REACTIVE DISTILLATION SIMULATION FOR PRODUCTION OF METHYL ACETATE: KINETIC MODEL PARAMETER OPTIMIZATION

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by

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LIST OF SYMBOLS

$f_{iL}^{\wedge}$	Liquid phase fugacity
$f_{iv}^{\wedge}$	Vapor phase fugacity
x_i	Liquid mole fraction
y_i	Vapor mole fraction
$\emptyset_{iL}^{\wedge}$	Partial liquid phase fugacity coefficient
$\emptyset_{iv}^{\wedge}$	Partial vapor phase fugacity coefficient
K	Phase equilibrium ratio
$a_{iL}^{\wedge}$	Liquid relative volatility
γ_i	Liquid phase activity coefficient
P_i^{sat}	Saturated partial pressure
P	Pressure
P_i	Partial pressure
Z	Compressibility factor
τ_{ji}	Tortuosity
G_{ji}	Gibbs free energy
γ_i^c	Critical activity coefficient
γ_i^r	Reference activity coefficient
ψ_i	Segment fraction
Θ_i	Area fraction
Γ_k	Concentration-polarization factor

LIST OF ABBREVIATIONS

Keq	Equilibrium Constant
NRTL	Non-Random Two Liquid
PI	Process Intensification
RD	Reactive Distillation
UNIFAC	UNIQUAC Functional-group Activity Coefficients
UNIQUAC	University Quasichemical Activity Coefficient
VLE	Vapor-Liquid Equilibrium
OHAC	Acetic Acid
MEOH	Methanol
MEOAC	Methyl Acetate
H_2O	Water

SIMULASI PENYULARAN REAKTIF UNTUK PENGHASILAN METHIL ASETAT: PENGOPTIMUMAN PARAMETER MODEL KINETIK

ABSTRAK

Disebabkan oleh banyak faedah penyulingan reaktif (PR) dalam sintesis kimia berbanding kaedah konvensional (reaktor diikuti dengan lajur penyulingan), PR telah menarik perhatian penyelidik di seluruh dunia untuk meneroka potensinya dalam industri kimia. Pelaksanaan PR sebagai teknologi intensifikasi proses (PI) dapat mengatasi kelemahan pada lajur penyulingan konvensional.

Pemodelan, simulasi dan pengoptimuman PR pada proses pengesteran asid asetik dan metanol yang digunakan untuk menghasilkan metil asetat telah dijalankan dengan menggunakan Aspen Plus V10. Lajur padat RadFrac telah dibangunkan dan disimulasikan yang mempunyai tindak balas dan pemisahan dalam satu lajur dengan 23 peringkat termasuk dandang semula dan pemeluwap. Selain itu, kaedah sifat Bukan Rawak Dua Cecair (BRDC), kadar alir suapan asid asetik dan metanol 0.03L/min, suhu suapan 25°C dan tekanan 1 atm masing-masing telah digunakan.

Alat sensitiviti dan pengoptimuman dalam Alat Analisis Model digunakan secara serentak dalam pengoptimuman parameter kinetik dan parameter operasi masing-masing. Pengoptimuman parameter kinetik seperti K-stoichiometry A dan K-stoichiometry B telah dikaji untuk mendapatkan penumpuan yang baik dengan data Giwa (2013). Untuk memaksimumkan ketulenan metil asetat, parameter operasi seperti kadar aliran suapan, nisbah refluks, dan tugas haba reboiler dikaji dan dioptimumkan.

Keputusan yang dioptimumkan menunjukkan keadaan optimum untuk memaksimumkan ketulenan metil asetat adalah pada kadar alir metanol

0.0472266kmol/jam, nisbah refluks 9, dan duti haba dandang semula 528.5Watt. Perbandingan antara Giwa (2013) dan kajian semasa mengenai lajur penyulingan reaktif telah dijalankan dengan membandingkan penukaran, ketulenan, dan duti haba dandang semula. Ketulenan metil asetat meningkat sebanyak 52.25% daripada 0.653108 kepada 0.984221 serta duti haba dandang semula diminimumkan sebanyak kira-kira 24.5% daripada 700Watt kepada 528.5Watt tetapi penukaran dikurangkan sebanyak 30% daripada 96.48% kepada 66.28%.

Dalam pembolehubah operasi yang disebutkan di atas, kadar alir suapan, nisbah refluks, dan duti haba dandang semula mempunyai kesan yang paling ketara ke atas ketulenan metil asetat dalam sulingan dan penukaran asid asetik. Selain itu, fungsi objektif pengoptimuman ini telah dicapai kerana anggaran nilai optimum kadar alir suapan, nisbah refluks, dan duti haba dandang semula telah digunakan untuk rum model yang dibangunkan. Oleh itu, objektif ini membuktikan bahawa nilai optimum Aspen Plus telah disahkan.

REACTIVE DISTILLATION SIMULATION FOR PRODUCTION OF METHYL ACETATE: KINETIC MODEL PARAMETER OPTIMIZATION

ABSTRACT

Due to the numerous benefits of the reactive distillation column (RD) in chemical synthesis over standard method (reactors followed by distillation columns), RD has drawn the attention of researchers all over the world to explore its potential in the chemical industries. Implementing RD as process intensification (PI) technology can overcome the disadvantages of the conventional distillation column.

The modeling, simulation, and optimization of the RD on the esterification process of acetic acid and methanol are used for producing methyl acetate have been carried out by using Aspen Plus V10. RadFrac packed column was developed and simulated which had the reaction and separation in one column with 23 stages included reboiler and condenser. Moreover, the Non-Random Two Liquid (NRTL) property method, feed flowrate of acetic acid and methanol of 0.03L/min, feed temperature of 25°C, and pressure of 1 atm respectively was used.

Sensitivity and optimization tools in Model Analysis Tools were used simultaneously in the optimization of kinetic parameters and operating parameters respectively. Optimization of kinetic parameters such as K-stoichiometry A and K-stoichiometry B were studied to get good convergence with the data of Giwa (2013). To maximize the purity of methyl acetate, operating parameters such as feed flowrate, reflux ratio, and reboiler heat duty are studied and optimized.

Optimized results showed the optimum condition to maximize the purity of methyl acetate is at methanol flowrate of 0.0472266kmol/hr, reflux ratio of 9, and reboiler heat duty of 528.5Watt. A comparison between Giwa (2013) and the present

study on RD column was carried out by comparing conversion, purity, and reboiler heat duty. The purity of methyl acetate increased by 50.7% from 0.653108 to 0.984221 as well as the reboiler heat duty is minimized by about 57.14% from 700Watt to 528.5Watt but the conversion is reduced by 30% from 96.48% to 66.28%.

