained from RADFRAC and RATEFRAC are similar with only a few differences under every simulation conditions. Moreover, through a simulation on methyl acetate system which was researched by Peng et al. (2002), the simulation results predicted by both RADFRAC and RATEFRAC matches with the experimental data by Popken et al. (2001). With this, it shows that RADFRAC is capable in simulating a reliable data for the synthesis of n-Butyl Acrylate as RATEFRAC shows more complexity compare to RADFRAC according to the past research by Baur et al. (2000).

The UNIQUAC thermodynamic model was used to describe liquid-liquid equilibrium with liquid activity coefficients calculated by UNIQUAC model and vapor association of AA was assumed to be ideal. According to Bouneb et al. (2010), UNIQUAC is preferred over NRTL because UNIQUAC is based on group contribution method which will be an advantage when it comes to calculations for distillation column. Finally, the kinetic model used was a simple pseudohomogeneous (PH) model. It was developed based on an activity-based Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach (Hougen and Watson, 1943; Hougen and Watson, 1947; Niesbach et al., 2012 & Niesbach et al., 2013). The (PH) model is similar to the power law of homogeneous reaction whereby the reaction rate is described by the concentration of reactants. Table 3.5 gives the summary of RD, thermodynamic and kinetic models studied by past researches. From their findings, every researches reported that for the different models being studied by each researches, the models agrees with the experimental data which was based on.

Table 3.5 Summary of RD, thermodynamic and kinetic models.

Esterification system	RD model	Thermodynamic model	Kinetic model	Reference
Acetic acid & n-hexanol	Equilibrium model	NRTL	Pseudo homogeneous	Schmitt <i>et al.</i> (2004)
Acetic acid & methanol	Not mention	UNIQUAC	Pseudo homogeneous	Kim and Han (2012)
Acetic acid & n-butanol	Equilibrium model	UNIQUAC	LHHW	Steinigeweg and Gmehling (2002)
	Equilibrium model	UNIQUAC-HOC	LHHW	Tian <i>et al.</i> (2012)
Acrylic acid & n-butanol	Non-equilibrium	UNIQUAC-HOC	LHHW	Niesbach <i>et al.</i> (2012); Niesbach <i>et al.</i> (2013)
Decanoic acid & methanol	Equilibrium model	UNIFAC	LHHW	Steinigeweg and Gmehling (2003)
Palmitic acid & isopropyl	Equilibrium & non-equilibrium model	UNIFAC	LHHW	Bhatia <i>et al.</i> (2007)

3.8 Summary

Based on the review done on the different types of reactions which were investigated in RDC by past researchers, we can summarize that up to date, not a single study on the recovery of acrylic acid through esterification process in RDC has even been carried out before. On the other hand, there was only a few study was done on the esterification process between acrylic acid and n-butanol in RDC (Niesbach *et al.*, 2012; Niesbach *et al.*, 2013). Thus, the study on the recovery of acrylic through esterification process in RDC is carried out in this research.

4. FINDINGS

The proposed prototype of reactive distillation column (RDC) was designed and fabricated based on the simulation work done by Zeng et al. (2006) and the design guidelines developed by Subawalla and Fair (1999). The RDC consisted of 3 main sections, the one meter each rectifying and stripping sections packed with SULZER EX for separation and the two meter reactive section packed with Amberlyst 15 catalyst in SULZER KATAPAK. The column was equipped with a reboiler at the bottom and a cooling water condenser at the top. Phase separation occurs upon condensation because of the heteroazeotropic behaviour of the test systems. Thus, a decanter was installed after the condenser for splitting the distillate to an organic and aqueous phase. The aqueous distillate was removed while the organic distillate was recycled. All the sections of the column are provided with a heating blanket, insulation and thermocouple.

The reactants, butanol (BuOH) and acrylic acid (AA) were fed to the RDC with controlled flowrate using peristaltic pumps. The feeds were introduced at a temperature of <100 °C. In a typical experiment, BuOH was introduced at the top and AA was fed at the bottom to achieve maximum conversion. After starting the reaction, the temperature in each section of the column was logged. The top product, bottom product and samples along the column were continuously withdrawn at certain time interval, weighed and analysed for their composition until the steady state was achieved (all the sections of columns attained the constant temperatures). The flowrates of the feed, bottom and overhead were measured and a complete material balance was performed. Butyl acrylate, water, BuOH and AA present in the sample was analyzed using gas chromatograph. All the experiments were carried out at atmospheric pressure. Both molar ratio of BuOH to AA was varied from 1-8 while the reflux ratio was varied from 3-7. Table 4.1 shows the AA conversion obtained at different operating parameters whereas Figure 4.1 and 4.2 show the AA conversion in the variation of molar ratio to BuOH to AA and reflux ratio. The maximum AA conversion of 99.6 % was achieved at a BuOH to AA molar ratio of 4 and reflux ratio of 5.

