SIMULATION OF REACTIVE DISTILLATION COLUMN FOR 2-ETHYL HEXYL ACRYLATE PRODUCTION FROM DILUTE ACRYLIC ACID

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SIMULATION OF REACTIVE DISTILLATION COLUMN FOR 2-ETHYL HEXYL ACRYLATE PRODUCTION FROM DILUTE ACRYLIC ACID

TAY HONG LUAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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JANUARY 2014

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Date : 21 JANUARY 2014

DEDICATION

To my family who has always been there through the hard times

&

To my friend, Jesslyn for the guidance and motivation
to finish this dissertation.

ACKNOWLEDGEMENT

I would never been able to finish my dissertation without the guidance of my supervisor, help from friends and support from my family.

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ABSTRAK

Asid acrylate (AA) adalah asid organik yang tak tepu, bertoksik dan berbahaya terhadap alam sekitar. Malangnya, asid acrylate (AA) cair biasanya dihasilkan sebagai by-produk dalam pelbagai kimia dan petrokimia proses seperti pembuatan ester acrylate. Di kalangan penyelidik, pemulihan AA cair daripada aliran air sisa telah menjadi satu isu yang popular untuk dibincang oleh sebab isu-isu economic and alam sekitar. Pelbagai teknik pengasingan konvensional seperti penjerapan, penyulingan, dan pengekstrakan telah digunakan untuk merawat air sisa dari industri. Namun, teknik-teknik tersebut mempunyai kelemahan mereka masing-masing. Pemulihan AA melalui penyulingan reaktif telah menjadi salah satu kaedah yang menggalakkan dan ekonomi lestari untuk merawat air sisa. Setakat ini, kajian mengenai pengeteran AA cair melalui penyulingan reaktif tidak dilaporkan oleh penyelidik. Oleh itu, kajian simulasi terhadap pengesteran 2-ethylhexanol dengan AA cair melalui penyulingan reaktif akan disampaikan dalam kertas kerja ini. Kesan-kesan seperti kepekatan asid acrylate, nisbak refluks, kadar bawah, dan pemuatan pemangkin telah diubah serta konfigurasi optimum bagi penyuligan reaktif telah dikaji dalam karya ini. Keadaan operasi terbaik dan optimum konfigurasi bagi penyulingan reaktif seperti 10wt% kepekatan asid acrylate, 0.1 nisbah refluks, 0.13kg/h kadar bawah dan 1.5kg/m bebanan pemangkin telah dikenal pasti daripada keputusan simulasi. Konfigurasi penyulingan reaktif yang terbaik untuk system pengesteran AA cair dengan 2-ethylhexanol adalah lengkap dengan 18 peringkat terdiri daripada 4 tingkat reaktif, 10 tingkat pelucutan dan 4 tingkat pengayaan telah direka. Pemulihan maksimum asid acrylate dalam pengeteran AA cair dengan 2-ethylhexanol adalah 83%.

ABSTRACT

Acrylic acid (AA) is an unsaturated organic acid, very toxic and hazardous to the environment. Unfortunately, dilute acrylic acid (AA) has commonly produced as a by-product in many chemical and petrochemical processes such as manufacturing of acrylic esters. The recovery of dilute AA from the wastewater streams has become a growing concern among researchers due to its economic and environmental issues. There are several conventional separation techniques such as adsorption, distillation and extraction were developed to treat the wastewater from the industries; however, they have their own drawbacks respectively. One of the promising methods to purify the wastewater and economically sustainable is through esterification process of the recovery acrylic acid with alcohols via reactive distillation column. To date, study about esterification by using dilute AA has not been reported in literature. In this present work, a simulation study of esterification reaction of 2-ethylhexan-1-ol and dilute AA via reactive distillation system in the presence of ion exchange resin catalyst was performed using Aspen Plus RADFRAC incorporated with thermodynamic model of UNIFAC. The effect of different operating variables such as Acrylic Acid concentration, reflux ratio, bottom rate, catalyst weight and optimum column configuration were studied in this present work. The best operating conditions and column configuration were identified with maximum recovery of acrylic acid was 83% for the feed concentration of 10wt% AA, 0.1 reflux molar ratio, 0.13kg/h bottom rate and 1.5kg/m of catalyst weight. The best column configuration for the esterification system of acrylic acid and 2-ethylhexanol consisted of 4 reactive stages, 10 stripping stages and 4 rectifying stages, contributing to 18 numbers of stages with each stage of condenser and reboiler.

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1 INTRODUCTION

1.1 Background and Motivation of study

Acrylic acid and acrylate esters are widely used in the chemical industry. The market demand for these chemicals is nearly 4 MillionMT/yr, roughly split equally between acrylic acids and acrylate esters (Novemer, 2010). The production of these components has received increasing attention in Asia-Pacific region such as, China and South Korea due to the growing demands in super absorbent polymers in the market. Besides, great demand of acrylate ester such as 2-ethylhexyl acrylate in water-based coating and dispersion systems also has reached 2.8 millionMT in 2005 (NexantChem Systems, 2006). Thus, the demand trend for acrylic acid and its derivatives is forecast to increase gradually 4% per year in Asia-Pacific till 2018 (MarketsandMarkets, 2010). These have attracted many global companies such as BASF (Germany), Dow Chemical Company (U.S.), Nippon Shokubai (Japan), and others to venture into these markets.

2-ethylhexyl acrylate (2EHA) is one of the common acrylate ester which is commercially produced from 2-ethylhexan-1-ol (2EHOH) and acrylic acid (AA) by esterification process. It is colourless, volatile liquid, slightly soluble in water and completely soluble in alcohols and ethers and most organic solvents. It is used as a monomer in chemical industry for the production of homopolymers and copolymers (Komon *et al*., 2012). Both homopolymers and copolymers are mainly processed further to aqueous polymer dispersions. The aqueous polymer dispersions are used in adhesives, printing inks and binder for paints. They are also applied in the manufacturing of elastomers, super adsorbent polymers, flocculants, fibres and plastics.

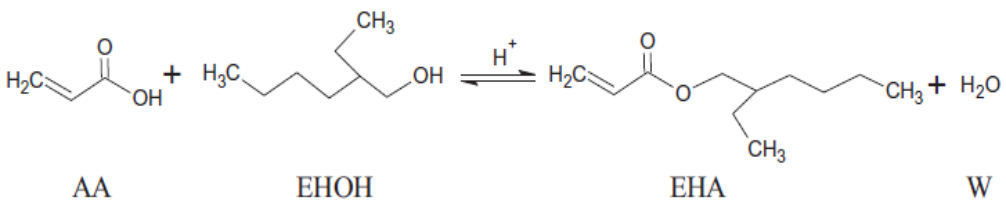
Acrylic acid, one of the reactant used to produce 2EHA is an unsaturated organic acid and is potentially a hazardous chemical to living species. It is released to the environment during the manufacturing of acrylic ester, water soluble resin and flocculants.In a typical acrylic manufacturing unit, the wastewater obtained from the quench tower containing high concentration of AA in the range of 4-10wt% along with several other toxicants of AA family such as acrylonitrile which is harmful to the environment (Kumar *et al*., 2010 Silva *et al*., 2003). The dissolved oxygen (DO) concentration of the receiving water stream polluted by the untreated wastewater can fall below the level necessary for normal aquatic organisms. Hence, removal of AA

from the wastewater is significantly important to protect the environment (Levec & Pintar, 2007).