In above mentioned operating variables, the feed flowrate, the reflux ratio, and reboiler heat duty have the most significant effect on the purity of methyl acetate in the distillate and the acetic acid conversion. Moreover, the objective function of this optimization was achieved as the estimated optimum value of feed flowrate, reflux ratio, and reboiler heat duty were used to rum the developed model. Thus, this objective proved that the Aspen Plus optimum values were validated.

CHAPTER 1

INTRODUCTION

1.1 Reactive Distillation

Distillation is the most commonly used method for the separation of homogeneous fluids mixture (Duroudier, 2016). Separation of distillation is depending on the difference in boiling points or volatility of the mixture's components. Most homogenous fluid mixtures may be separated almost completely by repeated vaporization and condensation (Duroudier, 2016). The benefit applying distillation over other alternative methods for separation of fluid mixture: 1) The ability to handle wide range of flowrate including extremely high or low flow rate, 2) The capability to separate feeds with a wide range of feed concentration, 3) The potential to produce high product purity (Duroudier, 2016). These benefits show that why distillation is the most widely used as separation technology as well as it is a versatile, robust and well-understood technique. Even though distillation is the oldest and most widely used as separation technology on an industrial scale, there are still significant improvements to be made.

Reactive distillation (RD) is especially attractive where chemical and phase equilibrium conditions coexist in systems. Within the same zone of a distillation column, the reactants are transformed while the products are being separated and recycle again at the same time (Kiss, 2013). It brought many advantages to chemical production especially for its high conversion and selectivity. Compared to traditional distillation, the effects of pressure and temperature on phase equilibrium and chemical kinetics are significantly more prominent in RD (Kiss, 2013). Low temperature with high volatilities might result in slow reactions that require large amount of catalyst to complete the conversion while high temperature may favor unwanted side reactions that makes it difficult to dire the reaction to completion (Kiss, 2013). RD is typically applied to equilibrium reactions, such as esterification, etherification, hydrolysis, and alkylation.

Process intensification (PI) is an engineering tool for improving process efficiency via the use of appropriate equipment and the development or redesign of innovative methods (Segovia-Hernández et al, 2015). Aims of PI are to reduce mass and heat transfer resistance and overcome thermodynamic limitations through the integrated design and operation (Segovia-Hernández et al, 2015). Other than that, this process substantially decreasing equipment volume, energy consumption, or waste formation, and ultimately leading to cheaper, safer, sustainable technologies (Stankiewicz, 2003). Based on Stankiewicz (2003), multifunctional reactors which combining at least more function in one unit operation that conventionally would perform in a separate piece can be example of process intensification technology as shown in Figure 1.1.

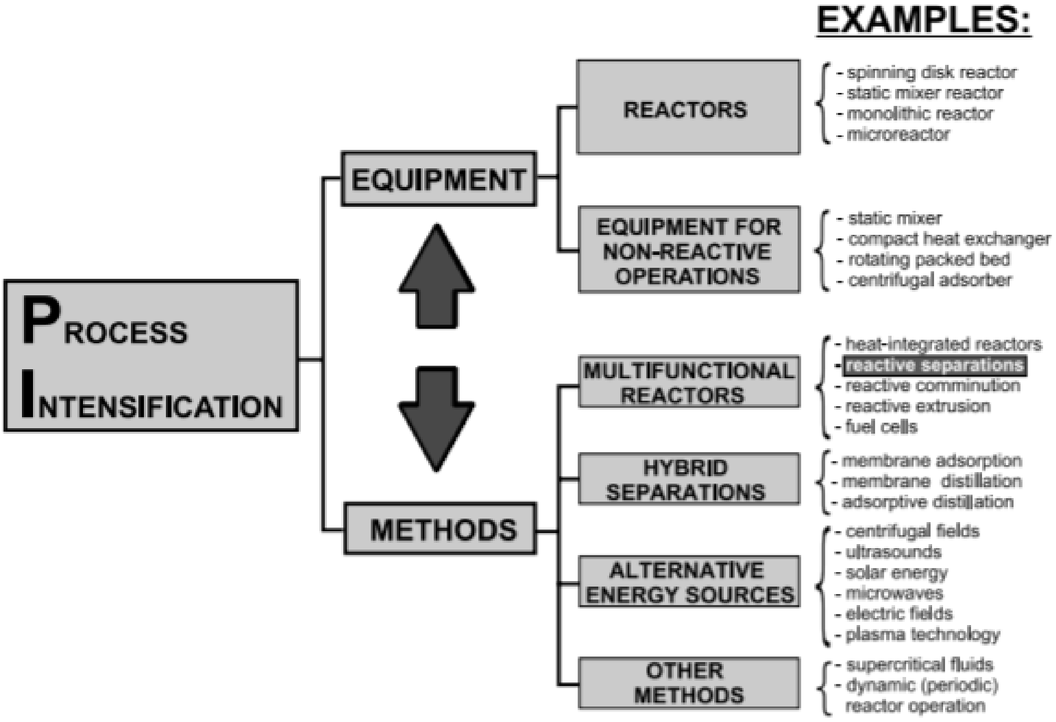


Figure 1.1 Process intensification and its components

1.1.1 Reactive Distillation Configuration

Reactive distillation (RD) has gained more attention due to its potential for process intensification. RD technology is the system that the reaction and distillation take place in the same zone where the reactants being converted with simultaneous separation of the products as shown in Figure 1.2 (Kiss, 2013). It have bought many advantage to chemical production especially for high conversion and selectivity (Mallaiah, Kishore and Reddy, 2017). RD is commonly used for reversible chemical processes in the liquid phase where the conversion of reactant is limited by reaction equilibrium. Production of methyl acetate is one of chemicals that can fully benefited from RD technology.