Table 4.1 AA conversion obtained at different operating condition.

Experiment No.	Molar ratio BuOH to AA	Feed flow rate, L/h		Reboiler temperature, °C	Reflux ratio, mol/mol	AA conversion, mol/mol
		BuOH	AA solution			
1	1	1.05	2.7	147	5	0.920
2	2	2.1	2.7	147	5	0.958
3	4	4.2	2.7	147	5	0.996
4	6	6.3	2.7	147	5	0.996
5	8	8.4	2.7	147	5	0.996
6	4	4.2	2.7	147	3	0.965
7	4	4.2	2.7	147	4	0.966
8	4	4.2	2.7	147	6	0.953
9	4	4.2	2.7	147	7	0.945

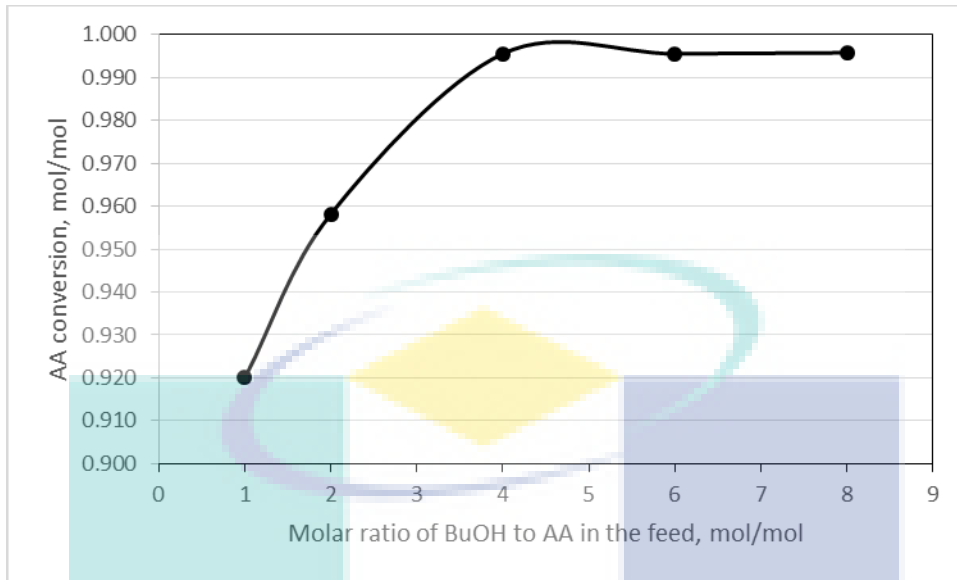


Figure 4.1 Effect of BuOH to AA feed molar ratio on the AA conversion.

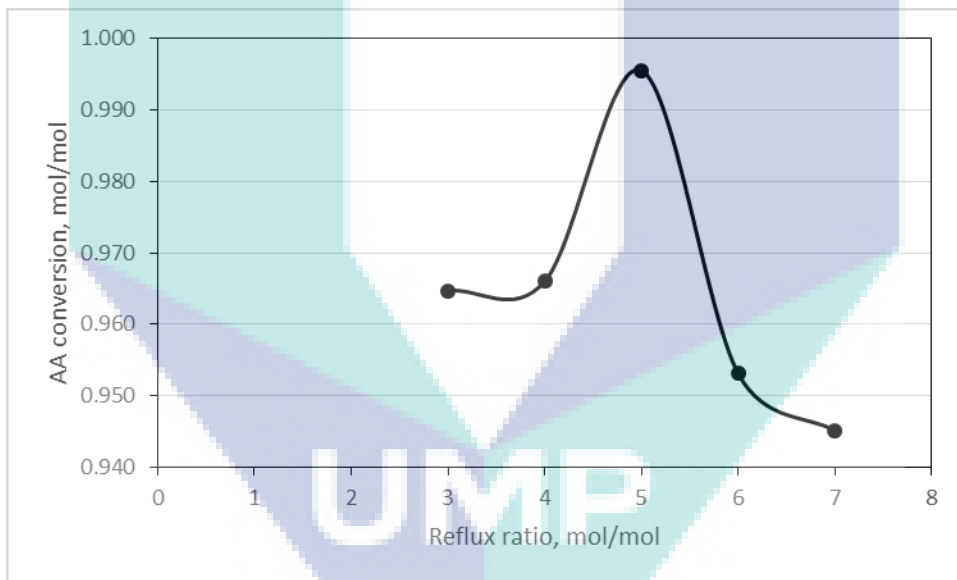


Figure 4.2 Effect of reflux ratio on the AA conversion.