Several treatment methods such as adsorption by activated carbon system (Kumar *et al*., 2010), wet air oxidation (WAO) (Silva *et al*., 2003), distillation and extraction (Arpornwichanop *et al*., 2008) are adopted to treat this type of wastewater. However, some of these methods are still suffering with the shortcomings of high operating cost and are inappropriate to treat the low concentration of wastewater with 4-15% of AA. Currently, wastewater from the industries is being treated using incineration process. Despite that, incineration is only suitable for highly concentrated wastewater at low flow rate (Kim & Ihm, 2011). On the other hand, recovery of AA from its dilute aqueous solution by using it as a reactant for esterification process could be a promising way (Singh *et al.*, 2006). The AA recovered from the wastewater can be used to produce a higher valued ester. This approach has brought much attention because it can save raw material cost and environmental problem.

1.2 Problem Statement

Esterification is a well-known chemical process that involves an acid and an alcohol to produce water and an ester as reaction product. To produce 2-ethyl hexyl acrylate, acrylic acid and 2-ethyl hexan-1-ol are esterified in a reversible equilibrium limited reaction shown in equation (1) (Komon *et al*., 2012):



(1)

Due to the reversible esterification reaction, the equilibrium of the esterification of the waste water containing AA with alcohol would be shifted away from the product. Excessive alcohol must be fed in to the reaction to shift the equilibrium to obtain ester as the reaction product. However, an excess alcohol feed have become the disadvantages due to the high cost separation process and recycled back after the reaction (Mueanmus *et al*., 2010). Currently, the production of 2-ethylhexyl acrylate (2EHA) is done by esterifying AA with 2-ethylhexanol (2EH) in conventional way by

using a continuous reactor followed by a series of separation units instead of using a RDC (Taylor & Krishna, 2000). Reactive distillation column (RDC) has become an attractive approach used to enhance an equilibrium limited esterification process in liquid phase (Buchaly et al., 2011) due to its special feature of insitu removal of product which can shift the equilibrium to the product side and yield the products, 2-ethyl hexyl acrylate. Figure 1 show (a) a typical conventional process consists of a reactor followed by a sequence of distillation columns. The mixture of A and B is fed into the reactor, where the reaction takes place in the presence of catalyst and reach equilibrium. A distillation train is required to produce pure products C and D. The unreacted components A and B will be recycled back to the reactor. (b) alternative reactive distillation column (RDC). The column consists of 3 sections of rectifying, reactive and stripping respectively. The rectifying section is at the top of the column followed by reactive section in the middle and lastly, the stripping section at the bottom of the column. The rectifying section is responsible to recover the reactant B from the product stream A while the stripping section is responsible to strip the reactant A from the product stream D.

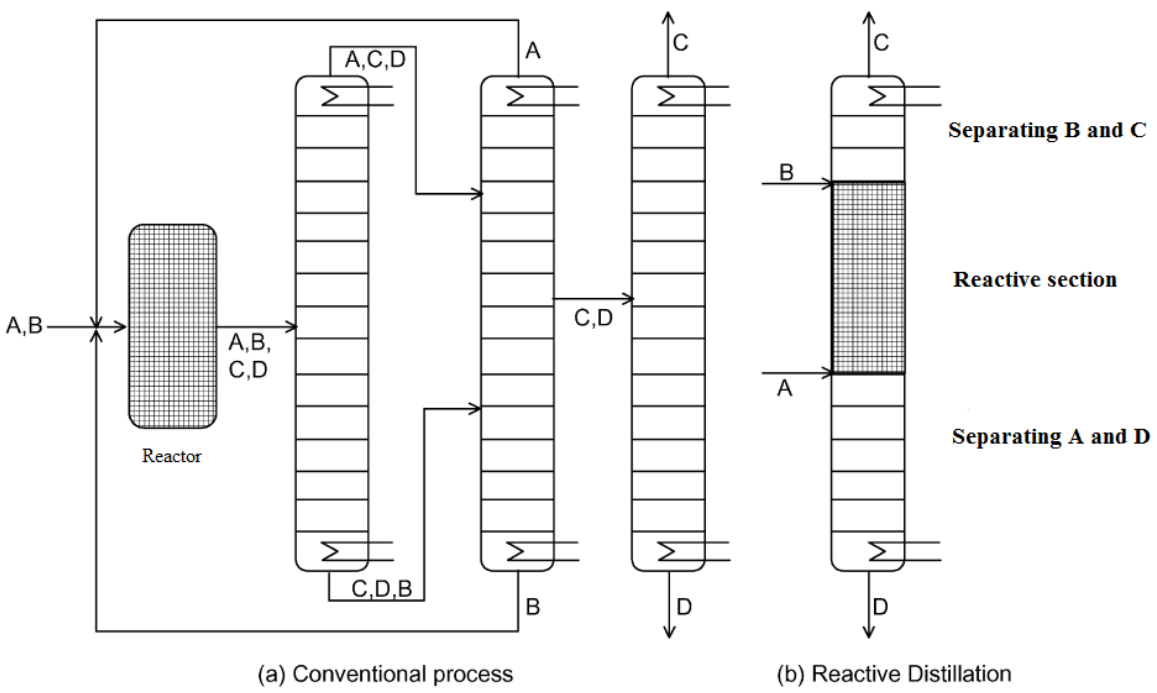


Figure 1. 1: Processing schemes for a reaction sequence $A + B \leftrightarrow C + D$ where C and D are both desired products. (a) Typical configuration of a conventional process consisting of a reactor followed by a series of distillation column. (b) The configuration of a

reactive distillation column. The components A, C, D and B have increasing boiling point (Taylor & Krishna 2000).

It is expected that esterification of waste water containing AA with 2-ehyl hexa-1-ol (2EHOH) in a RDC would be a promising method to recover AA. To the best of our knowledge, open literature about synthesis of 2-ethyl hexyl acrylate (2EHA) by reacting diluted acrylic acid with 2-ethyl hexan-1-ol (2EHOH) in a RDC is limited. Therefore, the present study focuses on the simulation study of the RDC for the production of 2EHA from the diluted AA and 2EHOH. The feasibility and practicability of AA recovery from the diluted aqueous solution using RDC are examined.