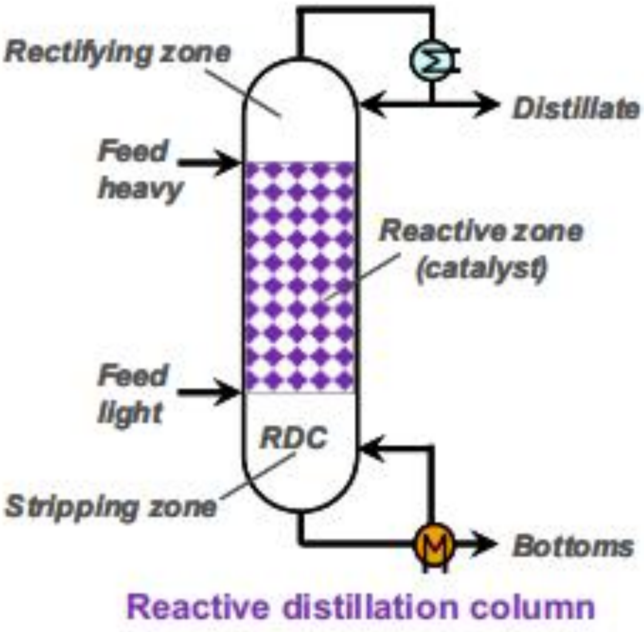


Figure 1.2 Reactive distillation equipment

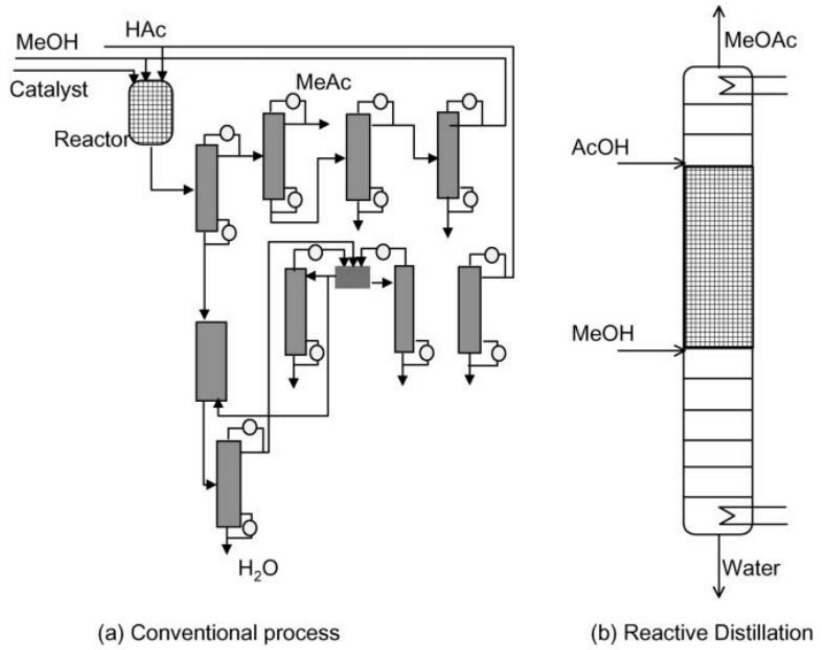
This development of RD was reduced the expenditure and energy requirement by approximately 20% when compared to the traditional of a reactor followed by a series of reactor (Segovia-Hernández et al, 2015). RD technology providing valuable synergistic effect that overcomes the equilibrium limitations of many reactions such as (trans-)esterification, etherification, hydrolysis, (de-)alkylation, (de-)hydration, (de)hydrogenation, amination, aldolization, condensation, isomerization, oligomerization, dimerization, amidation, and chlorination (Kiss, Jobson and Gao, 2019).

The first patents of RD which were for application of catalyzed esterification, are of 1920s. This catalyzed process was patented for the production of methyl-tert-butyl ether (MTBE), tertiary butyl alcohol (TBE) and cumene (Bascomb, 1993). This article focusing on MTBE production which involved the reaction between methanol and isobutene as well as involved cation exchange resin packing which contain acid cation exchange resin catalyst. MTBE separate as bottom product due to high boiling point compared to the unreacted reactants (Bascomb, 1993).

The introduction of in-situ reaction with distillation in a single vessel leads to a complex interactions between vapor-liquid mixture equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion and chemical kinetics (Taylor and Krishna, 2000). This makes the design of these systems to be difficult.

1.1.2 Comparison of Process in Conventional and Reactive Distillation

Conventional methyl acetate production process consisting of one reactor and nine distillation columns. Figure 1.3 (a) shows the conventional method in production of methyl acetate. To achieved high product purity, a huge number of distillation columns is needed due to formation of methyl acetate-methanol and methyl acetate-water azeotrope (Patil, 2007). In the RD implementation shown in Figure 1.3 (b) only involved one column and nearly 100% conversion of reactant is achieved in low operating cost and low energy consumption (Boodhoo and Harvey, 2013).



(a) Conventional process (b) Reactive Distillation

Figure 1.3 Processing schemes for the esterification of methanol and acetic acid

1.1.3 Advantages of Reactive Distillation

The RD technology can reduce the complexity of the conventional processes. By this way, the is typically much easier and cheaper to operate and maintain in industrial scale. Moreover, reducing equipment units used in the chemical production leads to a considerable reduction of capital cost (Kiss, 2013).

In addition, RD can minimize the formation of azeotrope of mixture especially on methyl acetate-methanol and methyl acetate-water azeotrope. Traditionally, huge number of distillation columns are needed to separate the azeotrope mixture (Patil, 2007). This technology will decrease the number of distillation column as well as the capital cost and lead to significant capital savings.

The RD is especially beneficial for exothermic reactions. One of the exothermic reactions is the formation of methyl acetate. The heat integration technique allows you to completely use the heat energy created by the chemical process. The heat released will be used in vaporization and reduce the duty of the reboiler as well as reduces the risk of runaway.

Moreover, the maximum conversion of reactants to products can be achieved nearly 100% with implemented RD technology. This increase in the conversion results in reducing forward rate by shifting of equilibrium to the right side (product). The selectivity of product also being improved because of removal of products from the reaction zone and avoided them to undergo side reaction.

The RD also can reduce the degradation of chemicals due to the lower residence time as compared to conventional reactor. The chemicals are exposed with the high temperature in shorter time compared to the conventional reactor. Also, RD be applying to do separation of close boiling point components which lead to increase the purity of the desired product.

1.1.4 Disadvantages of Reactive Distillation

Although RD is a new technology and brings many advantages to the production of chemical product, not all the chemicals manufacturing is suitable by using RD unit. The main drawback of RD is the process exhibits nonlinear characteristics such as multiple steady state and very sensitive to operating variables such as reflux ratio and reboiler heat duty due to the coupling between separation and chemical reaction (Wang and Wong, 2006).

Moreover, a suitable sequence of volatilities is necessary to ensure maximum reactant concentrations and low product concentrations in the reactive zone. RD can be applied only if the difference in boiling point between the reactants and the products is more than temperature of 20K (Kiss, 2013). Also, RD technology can reduce flexibility due to higher degree of integration as compared to classic units.

In addition, reactive azeotrope can be created when the reaction is fully compensates for the concentration difference generated by distillation. Reactive azeotropes can occasionally form distillation borders that make separation difficult.