The modeling and simulation were carried out using (a) Equilibrium Stage Model, RADFRAC available in ASPEN PLUS v9 software package. RADFRAC module in the steady state simulator based upon a rigorous equilibrium stage model for solving the mass balance, phase equilibrium, summation and energy balance (MESH) equations. The equilibrium model assumes vapor liquid equilibrium at each stage. The departure from equilibrium is accounted for by tray efficiency or height equivalent to theoretical plate (HETP). The RDC prototype testing data was used to validate the simulation results. It was found that Equilibrium Stage Model could give a reasonably good prediction to the column temperature and product compositions, resulting an error between the experimental data and the simulation results of <10 %. Figure 4.3 shows

the comparison of the predicted composition and temperature with the experimental data generated from the RDC operated at molar ratio BuOH to AA of 4 and reflux ratio of 5.

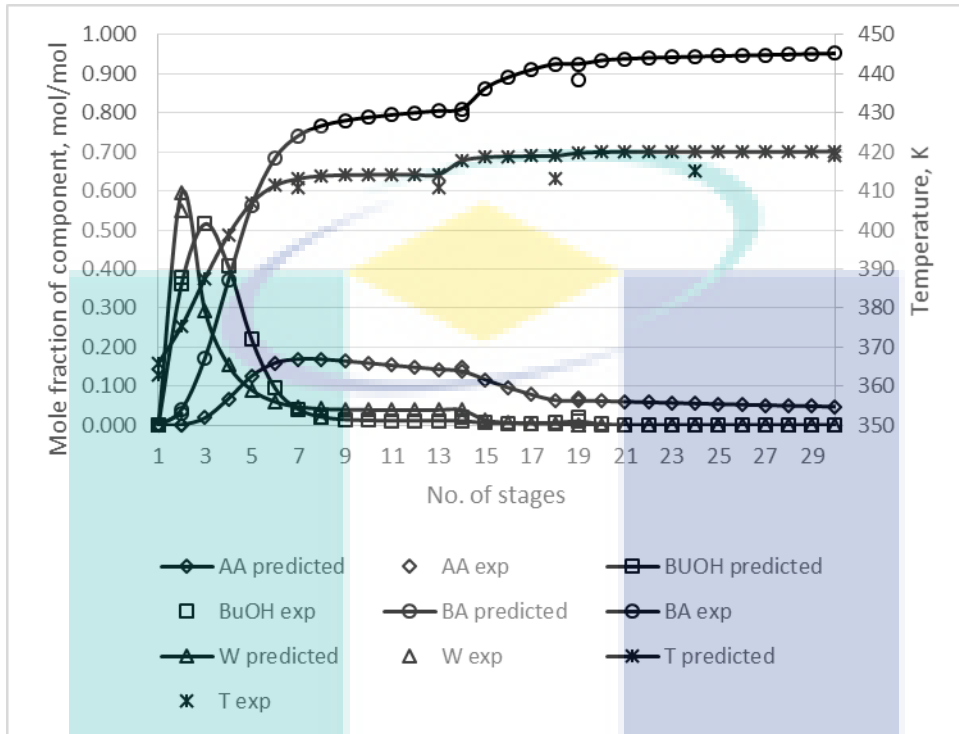


Figure 4.3 Comparison of the predicted composition and temperature with the experimental data generated from the RDC. Reboiler temperature= 420 K, molar ratio of BuOH to AA in feed= 4, reflux ratio= 5.

A technical optimized process which was developed by simulation using Equilibrium Stage Model. It is shown in Figure 4.4 and Figure 4.5 that the technically optimized process required only a rectifying section with six stages and a stripping section of four stages.