1.3 Objectives

The objectives of the present study include:

- To examine the efficiency of AA recovery from the diluted aqueous solution using RDC
- To investigate the effect of different important operating parameters for the reactive distillation column (RDC).

1.4 Scope of Study

In the present research, an intensive simulation study of the esterification of acrylic acid with 2-ethyl haxan-1-ol heterogeneously catalysed by acidic ion-exhange is performed using Aspen Plus version 7.0. Equilibrium model (RADFRAC) is chosen to simulate the RDC with the incorporation of suitable thermodynamic properties and reaction kinetics.

The verification is first done on esterification of acrylic acid and other alcohols from the past researchers to check the accuracy of the model. After obtaining validated model, it is adopted for the simulation study for esterification of acrylic acid and 2-ethylhexanol via RDC. Then, the practicability of the reaction is examined through the acrylic acid conversion in the RDC.

In this study, several operating parameters such as concentration of AA in the feed, reflux ratio, bottom rate, and catalyst weight are varied during the simulation studies. The ranges of these parameters are concentration of AA (10wt%-30wt %),

reflux molar ratio (0.1-0.2), bottom rate (0.01-0.13 kg/h), and catalyst weight (0.5-2.0 kg/m). The best operating condition to maximize the AA recovery is identified. Besides that, the column configuration for RDC is determined in this present paper work.

1.5 Organisation of this Partial Thesis

This partial thesis is divided into four chapters. Chapter 1 (introduction) presents a brief description about the demands of acrylic acids and acrylate esters in Asia-Pacific. The harmful of wastewater discharged containing acrylic acid to the environment and the conventional processes used to treat this wastewater is also briefly discussed. This chapter includes the problem statement that provides some guidelines for identifying the research directions and objectives. The objectives and scopes of study are then elucidated in detail. Finally, the organization of the partial thesis is given.

Chapter 2 (Literature review) provides information the shortcoming of the conventional method used to purify the wastewater, recovery of carboxylic acid through esterification reaction and application of RDC in esterification system are discussed, and several important considerations such as catalysts, kinetics thermodynamics and modelling for the RDC implementation are surveyed.

The simulation procedures are illustrated in detail in chapter 3 (Methodology). In this chapter, an appropriate RD model is chosen to simulate the RDC by incorporating the suitable thermodynamic properties and reaction kinetics of the esterification system. A step-by-step guide for the simulation study is also included.

Chapter 4 discusses the results obtained from the simulation. The accuracy of the model is discussed based on the model validation results. performed to check the. The validated model is then applied for the simulation of the esterification of acrylic acid and 2-ethyl hexan-1-ol under different operating parameters such as concentration of acrylic acid (10-30wt%), reflux ratio (0.1-0.2), bottom rate (0.01-0.12 kg/h), and catalyst weight (0.5-2.0 kg/m). The results are deliberated to identify the most significant effect, the best operating parameter and column configuration that yield highest conversion.

Chapter 5 summarises the thesis for the simulation studies and suggestions are outlined to develop in future work.

2 LITERATURE REVIEW

2.1 Overview

This chapter presents the literature review from past researchers about the problem of acrylic acid discharged into the water stream; types of wastewater treatment method; recovery of carboxylic acid via esterification system; reactive distillation technology; application of RDC in esterification system; catalyst in esterification system and modelling of reactive distillation.

2.2 Introduction

Various types of wastewater containing toxic and hazardous organic compounds are generated by the chemical and petrochemical industries. Acrylic acid is one of the hazardous organic acids that presents in this industrial wastewater. It brings harmful effects to the living species such as irritation to the skin, eyes and respiratory system. In a typical AA manufacturing plant, the wastewater containing concentration of AA in the range of 10-20% is being produced (Kumar *et al*., 2010). The discharge of this waste water would create a lot of complications to the environment due to high toxicity of organic compound. The level of dissolved oxygen (DO) concentration of the water streams should be below the level that necessary for the aquatic life to survive (Lin *et al*., 1996).The waste elimination matter has gained a lot of concerns from the researchers (Debellefontaine & Foussard, 2000). The industrial wastewaters must be treated to a level which is safe to be disposed to the natural water streams (Levec & Pintar, 2007).

2.3 Type of Industrial Wastewater Treatments

Several conventional separation techniques such as activated sludge treatment (Lin *et al*., 1996), distillation and extraction (Arpornwichanop *et al*., 2008) are adopted to treat the wastewater containing acrylic acid from the industries. Adsorption and wet air oxidation are the treatment methods under research (Kumar *et al*., 2010; Silva *et al*., 2003).

Activated sludge treatment is a type of traditional biological method used to recover AA from wastewater. The activated sludge system is not a complex treatment

and this eventually makes it relatively low cost to operate (Lin *et al.*, 1996). However, the microorganism in the activated sludge system requires a long residence time to degrade the pollutants. Thus, the biological sludge system can only deal with relatively low concentration of organic compounds. Moreover, this treatment is not suitable to treat the toxic contaminants due to biomass poisoning (Kim & Ihm, 2011). The conventional distillation is also used to purify the wastewater; however it is highly uneconomical because of large amount of water is required to vaporize from dilute aqueous solution due to the high latent heat of vaporization of water which makes it impractical (Gangadwala *et al*., 2008). Acoording to Ashton (2013), the conventional distillation managed to recover low concentration of acetic acid from wastewater, which in the range of 0.4-0.8wt%. Besides, the extraction also suffers from several drawbacks such as the separation process is limited by phase separation and distribution of components involved in the reacting system (Bianchi *et al.*, 2003). This method is used to recover AA from wastewater in the range of 7-12wt% (Shin *et al*., 2008).

Kumar *et al*. (2010) have used powdered activated carbon (PAC) as an adsorbent in their research work to remove AA from wastewater. They have found that adsorption treatment for recovery of AA from wastewater to be efficient and relatively low cost. Aluminium, alumina, titanium dioxide and clay minerals are a few examples of the adsorbent for the treatment used in laboratory scale adsorption experiment. Despite that, adsorption approach can only be used to treat low concentration of organic compounds present in wastewater.

Due to development of innovative technology, wet air oxidation (WAO) separation technique has been adopted to treat the wastewater and substituted the adsorption and activated sludge methods. The main reason WAO has replaced adsorption method is because it can remove high concentration of organic compounds in chemical wastewaters (Li *et al*., 1991). The WAO processes have the ability to break the organic compounds to simpler, easily treated materials before they are released into the environment. In general, it has a very limited interaction with the environment, which makes it environmental friendly (Levec & Pintar, 2007). Typical operating conditions were needed for WAO processes: high temperature at 200- 325˚C and high pressure at 50-175 bar to partially oxidize the organic pollutants into biodegradable intermediates to carbon dioxide, water and innocuous end products (Kim *et al.*, 2011).