Furthermore, operating window constraints can occur due to both reaction and separation processes take place at the same conditions. As a result, appropriate conversion must be attained under distillation-friendly operating condition (Kiss, 2013).

1.2 Synthesis of Methyl Acetate

Methyl acetate is a carboxylate ester with the formula of CH_3COOCH_3. This ester having molecular weight of 74.08g/mol, boiling point of 57.1^{O}C and melting point of -98.7 ^{O}C (Green and Southard, 2019). It is a flammable liquid with a pleasant odour reminiscent of some glues and nail polish removers. Methyl acetate is used as solvent in chemical industries because it is weakly polar and lipophilic which having solubility of 25% in water at room temperature. Its solubility in water increases dramatically at high temperature. In present of strong aqueous bases or acid, methyl acetate is unstable (Giwa, 2013).

Methyl acetate can be produced via the carbonylation of methanol as a by-product of the production of acetic acid. Other than that, esterification of acetic acid with methanol in present of heterogeneous or homogeneous catalyst is intensified process in producing methyl acetate (Giwa, 2013). This paper is focusing on esterification reaction to produce methyl acetate. This synthesis of methyl acetate from esterification of methanol and acetic acid using heterogeneous Amberlyst®15 catalyst has been studied experimentally by Lux et al. (2015). Methyl acetate synthesis through RD has been studied experimentally and simulationly by Mallaiah, Kishore and Reddy (2017). Esterification reaction is expressed by equation below:

$$CH_3COOH + CH_3OH \leftrightarrow CH_3COOCH_3 + H_2O$$

The esterification of methanol and acetic acid to form methyl acetate is a reversible equilibrium-controlled reaction and it is exothermic reaction. There are many types of rate kinetics model equation for heterogeneous catalyst reaction such as adsorption base kinetics model and pseudo homogeneous kinetic model (Lux et al., 2015). This reaction occurs only in liquid phase in RD. These reactions will produce two azeotrope mixture which are methyl acetate-methanol and methyl acetate-water azeotrope. Traditionally, huge number of distillation columns are needed to separate the azeotrope mixture (Patil, 2007).

Based on Figure 1.4, the RD units can be divided into three zones which are rectifying zone, reactive zone and stripping zone. Two feed set-ups used for RD where acetic acid is feed on the top of reactive section while methanol is feed at bottom of reactive section. Simulation of catalytic distillation model can be performed by using Aspen Simulation platform.

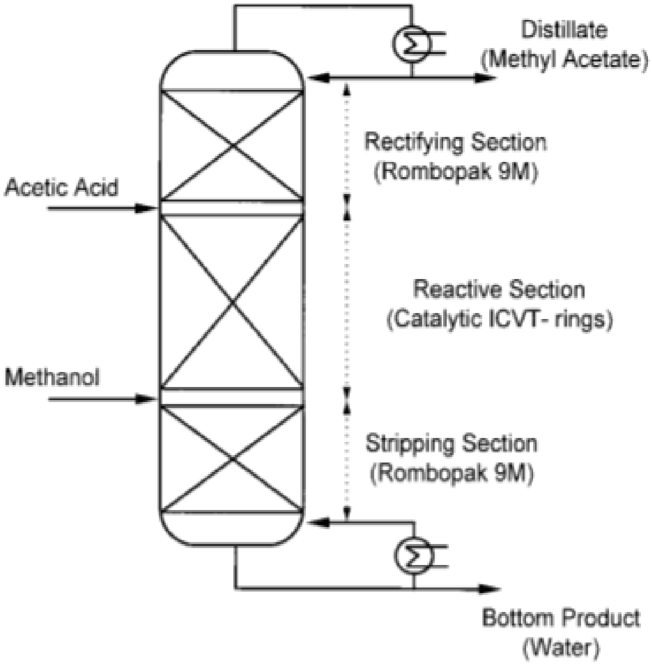


Figure 1.4 Reactive distillation unit

1.3 Problem Statement

Formation of azeotropes mixture between methyl acetate-methanol and methyl acetate-water is the most challenging faced in the methyl acetate production. Conventionally, this problem can be solved by applying one reactor followed by nine distillation column which can increase the operating cost as well as cost of equipment. Moreover, this challenge also promoted to less purity of the product. Thus, implementation of RD technology in the methyl acetate production indirectly can avoid the formation of azeotropes as well as utilized the pure product.

Nowadays, RD technology become more selective used compared to conventional distillation in the industrial activities especially in manufacturing of methyl acetate. Many researchers are studied for RD technology for MTBE and methyl acetate production. Numerous studies are carried out in the field of RD modeling as reviewed by Taylor and Krishna (2000). Chosen of the catalyst packing such as Amberlyst 15 in the RD technology also have beens studied. KATAPAK-S and KATAPAK-SP can be apply to RD technology which use to immobalize the catalyst packing to vary the catalyst fraction and the separation efficiency as discussed in Götze et al. (2001). Further research activities also focus on modeling and optimizing the RD technology to develop most efficient technology in the methyl acetate. RD designing previously involves complex calculation and rate of kinetic reaction. In this work, optimization of RD system has studied to optimize the kinetic parameter on methyl acetate production.

There are many factor that contribute to the RD technology on methyl acetate production. Reflux ratio and reboiler duty of RD model are the factor can maximize the mole fraction of distillate product at top product column. In methyl acetate production, acetic acid feed and methanol feed temperature also can be a factor that influence the production. Varying the temperature above the boiling point of feed will convert into gas phase that can reduce the reaction rate and led to reduce in reactant conversion (Mallaiah, Kishore and Reddy, 2017).

Therefore, Aspen Plus which is an effective and reliable simulation tool is used to study the effect of kinetic and operating parameters in kinetic model on esterification reaction based on the yield of methyl acetate production. Moreover, the optimization process can be done through sensitivity analysis to determine its optimum operating condition. The scope of this work also includes the comparison of reference study and present study on intensified methyl acetate plant (RD) in Aspen Plus.