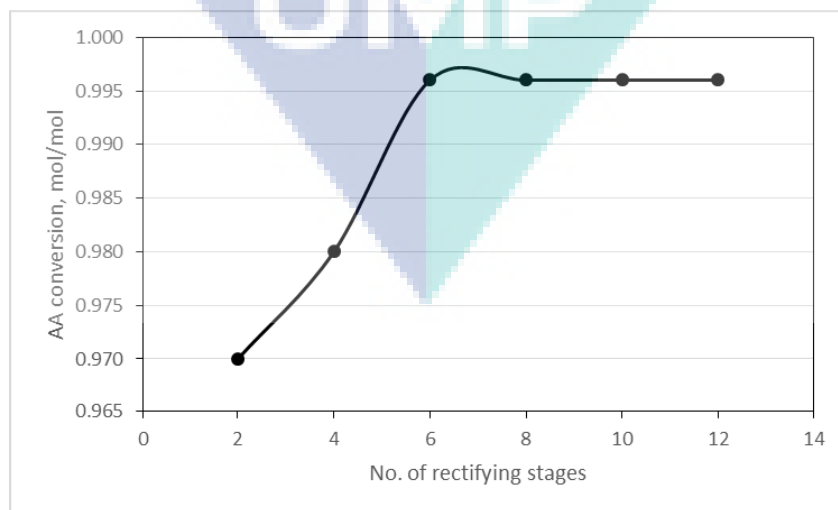


Figure 4.4 Effect of number of rectifying stages on the AA conversion.

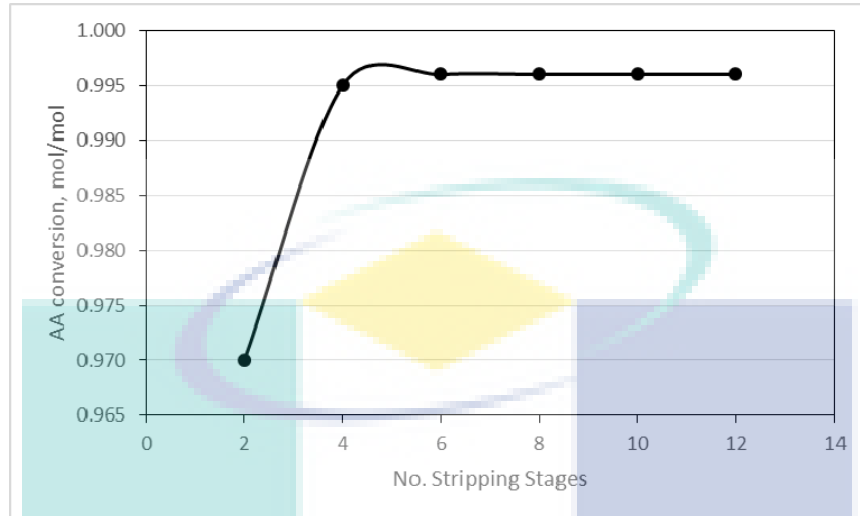


Figure 4.5 Effect of number of stripping stages on the AA conversion.

5. CONCLUSION

The RDC was successfully designed and fabricated. It was tested for the esterification of acrylic acid in the wastewater with butanol at different molar ratio of butanol to AA and reflux ratio. The best AA conversion of 99.6 mol% was achieved when the BuOH to AA molar ratio and reflux ratio were 4 and 5 respectively. The testing data was used to validate the simulation results generated using Equilibrium Stage Model in ASPEN PLUS. The technical optimised process determined through simulation showed that the required number of rectifying and stripping stages were only 6 and 4 respectively to give the adequate separation.

ACHIEVEMENT

- i) Name of book chapter: S.Y. Chin, M. R. Kamaruzaman and M.A.A. Ahmad. (2016). Converting Dilute Acrylic Acid to Ester in a Reactive Distillation Column: A New Method to Treat Waste Water Containing Acrylic Acid in Petrochemical Industries. Chapter 1, Industrial Waste: Management, Assessment and Environmental Issues. Nova Science Publishers, USA. **(Appendix B)**
- ii) Human capital development: 1 Research Assistant (Miss Hong Chi Shien)
- iii) Packing sponsorship by Sulzer Packing Singapore **(Appendix C)**
- iv) Patent application: Patent search report was obtained. In the process to pursue to the next step of the application. **(Appendix D)**

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APPENDIXES

Appendix A Operating Manual of RDC

Appendix B Book Chapter: S.Y. Chin, M. R. Kamaruzaman and M.A.A. Ahmad. (2016). Converting Dilute Acrylic Acid to Ester in a Reactive Distillation Column: A New Method to Treat Waste Water Containing Acrylic Acid in Petrochemical Industries. Chapter 1, Industrial Waste: Management, Assessment and Environmental Issues. Nova Science Publishers, USA.

Appendix C Packing Sponsorship by Sulzer Singapore Pte Ltd

Appendix D Patent Search Report

The logo for UMP (Universiti Malaysia Perlis) is a large, downward-pointing arrow shape. It is composed of four triangular sections meeting at a central point. The top-left and bottom-right sections are light blue, the top-right and bottom-left sections are light purple, and the central white area contains the letters 'UMP' in a bold, white, sans-serif font.

UMP