Unfortunately, the severe operating condition of WAO has caused high capital cost and energy consuming (Oliviero *et al.*, 2001).

Recovery of AA by esterification process with the aid of reactive distillation could be one of the most promising and interesting treatment method used to purify industrial wastewater. Ragaini *et al*. (2006) have reacted the dilute acetic acid (4.5-15%wt) with alcohol in the presence of catalyst to produce ester. The main advantage to treat the wastewater by using esterification is that it can produce a good value of ester on top of reducing the environmental problem.

2.4 Recovery of Carboxylic Acid via Esterification Reaction

Acetic acid has been successfully recovered from dilute aqueous solutions through esterification with methanol by using RDC (Singh *et al.*, 2006). Besides that, other acids such as lactic acid, adipic acid, mystiric acid, succinic acid, chloroacetic acid, glycolic acid and trifluroacetic acid can also be recovered from their dilute solution with RDC (Yogesh & Singh, 2008).

The recovery of acetic acid (30% wt) with methanol by reactive distillation in the presence of ion exchange resin catalyst has been investigated by Singh *et al*. (2006) for both the simulation and experimental studies. A pseudohomogeneous kinetic model was used during the simulation. The studies on the effect of the operating parameters such as reboiler duty, feed flow rate and feed composition also have been covered in the simulation study. The results showed a quantitative recovery as high as 80% of acetic acid for the feed concentration of 30%wt in a laboratory column. Besides that, the researchers have also proposed three feasible alternative of configuration to complete recover the acid in the system.

Similarly, Saha *et al*. (2000) have also studied the effect of operating variables, such as, feed flow rate, feed location, reflux ratio, molar ratio of reactant and the effect of recycle of water on the recovery of 30% acetic acid by reacting with n-butanol and iso-amyl alcohol respectively in a RDC using ion-exchange resin, Indion 130 cation exchange resin, as a catalyst. The results showed that at 1:2 molar ratio of acetic acid to butanol, approximately 58% conversion of acetic acid was realized; while at 1:2 molar ratio of acetic acid to iso-amyl, almost closely of 51% conversion of acetic acid was

achieved. The best result was obtained when the column was operated in counter current mode.

Bianchi *et al*. (2003) have presented the recovery of a diluted acetic acid (6wt %) by reacting with n-butanol and 2-ethylhexanol in a simple glass reactor. The peculiarity of this method is the presence of large amount of water at the beginning of the reaction. The esterification reaction in the glass reactor is thermodynamically favourable as it has the ability to shift the reaction equilibrium towards the ester and not towards the reagent.

The feasibility of recovery of trifluroacetic acid (TFA) from dilute aqueous solution by reactive distillation has been studied by Yogesh and Singh (2008). The experimental investigation was carried out by reacting the recover TFA with 2-propanol via RD in batch and continuous modes. The experiments result show an increased conversion of TFA and it is confirmed that through simulation with either incorporated equilibrium stage model or non-equilibrium stage model, the recovery system can yield greater than 97% recovery.

2.5 Reactive Distillation Technology and Applications

The concept of reactive distillation for esterification process has been introduced by Backhaus starting in 1921. Despite the fact that the basic concept of combining reaction and distillation is old, there has been an enormously growing interest in the design and operation of RD process in recent year. In RD column, the chemical reaction and separation by distillation occurs simultaneously in one unit operation (Niesbach *et al*., 2012). A RDC consists of a reaction section in the middle with non-reactive rectifying and stripping sections at the top and bottom respectively. The task of rectifying section is to recover reactant B from the product C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section, the products are separated in situ, driving the equilibrium to the right and preventing any undesired side reaction between the reactants A (or B) with the product C (or D). The components A, C, D, and B have increasing boiling points. The general configuration of RDC is shown in figure 2.1 (Shinde *et al*., 2011).

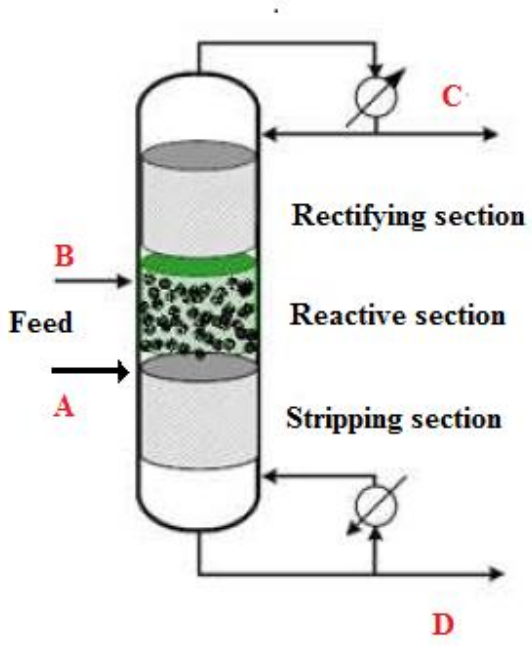


Figure 2. 1: The general configuration of Reactive Distillation (RD).

The development of innovative reactive distillation based on ecologic and economic aspects has evolved into a promising process alternative to conventional sequential processes especially for equilibrium limited and consecutive reactions (Steinigeweg & Gmehling, 2002). RD is successfully implemented in several reactions, for examples, etherification, esterification, alkylation, hydrogenation, hydration and hydrolysis that incorporated with solid heterogeneous catalyst, in another term RD is also called as catalytic distillation process (Murat *et al*., 2003).

Reactive distillation (RD) has many distinctive advantages and it is summarized as follows (Taylor & Krishna, 2000; Murat *et al.*, 2003; Tuchlenski *et al.*, 2001):

- Reduction in capital investment. This is because the two process steps can be carried out in the same unit operation. Besides that, the amount of equipment such as pump, piping and instrumentation also can be reduced significantly.
- Increased conversion of reactants. The in-situ removal of products from the reactive zone has pushed the chemical equilibrium to the forward direction based on Le Chatelier's Principle. The forwarded chemical equilibrium in the reaction has results a significant yield of products.

- Improved products selectivity. The products selectivity can be improved due to fast removal of reactants or products from the reactive zones. The maintaining low concentration of one the reagents can lead to reduction of the rates of side reactions and thus improved the selectivity of the desired products.
- Lower energy consumption. If esterification is an exothermic reaction, the heat of reaction can be used for vaporisation of liquid and hence, the reduction of reboiler duties can cause the energy consumption to be lowered.
- Avoidance of azeotrope. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes to be "reacted away" in a single vessel.
- Environmental friendly

Besides the above-mentioned advantages of RD, there are several constrains and difficulties for implementing RD technology.