1.4 Objective

The objective of this research:

i. To investigate the effect of parameter in kinetic model on production of methyl acetate
ii. To determine the optimum operating condition for the system through sensitivity analysis
iii. To compare the performance of reference study and present study based on conversion, purity and reboiler heat duty (energy analysis)

1.5 Scope of Project

Application of RD has been widely studied due to its ability to perform both reaction and separation simultaneously for chemical production process including methyl acetate production. Thus, understanding the parameter that affect the mole fraction of desired product and performance of the RD technology is crucial. The scope of this project is to investigate the effect of kinetic parameter such as K-stoichiometry A and K-stoichiometry B on the mole fraction of desired product. Moreover, this project also performs to determine the optimum operating parameter such as methanol feed flowrate, reflux ratio and reboiler duty through sensitivity analysis in Aspen Plus. The results from the best optimum parameter are compare between the reference study based on conversion, purity, and energy analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Development of Reactive Distillation on Methyl Acetate Production

RD technology is proven to be an efficient process for the esterification reactions including methyl acetate production. Implementation of RD technology in this production can overcome the limitations in the conventional method. RD is an integrated operation that combines reaction and separation into single unit, which allowing for simultaneous product production and removal, improving productivity and selectivity, reducing energy use, eliminating the need for solvents and high efficiency system with green engineering features (Boodhoo and Harvey, 2013). Many researchers have studied on implementation of RD technology on methyl acetate production

Mallaiah, Kishore and Reddy (2017) have studied on catalytic distillation for esterification process of acetic acid with methanol for both experimental and simulation. The experimental setup of RD column is shown in Figure 2.1. The total height ofcolumn is 3 meter and inner diameter is 50mm. The middle of reaction zone is packed with stuctured of Karapak-S Indion 180 ion exchange resin solid catalyst. The pseudo-homogeneous (UNIQUAC) kinetic model has been developed for esterification process and the simulation have been done using Aspen Plus version 7.3. This paper studied the effect of various operating conditions such as reboiler temperature, reflux ratio and different feed flow rate of feeds on methyl acetate production. From this paper, the simulation results recorded are closely match with enviromental result. It found that, 99.8% of methyl acetate formed from simulation while experiment data recorded around 95%. Both experiment and simulation give the same value of reflux ratio of 2 that achieved maximum conversion of acetic acid. The comparison on graphical information of temperature profile, reflux ratio and liquid composition was given.

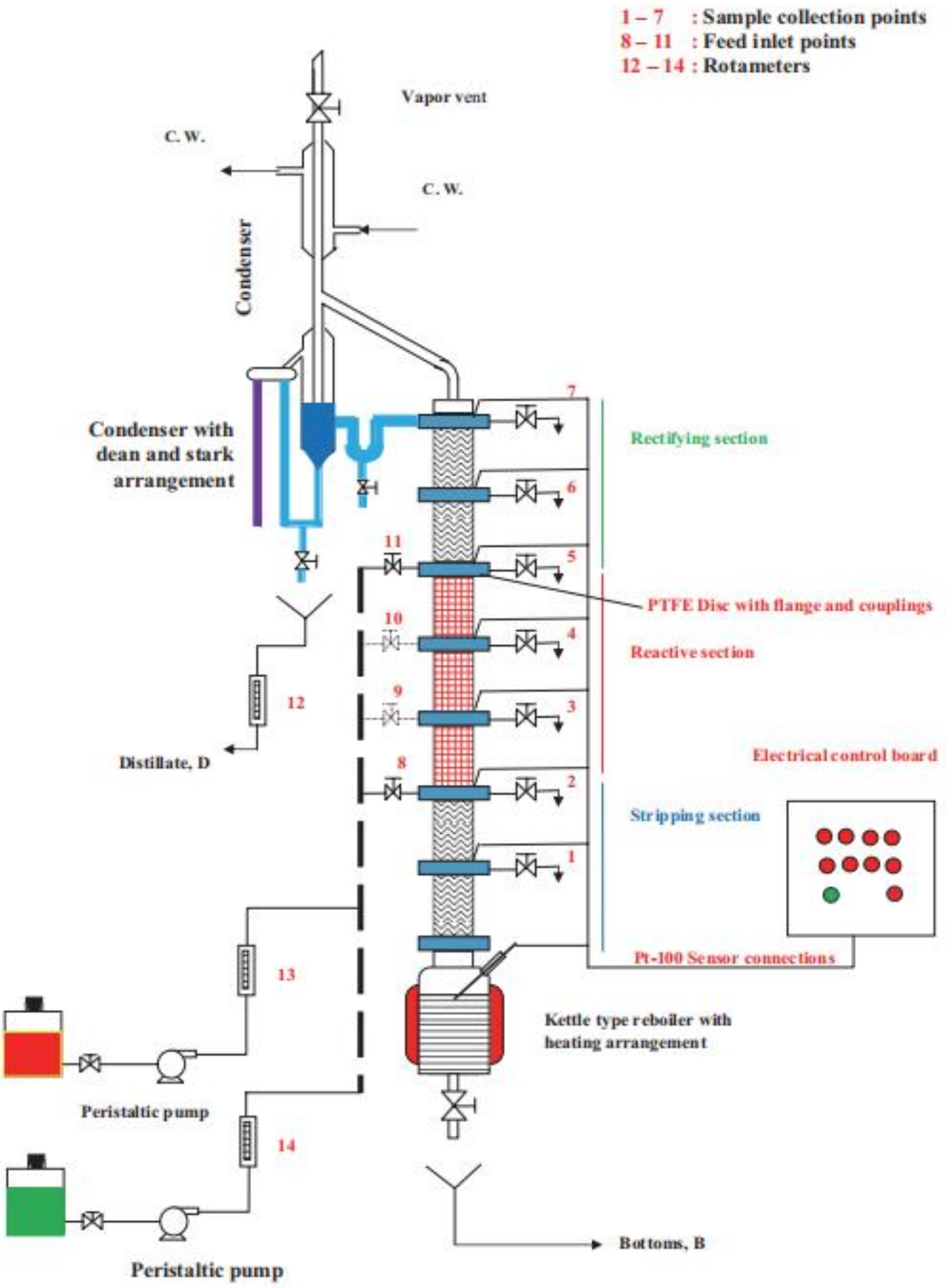


Figure 2.1 Experimental setup of RD column

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Huss et al (2003) have desribed a hierarchy of methods, models and calculatuion techniques that support the design of RD column for the production of methyl acetate. The results shows the effects of reflux ratio and kinetic parameters on the conversion in the RD. Assuming reaction equilibrium will ease to design a column operating and promoted high purity of methyl acetate. Sensitivity studies on verified kinetic model with using Wilson model givr the region of multiple steady states at optimum reflux ratio. Damkohler number also give the effect on conversion when operated far from optimum reflux ratio (Huss et al., 2003). The calculations and findings is match closely and obey the investigated on the Bessling et al. (1998). The equilibrium design profile, reflux ratio profile, conversion acetic acid profile, multiple steady state profile, and comparision pf column profiles are given. Figure 2.2 shows the final design and simulation summary that developed by Huss et al (2003).

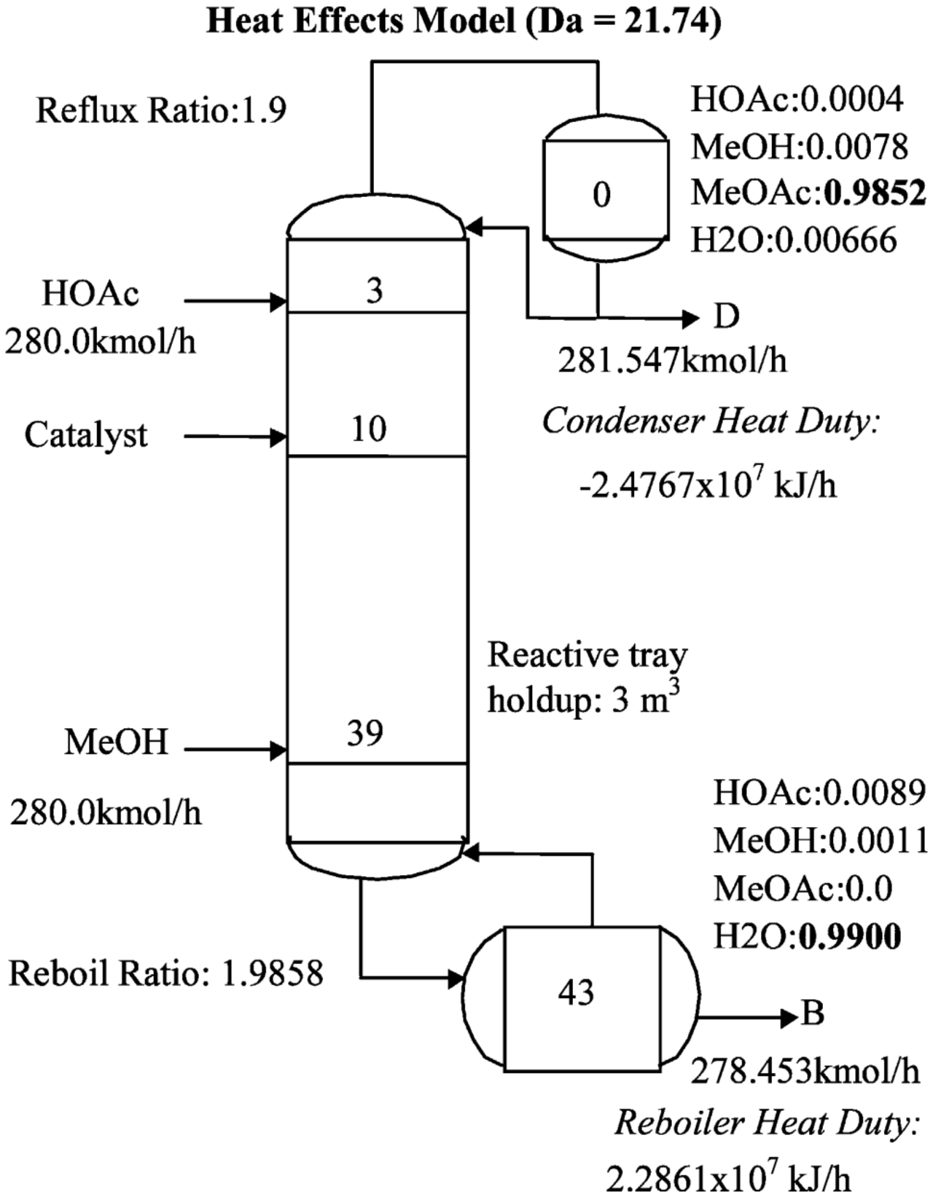

Figure 2.2 Final design/simulation summary for RD of methyl acetate production

2.2 Vapor Liquid Equilibrium for Multicomponent Distillation

Vapor Liquid Equilibrium (VLE) calculations are usually carried out for separation processes. The prediction of VLE for multicomponent is more complicated than the prediction of pure component. The phase equilibrium relation is one of the essential features required for the calculation of separation processes, and useful equations for describing these relationships have been provided (Henley, Seader and Roper, 2011).

Efficient design of RD equipment requires quantitative understanding of VLE in multicomponent mixtures as expressed through vapor-phase fugacity coefficients and liquid-phase activity coefficients (Henley and Seader, 1991).

2.2.1 Fundamental Equations for the Vapor Liquid Equilibrium Relation

To describe the phase equilibrium of system of N components at temperature (T), pressure (P) and at equilibrium, the vapor phase fugacity is equal to the liquid fugacity for every component (Henley, Seader and Roper, 2011).

$$f^{\wedge}_{iv} = f^{\wedge}_{iL} \tag{2.2.1}$$

For $i = 1,2,3, \dots . N$

Equation of states in both phase

$$\emptyset^{\wedge}_{iL} = \frac{f^{\wedge}_{iL}}{x_i P} \tag{2.2.2}$$

$$\emptyset^{\wedge}_{iv} = \frac{f^{\wedge}_{iv}}{y_i P} \tag{2.2.3}$$

Substitute equation of states (2.1.2) and (2.1.3) into equation (2.1.1)

$$f^{\wedge}_{iv} = f^{\wedge}_{iL} \tag{2.2.4}$$

$$\emptyset_{iv}^{\wedge} y_i = \emptyset_{iL}^{\wedge} f_{iL}^{\wedge}$$

$$K = \frac{\emptyset_{iL}^{\wedge}}{\emptyset_{iv}^{\wedge}} \tag{2.2.5}$$

Equation of states in vapor phase and activity coefficient in liquid phase,

$$f_{iv}^{\wedge} = f_{iL}^{\wedge} \tag{2.2.6}$$

The vapor phase fugacity can be written in terms of vapor phase fugacity coefficient $\emptyset_i^{\wedge}$, vapor mole fraction y_i and total pressure P as following.

$$f_{iV}^{\wedge} = \emptyset_{iv}^{\wedge} y_i P \tag{2.2.7}$$

$$a_{iL}^{\wedge} = \frac{f_{iL}^{\wedge}}{f_{iv}^{o}} \tag{2.2.8}$$

Also, the liquid phase fugacity can be written in terms of liquid phase activity coefficient γ_i, and liquid mole fraction x_i as following:

$$f_{iL}^{\wedge} = \gamma_i x_i f_{iL}^{o} \tag{2.2.9}$$

$$ln \frac{f_{iL}^{o}}{f_{isat}^{o}} = \frac{V}{RT}(P - P_i^{sat})$$

$$f_{iL}^{o} = f_{isat}^{o} exp^{\frac{V}{RT}(P - P_i^{sat})}$$

$$\emptyset_i^{osat} = \frac{f_i^{osat}}{P_i^{sat}} \tag{2.2.10}$$

$$f_{iL}^{o} = \emptyset_i^{osat} P_i^{sat} exp^{\frac{V}{RT}(P - P_i^{sat})}$$

$$\emptyset_{iv}^{\wedge} y_i P = \gamma_i x_i \emptyset_i^{osat} P_i^{sat} exp^{\frac{V}{RT}(P - P_i^{sat})} \tag{2.2.11}$$