- Volatility constraints. Appropriate volatility of reagents and products is a must to maintain the high concentrations of reactants and low concentrations of products in the reactive zone.
- Residence time requirement. The residence time for the reaction is long in the reactive zone requires a large column size with large tray hold-ups. This may cause RD to be more non-economic than the conventional reactor-separator arrangement
- Scale up to large flows. It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed RD columns.
- Process conditions mismatch. In some processes the optimum conditions of temperature and pressure for distillation may be far from the optimum reaction and vice versa.
- Liquid phase conditions. Wet catalysts pellets are necessary if the chemical reaction is take place in liquid phase.

- Long lifetime of catalyst needed. As it is very expensive to change the catalyst in the structured catalytic packing in RDC. A long lifetime of catalysts is strongly required.

Esterification is a well-known chemical process that involves two reactants; an alcohol and an acid in the presence of acid catalyst which produce an ester as reaction product. This process has attracted a lot of researchers' attention to make it as a subject for extensive investigation (Syed Azhar *et al*., n.d.).

Steinigeweg and Gmehling (2002) have presented a study of the development of heterogeneously catalysed RD process for the production of n-butyl acetate using the reliable thermodynamic and kinetic data. The reaction was catalysed by strongly acidic ion-exchange (Amberlyst 15). The experimental results were compared with the simulation results which indicate that an equilibrium stage model is able to describe the experiments quantitatively. On the other hand, the influence of design factors such as feed location, use of prereactor, number of reactive and nonreactive stages were determined by the help of simulation study. The same conclusion was shown from the study of feasibility of RDC for producing n-butyl acetate using different heterogeneous catalyst; for example, surface-sulfonated ion-exchange resin Amberlyst 46 (Hui *et al*., 2012). From the simulation results, n-butanol conversion and n-butyl acetate purity have reached greater than 96% at the optimal conditions.

The esterification of acetic acid with ethanol has been widely investigated by researchers, mainly because it is an important organic solvent used in the chemical industry (Lai *et al*., 2008). Both Kirbaslar *et al*. (2000) and Calvar *et al*. (2007) have studied the reaction kinetics of the esterification process of ethanol with acetic acid which catalysed by heterogeneous and homogeneous catalysts at the temperature range of 303.15˚C to 353.15˚C. Besides that, they have also done several investigations on the effect of the operation parameters such as reflux ratio, feed flow rate and vapor rate on the production of ethyl acetate. Kirbashlar *et al*. (2000) showed the results of highest ethyl acetate composition is obtained when the packed bed reactive column operated in continuous mode; while Calvar *et al*. (2007) showed that the purity of ethyl acetate in distillate is limited by the azeotropic composition. As for Lai *et al*. (2008), production of high purity of ethyl acetate has been researched experimentally. A product of more than 99% of ethyl acetate and less than 100ppm of acetic acid is expected to achieve as

the specification. The results of six experiment run show that with the proper design of reactive distillation, a highly purity of ethyl acetate will be obtained.

As a summary, the application of RDC in esterification systems is acknowledged by a lot of past researchers because it can produced a good value of esters as final product at optimum operating conditions. The application of RDC in esterification systems have been summarized in the Table 2.1.

Table 2. 1: The application of RDC for the esterification systems.

Esterification system	**Type of catalyst**	**References**
$n-Butanol + Acrylic\ \ acid \rightarrow n-Butylacrylate + Water$	Amberlyst 15	Niesbach *et al.*, 2012
$n-Butanol + Acetic\ \ acid \rightarrow n-Butylacetate + Water$	Amberlyst 36 Wet	Hui *et al.*, 2012
	Amberlyst 15	Steinigeweg & Gmehling, 2002
$Ethanol + Acetic\ \ acid \rightarrow Ethylacetate + Water$	Amberlyst 15	Kirbashlar *et al.*, 2000
	Acetic acid (homogeneous); Amberlyst 15 (heterogeneous)	Calvar *et al.*, 2007
	No information	Kenig *et al.*, 2001
	Amberlyst 36 Wet	Lai *et al.*, 2008
$1-Propanol + Propionic\ \ acid \rightarrow n-Prorylpropionte + Water$	Amberlyst 46	Buchaly *et al.*,

		2012
$n-\text{Hexanol} + \text{Acetic acid} \rightarrow \text{Hexylacetate} + \text{Water}$	Amberlyst CSP2	Schmitt *et al.*, 2004
$\text{Methanol} + \text{Decanoic acid} \rightarrow \text{Decanoate} + \text{Water}$	Amberlyst 15	Steinigeweg & Gmehling, 2003

2.6 Catalysts in Esterification System

Catalysts were added into the liquid phase esterification in order to speed up the rate of reaction and increase the conversion of the reactants (Ahmed Zeki *et al*., 2010). The kinetic model and reaction mechanism for carboxylic acids esterification over homogeneous acids and heterogeneous catalysts have been well documented in the literature (Miao & Shanks, 2011).

The mechanism for homogeneous catalysis in esterification reaction involves protonation of carboxylic acid, which activates it for the reaction with the nonprotonated alcohol to yield a tetrahedral intermediate that, by decomposition. This will result in the production of ester and water. The slow step of the reaction is the nucleophilic attack of the alcohol on the protonated carbonyl group of the carboxylic acid (Liu *et al.,* 2006).

Two mechanisms have been proposed for esterification on heterogeneous acid catalysts: a single-site mechanism (Eley-Riedel, E-R) and a dual site mechanism (Langmuir-Hinshelwood type, L-H) (Miao & Shanks, 2011). The schematic diagram for the heterogeneous catalysis reaction mechanism is shown in Figure 2.2. In heterogeneous catalysis reaction, there are seven steps involved in the reaction mechanism. Steps 1 and 2 show the diffusion of the reactant form the bulk fluid into the external and internal surface of the catalyst pellet respectively. Similarly for steps 6 and 7, it shows the diffusion of reactant out from the external and internal surface of the catalyst pellet back into the bulk fluid respectively. Step 3 shows the adsorption of the

reactant A onto the catalyst surface continue by step 4 shows the reaction on the surface of the catalyst and lastly step 5 which is desorption of the product from the catalyst surface (Fogler, 1999).