2.2.2 Ideal Vapor Liquid Equilibrium

VLE is one of the most important fundamental properties in simulation, optimization, and design of any distillation process. The mixture is called ideal if both liquid and vapor are ideal mixtures of ideal components, thus the partial pressure of component P_i is proportional to its mole fraction in vapor phase according to Dalton's law (Henley and Seader, 1991):

$$P_i = y_i P \tag{2.2.12}$$

$$P_i = x_i P_i^{sat} \tag{2.2.13}$$

For and ideal mixture, the equilibrium relationship for any component is defined as:

$$K = \frac{y_i}{x_i} \tag{2.2.14}$$

Combination of equation (2.1.12) and (2.1.13) gives the Raoult's law expression of K-value:

$$K = \frac{P_i^{sat}}{P} \tag{2.2.15}$$

The ideal gas mixture is an imaginary gas mixture, and every component of the ideal gas mixture obeys the ideal gas law equation (2.1.16) in pure state. However, the real gases do not obey the ideal gas law expect at very low pressures (Henley, Seader and Roper, 2011).

$$Z = \frac{PV}{RT} = 1 \tag{2.2.16}$$

2.2.3 Non-Ideal Vapor Liquid Equilibrium

For non-ideal mixture or azeotropic mixture additional variable γ_i (activity coefficient) appears in vapor-liquid equilibrium equation.

$$y_i = \frac{\gamma_i P_i^{sat}}{P} x_i \qquad (2.2.17)$$

When, γ_i represents degree of deviation from reality.

When $\gamma_i = 1$, the mixture is said to be ideal while for non-ideal, $\gamma_i \neq 1$. This exhibits either positive deviation from Raoult's law, $\gamma_i > 1$ or negative deviation from Raoult's law, $\gamma_i < 1$.

2.3 Calculation on Activity Coefficient

Predictions of liquid properties based on Gibbs free-energy models for predicting liquid-phase activity coefficient is developed and important for design calculation for non-ideal distillation. This activity coefficient is needed to further be used for calculation of VLE for non-ideal mixture. Most models available in literature for the activity coefficient are the correlating type (Van Laar, Margules, Redlich-Kiser, Non-Random Two Liquid (NRTL), Wilson, UNIQUAC and UNIFAC model), indicate that experimental data are needed to calculate certain empirical parameters for all these model (Faúndez and Valderrama, 2009). In this work, the main equations for three models (NRTL, UNIFAC and UNIQUAC) are being studied.

2.3.1 Non-Random Two Liquid (NRTL) Model

The NRTL equation developed by Renon and Prausnitz in 1968 which represents an extension of Wilson's concept to multicomponent liquid-liquid, vapor-liquid and vapor-liquid-liquid systems (H. and J.M., 1968). This model uses three binary interaction parameters for each binary pain in multicomponent mixture-pairs. For N-components system, it is required $\frac{N(N-1)}{2}$ molecular binary pair.

The following equations represent NRTL model (Henley, Seader and Roper, 2011):

$$ln\,\gamma_i = \frac{\sum_{j=1}^{C}\tau_{ji}G_{ji}x_j}{\sum_{j=1}^{C}G_{ji}x_j} + \sum_{j=1}^{C}\left[\frac{x_jG_{ij}}{\sum_{k=1}^{C}G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{k=1}^{C}\tau_{ki}G_{kj}x_k}{\sum_{k=1}^{C}G_{kj}x_k}\right)\right] \tag{2.3.1}$$

$$G_{ij} = exp\,(-a_{ji}\tau_{ji}) \tag{2.3.2}$$

The coefficients of τ are given by

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{2.3.3}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{2.3.4}$$

where the double-subscripted g values are energies of interaction for molecule pairs. for and ideal solutions, $\tau_{ji} = 0$. The activity coefficient parameter, a_{ji} characterizes the tendency of species j and i to be distributed nonrandomly (Henley, Seader and Roper, 2011). Below shows the common value of a_{ji}:

Table 2.1 Common value of activity coefficient, a_{ji}

a_{ji}	Function
0	Local mole fractions equal to overall solution mole fractions
0.2	Hydrocarbon and polar species
0.3	Nonpolar compounds
0.4	Saturated hydrocarbon and homolog perfluorocarbons
0.47	Alcohols

2.3.2 Universal Quasichemical (UNIQUAC) Model

Abrams and Prausnitz (1975) used statistical mechanics to derive an expression for excess free energy to develop the University Quasichemical Activity Coefficient model (UNIQUAC) (Abrams and Prausnitz, 1975). This model distinguishes two contributions termed configurationally (C) and (R).

$$ln\,\gamma_i = ln\,\gamma_i^c + ln\,\gamma_i^r \tag{2.3.5}$$

The combinatorial part basically contributes for non-ideally of a mixture that arise due to differences in size and shape of constituent molecular species whereas residual contribution due to differences in intramolecular forces.

Combinatorial component $\ln\gamma_i^c$:

$$ln\,\gamma_i^c = ln\frac{\psi_i}{x_i} + \left(\frac{z}{2}\right) q_i\, ln\frac{\theta_i}{\psi_i} + l_i - \left(\frac{\psi_i}{x_i}\right)\sum_{j=1}^{C} x_j l_j \tag{2.3.6}$$

Residual component $\ln\gamma_i^r$:

$$ln\,\gamma_i^r = \sum_{k}^{n} v_k^{(i)}\left(ln\,\Gamma_k - \Gamma_k^{(i)}\right) \tag{2.3.6}$$

where,

$$\psi_i = \frac{x_i r_i}{\sum_{i=1}^{C} x_i r_i} = segment\ fraction \tag{2.3.7}$$

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^{C} x_i q_i} = area\ fraction \tag{2.3.8}$$

$$l_j = \left(\frac{z}{2}\right)\left(r_j - a_j\right) - \left(r_j - 1\right) \tag{2.3.9}$$

Lattice coordination number, $z = 10$

2.3.3 UNIFAC Model

Frendenslund, Jones and Prausnitz (1975) described UNIQUAC Functional-group Activity Coefficients model (UNIFAC). This method system for prediction of non-electrolyte activity estimation in non-ideal mixtures. UNIFAC model is applied functional group of the molecules to calculate the activity coefficient (Fredenslund, Jones and Prausnitz, 1975). For example, in a solution of toluene and acetone, its contributes to 5 aromatic CH groups, 1 aromatic C group and1 CH_3 group from toluene while for acetone, it contribute to 2 CH_3 groups and 1 CO carbonyl group (Henley, Seader and Roper, 2011).