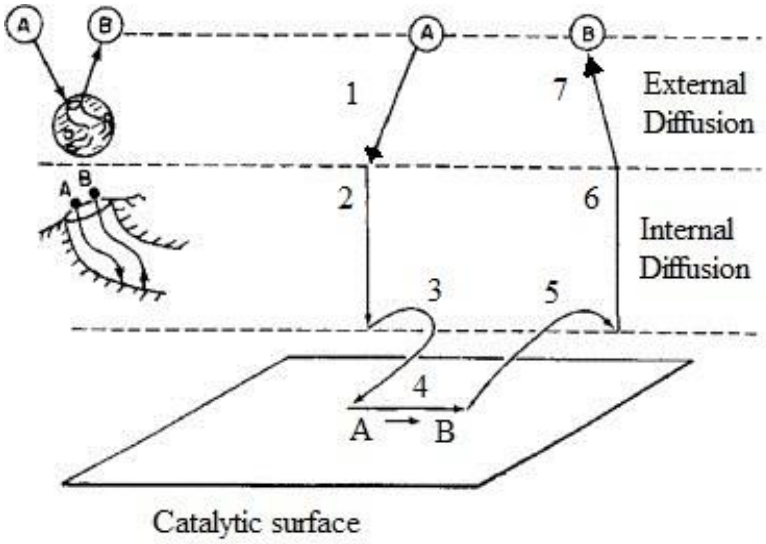


Figure 2. 2: The heterogeneous catalysis reaction mechanism

2.6.1 Homogeneous Catalyst

In esterification reaction, strong mineral liquid acids, such as sulphuric acid and p-toluenesulphonic acid are widely applied in the reaction. The catalytic activity of homogeneous catalysts is extremely high (Peters *et al.,* 2006). Despite a strong catalytic effect, the use of homogeneous catalyst, for example sulphuric acid has posed several drawbacks which include the generation of large amount of toxic wastewater, equipment corrosion and loss of catalyst (Yogesh & Singh, 2011; Chen *et al*., 1999).

Production of n-propyl acetate by reactive distillation which catalysed with homogeneous acidic catalyst, sulphuric acid was carried out experimentally by Brehelin *et al.* (2007). The results from the experiment showed that the acetic acid conversion has reached 79% with molar purity of n-propyl acetate of 64% have been achieved. Besides that, the researchers have done a simulation study for the optimum design of reactive distillation to obtained optimum production. The simulation results have shown a good agreement with experimental data.

Synthesis of acetic esters, including methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate using *p*-toluene sulphonic acid (PTSA) with sulfuric group as homogeneous catalyst was studied by Yao *et al.* (2009) in a microchanels reactors.

The highest yields of esters happened when the reaction temperature was near to the lowest boiling point of the components. The experimental results showed that the yields reached 74.0, 70.1, 97.2, and 92.2% for methyl acetate, ethyl acetate, n-propyl acetate n-butyl acetate production respectively.

The esterification kinetics of acetic acid with ethanol in the presence of sulfuric acid as homogeneous catalyst was studied by Ahmad Zeki *et al*. (2010). The investigation was carried out experimentally with isothermal batch at temperature of 50-60˚C. It was found that the rate constant and conversion at a certain mole ratio increased when the temperature of the reaction increased. From the results, it is found that the maximum conversion, approximately 80% as obtained at 60˚C for molar ratio of 10:1 ethanol to acetic acid.

2.6.2 Heterogeneous Catalyst

Zeolites, heteropolyacids, sulfated, metal oxides and ion exchange resin such as Amberlyst are some of the examples of solid acid catalyst used in many chemical industries (Shanmugan *et al*., 2004). According to Toor *et al*. (2011), ion exchange organic resin such as Amberlyst 35, Amberlyst 36, and Dowex 50W are the most popular solid catalyst used to produce esters. It is found that ion-exchange resins offer better selectivity toward the desired products compared to homogeneous. The drive to develop green processes has led to the development of solid acid catalysts to a significant increase in research studies both in academic and industrial section. These materials can substitute the corrosive liquid acids which are used in the industry in the olden days. Heterogeneous catalysts offer a few distinct advantages over catalysis by homogeneous catalysts (Teo & Saha, 2004):

- Environmental friendly due to corrosive environment eliminated.
- The purity of the products is higher as the side reactions can be completely eliminated or significantly less.
- Easy removal of catalyst from the reaction mixture by filtration.

In order to maintain the economic viability, suitable heterogeneous system must not only minimize the production of waste but should also exhibit high activities and selectivities comparable to the existing homogeneous route (Wilson & Clack, 2000).

Sert and Atalay (2012) have studied the liquid esterification of acrylic acid with different alcohols, such as butanol, iso-butanol, and hexanol in a batch reactor with zirconia supported tungstophosphoric acid (TPA) as heterogeneous catalysts. The study indicates that zirconia supported TPA catalysts has a high catalytic activity and thermal stability. The activity of the catalyst was found to depend on TPA loading and calcination temperature. The results showed that at 25% loading of TPA and calcination temperature of 650% are the most efficient catalysts since it gave more than 33%, 31% and 27% conversion of acrylic acid for the production of butyl, iso-butyl and hexyl acetate respectively.

The development of kinetic model and thermodynamic study of esterification of 2-ethanol and acrylic acid in a batch reactor with the presence of heterogeneous catalyst have been demonstrated by Komon *et al*. (2012). The catalysts selection of ion exchange resins, for instances Amberlyst 39, Amberlyst 46, Amberlyst 70 and Amberlyst 131 have been given special attentions. Amberlyst 70 showed the best performance as its active acidic sites is much stronger than other used catalysts. The kinetic of acrylic acid esterification with 2-ethanol was found to be second order and a quasi-homogeneous model was used to describe the reaction catalysed by Amberlyst 70.

Esterification kinetics of acetic acid with methanol have investigated by Jagadeeshbabu *et al.* (2011) with solid acid catalysts in an isothermal batch reactor at temperature range from 333˚C to 353˚C. The researchers have used several different types of ion exchange catalysts such as Indion 130, Indion 190 and Amberlyst 13 Wet for the esterification of acetic with methanol. It was found that Indion 130 was an effective catalyst for acetic esterification compared to other used catalysts. This is because Indion 130 was observed to give maximum conversion of 68.18%, followed by Indion 190 which gave maximum of 66.76% conversion and lastly the maximum conversion of 56.37% for Amberlyst 15 Wet catalyst. Various parameters, for example reaction temperature, reaction time, catalyst loading, molar ratio and speed of mixing were studied too. The rate equation was developed and can be used in simulation and design of the ethyl acetate production in catalytic distillation column.

2.7 Modeling of Reactive Distillation

In the past two decades, the development of various techniques for reactive distillation column (RDC) has been explored by many researchers due to the increasing popularity of RDC in many chemical industries (Okur & Bayramoglu, 2001). To model a RDC, a few assumptions must be set based on the RD model used (Taylor & Krishna, 2000). The appropriate thermodynamic and kinetic models are required to complement the RDC model for accurate prediction.

There are two type of RD model which are equilibrium model (EQ) and non equilibrium model (NEQ) have been presented in the open literature (Niesbach *et al*., 2012). Most of the reactive distillation mathematical models are originally derived from traditional distillation calculation, which are based on equilibrium model (Murat *et al*., 2003). According to Taylor and Krishna (2000), the equations that associated with the equilibrium stage model are known as MESH equation. MESH being an acronym referring to the different type of equation: Material balance, Equilibrium relationship, Summation equation and Heat (energy) balance. However, the NEQ model are referred as MERSHQ equations: Material balance, Energy balance, Rate equation of mass and heat transfer, Summation equation, Hydraulic equation for pressure drop and Equilibrium equations (Taylor *et al*., 2003). In NEQ model, hardware design information must be specified so that the mass and heat transfer coefficients, interfacial areas and liquid holdups can be calculated (Baur *et al*., 2003). This has increased the complexity for using NEQ model instead of the simplify EQ model.

For a reaction catalysed with heterogeneous catalyst, the reactants first needs to travel from the bulk fluid, to the surface of the catalyst by diffuse into the pores of the catalyst and being adsorbed onto the catalyst surface (Fogler, 1999, p.592). There are three type of kinetic model used to describe the kinetic of the reaction: pseudohomogeneous; Langmuir Hinshelwood and Eley Rideal. In pseudohomogeneous model, the adsorption of the reactants on the surface of catalyst is assumed negligible. On the other hand, LH and the ER models both include the adsorption effects of the species in the reactant which makes it more complicated than PH model. Besides that, Komon et al. (2012) also applied pseudohomogeneous model to describe the esterification of 2-ethylhexanol (2EHOH) and acrylic acid (AA) which catalysed by ion

exchange resin of Amberlyst 70. A general kinetic expression for PH model is written as (Qu *et al*., 2009):

$$R = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = k_a[\alpha_{AA}\, \alpha_{EHOH} - (\frac{1}{K_a})\alpha_{AA}\alpha_W]$$

Where m_{cat} is the catalyst mass, v_i is the stoichiometric coefficient of the ith component, n_i the number of moles of the ith component, t is the time, k_a is the forward reaction rate constant and α_{AA} , α_{EHOH} and α_W are the activity of acrylic acid, 2-ethyl hexanol and water respectively. The reaction constant is expressed using Arrhenius equation:

$$k = k_o \exp(-\frac{E}{RT})$$

Where k_o is the frequency factor, E is the reaction activity coefficient, R is the gas constant and T is the absolute temperature.

Bhatt and Patel (2012) studied generalized modeling and simulation of reactive distillation for esterification of acetic acid and butanol. The reaction was catalysed heterogeneously by a strong acidic ion-exchange resin, Amberlyst 15. A Pseudohomogeneous model has chosen to describe the esterification reaction which catalysed by solid catalyst. In the study, the researchers have used equilibrium stage model incorporated together with thermodynamic property of UNIQUAC to simulate the reactive distillation. The simulation results were validated with the experimental data that available in the literature. From the simulation results, 1% higher value of butyl acetate was achieved compared to the experimental data.

Okur and Bayramoglu (2001) have investigated the effect of the liquid-phase activity model on the simulation of ethyl acetate production by reactive distillation. In the previous work, researchers have adopted an EQ model to model the synthesis of ethyl acetate. NEQ is more complex to be used compared to EQ model, although NEQ model will give a more accurate result. This is because of large number of parameters such as mass transfer coefficient; heat transfer coefficient and interfacial area have to be estimated for the modelling.

Besides that, modelling and simulation research study of ethyl acetate with RDC using ASPEN PLUS has been done by Lone and Ahmad (2012). Researchers have used RADFRAC model to simulate the RD column. According to the simulation results, RD column helps in achieving products of high purity and higher conversion of reactants compare to the old conventional method. From all the studies, it has shown that application of RDC in esterification has been very beneficial to the process.

The thermodynamic models and kinetic models used during the RD simulation studies are summarized in Table 2.2:

Table 2. 2: The thermodynamic models and kinetic models adopted for RD simulation

Esterification System	**Thermodynamic model**	**Kinetic Model**	**Reference**
		Heterogeneous	
Acrylic acid and 2-ethylhexan-1-ol	UNIFAC	Pseudohomogeneous	Komon et al., 2012
Acrylic acid and n-butanol	UNIQUAC-HOC	LHHW	Niesbach et al., 2013
Acetic acid and n-butanol	UNIQUAC	Pseudohomogeneous	Steingweg & Gmehling, 2002
	UNIQUAC	LHHW	Hui et al., 2012
Acetic acid and ethanol	UNIFAC	Not available (NA)	Guatam et al., 2013
	UNIFAC	NA	Okur & Bayramoglu, 2001
	NRTL	NA	Kenig et al., 2001

3 METHODOLOGY

3.1 Overview

This chapter presents the procedure for the simulation of a reactive distillation (RD) column using Aspen-Plus version 7.0. The guidelines and sequences for model validation and the studies of the effect of important operating parameters are delineated.

3.2 Modeling of Reactive Distillation (RD) Column

The modelling and simulation of the RDC was carried out by using ASPEN PLUS™ V7. There are two different categories of RD models have been developed in the literature (Niesbach *et al*., 2012) to design the RD column: the equilibrium stage model (EQ), in which the vapor and liquid phases are assumed to be in equilibrium and non-equilibrium stage model (NEQ) in which the finite mass transfer rates across the vapour-liquid interface are accounted for. In this work, EQ model is chosen to describe the RD column instead of NEQ model. An inbuilt model known as RADFRAC in the ASPEN PLUS™ which is based on a vigorous equilibrium stage model was used to simulate the RD column (Aspen Tech, 2006). RADFRAC is being chosen due to its ability to predict a comparable result with experimental data despite its simplicity (Peng *et al.*, 2002). Besides that, RADFRAC is chosen also because of there is not much information about the hardware design of a reactive distillation available in the open literature. Without the complete equipment design details such as diameter, height and type of packing, it is impossible to estimate the mass transfer coefficient and the interfacial areas.

In EQ model, the exiting vapour and liquid streams of each stage are assumed to be thermodynamically equilibrium. Schematic diagram of an equilibrium stage model was shown in Figure 3.1. There are some assumptions need to simplify the model (Peng *et al.*, 2002):

- The phases in each segment of RDC are well mixed.
- The condenser and the reboiler at top and bottom of RDC respectively are treated as equilibrium stages.

- For a heterogeneous catalysed reaction, a pseudo-homogenous reaction is assumed. So that, reaction and diffusion inside the catalyst are not considered.
- The heat transfer coefficients are assumed to be constant for all segments.
- The finite-flux mass transfer coefficients are assumed to be the same as the low-flux mass transfer coefficients.