This UNIFAC method is based theoretically on UNIQUAC equation. The activity coefficient for species in a multicomponent mixture consists of combinational and residual parts same ad equation (2.2.5) (Henley, Seader and Roper, 2011).

$$ln\,\gamma_i = ln\,\gamma_i^c + ln\,\gamma_i^r$$

Combinatorial contribution γ_i^c is contribute from differences between molecular size while residual contribution γ_i^r is taking into account to molecular interactions (Fredenslund, Jones and Prausnitz, 1975).

Combinatorial component $\ln\gamma_i^c$ same as (2.2.6):

$$ln\,\gamma_i^c = ln\frac{\psi_i}{x_i} + \left(\frac{z}{2}\right) q_i\, ln\frac{\theta_i}{\psi_i} + l_i - \left(\frac{\psi_i}{x_i}\right)\sum_{j=1}^{C} x_j l_j$$

Z is the coordination number of the system and it relatively give a constant value of 10

Residual component $\ln\gamma_i^r$:

$$ln\,\gamma_i^r = \sum_{k}^{n} v_k^{(i)}\left(ln\,\Gamma_k - \Gamma_k^{(i)}\right) \qquad (2.3.10)$$

where Γ_k is residual activity coefficient of group k and $\Gamma_k^{(i)}$ is the same quantity but in reference mixture that contains only molecules of type i. Both Γ_k and $\Gamma_k^{(i)}$ have the same equation form.

$$ln\,\Gamma_k = Q_k\left[1 - ln\left(\sum_m \theta_m T_{mk}\right) - \sum_m \frac{\theta_m T_{mk}}{\sum_n \theta_n T_{nm}}\right] \tag{2.3.11}$$

$$\theta_m = \frac{X_m Q_m}{\sum_m X_n Q_m} \tag{2.3.12}$$

$$X_m \frac{\sum_j v_m^{(i)} x_j}{\sum_j \sum_n v_n^{(i)} x_j} \tag{2.3.13}$$

$$T_{mk} = exp^{\left(-\frac{a_{mk}}{T}\right)} \tag{2.3.14}$$

2.4 Reaction Kinetic in Reactive Distillation

Methyl acetate can be produced by esterification of liquid phase of acetic acid and methanol in presence of acid catalyst (sulfuric acid if sulfonic acid ion exchange resin) at pressure of 1 atm. The reaction is

$$CH_3COOH +\ CH_3OH \overset{K_{eq}}{\longleftrightarrow} CH_3COOCH_3 + H_2o$$

The phase of reaction was liquid and the basis of the equilibrium constant (K_{eq}) calculated from Gibbs free energy was taken to be molarity (Giwa, 2013). Kinetics rate equation for methyl acetate synthesis is depends on catalyst nature (homogeneous catalyst or heterogeneous catalyst). Based on Huss et al. (2003) the activity-based rate model for the reaction chemistry is

$$r = k_f\left(C_{HOAc}C_{MeOH} - \frac{C_{MeoAc}C_{H20}}{K_{eq}}\right) \tag{2.4.1}$$

The reaction equilibrium constant and the rate constant can be presented as:

$$K_{eq} = 2.32exp^{\left(\frac{782.98}{T}\right)} \tag{2.4.2}$$

$$k_f = 9.732x10^8exp^{\left(-\frac{6287,7}{T}\right)} \tag{2.4.3}$$

where T=K, k_f = h^{-1}

2.4.1 Homogeneous Catalyst Reaction

Liu et al. (2006) proposed rate expression of esterification reaction of methanol with acetic acid using homogeneous sulfuric acid catalyst, that give linear kinetis on catalyst concentration (Liu, Lotero and Goodwin, 2006). Ganesh et al. investigated the kinetics of reversible liquid phase esterification of acetic acid with mmethanol using sulfuric acid catalyst in an isothermal batch reactor (Ganesh et al., 2011).

The homogeneous catalyst esterification reaction of methanol and acetic acid using acetic acid catalyst is studied by Pöpken et al. and the proposed kinetics equation is (Pöpken, Götze and Gmehling, 2000):

$$r = \frac{1}{v_i}\frac{dn_i}{dt} = a_{HOAc}^{a}(k_1 a_{HOAc} a_{MeOH} - k_{-1} a_{MeoAc} a_{H2O}) \tag{2.4.4}$$

$$a_i = \gamma_i x_i \tag{2.4.5}$$

2.4.2 Heterogeneous Catalyst Reaction

Heterogeneous catalysis is associated with the ability of solid surfaces to form and break bonds with molecules from their surroundings. Solid surfaces accelerate a wide range of chemical processes especially for esterification process. A solid catalyst has three distinct roles. It begins by adsorbing the reactants and cleaving the necessary bonds. The surface then holds the reactants close proximity so they can react, and finally it allows the products to desorb back into the surrounding phase (Withers, 2008).

Reaction catalyzed by Amberlyst 15 described with boteh pseudo homogeneous model and adsorption-based model (Pöpken, Götze and Gmehling, 2000). Both models written as:

Pseudo homogeneous model:

$$r = \frac{1}{v_i}\frac{dn_i}{dt} = m_{cat}(k_1 a_{HOAc} a_{MeOH} - k_{-1} a_{MeoAc} a_{H2O}) \tag{2.4.6}$$

where the ion-exchange resin is thought to act as a source of solvated protons.

Adsorption-Based Model:

$$r = \frac{1}{v_i}\frac{dn_i}{dt} = m_{cat}\left(\frac{k_1 a'_{HOAc} a'_{MeOH} - k_{-1} a'_{MeoAc} a'_{H2O}}{(a'_{HOAc} + a'_{MeOH} + a'_{MeoAc} + a'_{H2O})^2}\right) \tag{2.4.7}$$

$$a'_i = \frac{K_i a_i}{M_i} \tag{2.4.8}$$

$$k_i = k_i^o exp\left(\frac{-E_A}{RT}\right) \tag{2.4.9}$$

where M_i is molar mass of the component i, whereby rate constants k_1 and k_{-1} are temperature dependent.