The equation model used in the EQ model is known as MESH equations. MESH equation is a term formed from the initial letter of different types of equation. M stands for the material balance equation; the total material balance takes the form (Taylor & Krishna, 2000):

$$\frac{dUj}{dt} = V_{j+1} + L_{j-1} + F_j - (1+r_j^V)V_j - (1+r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i\,.m}\, R_{m\,.j}\varepsilon_j$$

The component material balance is:

$$\frac{dUjxi,j}{dt} = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j+1} + F_{jz_{i,j}} - (1+r_j^V)V_{i\,y_{i,j}} - (1+r_j^L)L_j x_{i,j} + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i\,.m}\, R_{m\,.j}\varepsilon_j$$

In the material balance equation given above, L represents the liquid phase molar flow rate (mol/s) F represents the feed flow rate (mol/s), z represents the mole fraction of the component in the feed, *i* represents the component index, *j* represents the segment index, $v_{i,m}$represents the stoichiometric coefficient of the component *i* in reaction *m* and U_j represents the hold-up on stage *j*. U_j is only considered for the hold-up for liquid phase however for component material balance, vapor hold-up is neglected.

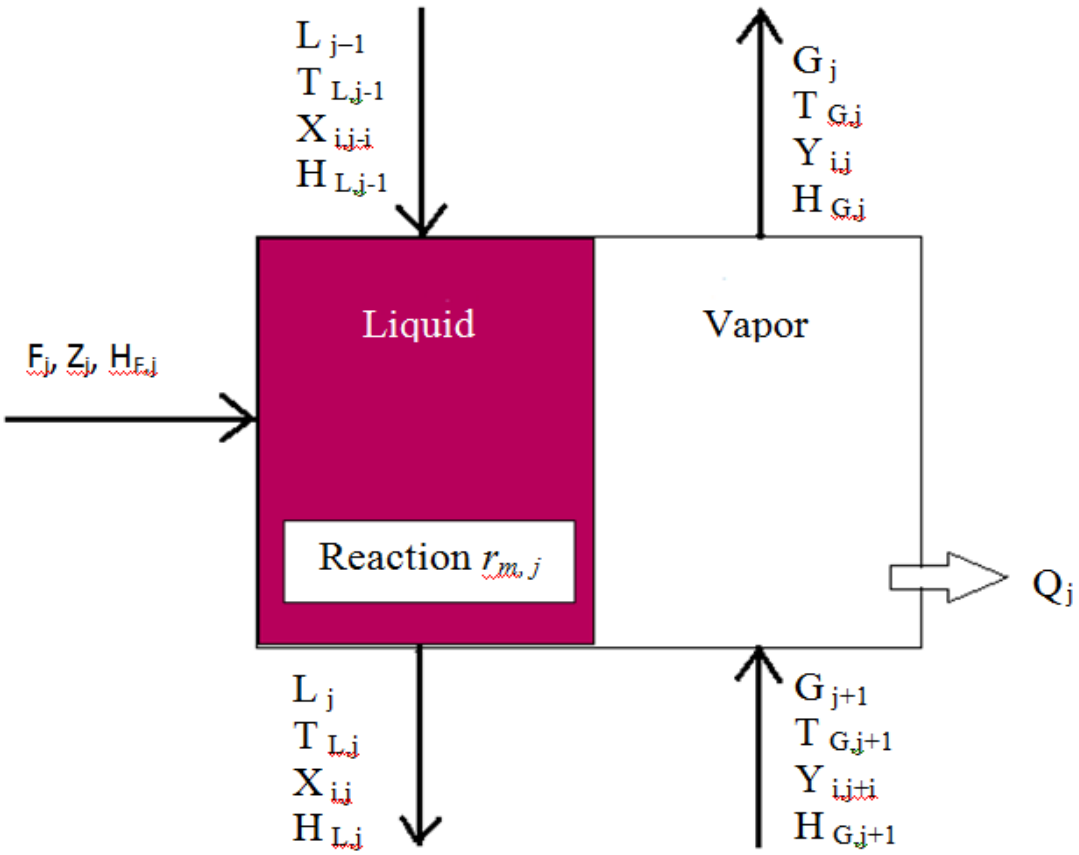


Figure 3. 1: The equilibrium stage model

The E equation stands for the equilibrium relationship (to express the assumption that the streams leaving the stage are in equilibrium with each other):

$$y_{i\,.j} = K_{i\,.j} x_{i\,.j}$$

The S equation stands for the summation equation:

$$\sum_{i=1}^{c} x_{i\,.j} = 1, \sum_{i=1}^{c} y_{i\,.j}$$

The H equation stands for the heat or enthalpy balances:

$$\frac{dUj\,Hj}{dt} = V_{j+1}H_{j+1}^{V} + L_{j-1}H_{j-1}^{L} + F_j H_j^{F} - (1+r_j^{V})V_j H_j^{V} - (1+r_j^{L})L_j H_j^{L} - Q_j$$

Where H is molar enthalpy (J/mol) and Q is heat duty (J/s)

3.3 Reaction Kinetics

The esterification of acrylic acid (AA) and 2-ethylhexanol (2EHOH) is catalysed with ion exchange resin, Amberlyst 15. For a reaction occurred in the presence of heterogeneous catalyst, the reactants first needs to travel from the bulk liquid, to the surface of the catalyst. Fogler (1999, p.592) states that from the external surface of the catalyst, the reactants still needs to diffuse into the pores of the catalyst and lastly being adsorb onto the internal surface of the catalyst. By assuming that the adsorption of the reactant onto the catalyst surface and mass transfer resistances were negligible, the esterification AA and 2-etyhlhexanol was represented by the pseudohomogeneous kinetic model by Ahmad (2013). The rate of reaction expression of the acrylate formation is described as:

$$-r_{EHA} = k(C_{AA}C_{2EHOH} - \frac{C_{EHA}C_{H2O}}{K_{eq}})$$

Where K_i is adsorption constant of the *i*th component; K_{eq} is equilibrium constant $-r_{EHA}$ is rate of ethylhexyl acrylate ($(dm^3)^2$/mol.g.min); and C_i is concentration of ith component (mol/dm^3).

Although PH model does not take into account the adsorption effect of the species in the reactant medium, it has been successfully used in high polar reaction media. It has been shown for esterification and etherification reactions, the presence of water has an significant influence on the kinetic since it is preferable to be absorbed by the resin due to its small molecular size and high polarity (Steinigweg & Gmehling, 2003).

3.4 Thermodynamic Aspect

The mixtures in the reaction are highly non-ideal. Phase equilibrium model such as UNIFAC (Universal Functional Activity Coefficient), UNIQUAC (Universal Quasi-chemical equation) and NRTL (Non Random Two Liquid) are used to predict the non-ideality factor which is the activity coefficient (Schwarzer, 2006). In this research, thermodynamic model plays a very important role to predict the activity coefficients. The UNIFAC group contribution group (Fredenslund *et al*., 1975, 1977) has proven that

UNIFAC is a fast and reliable tool to predict the liquid phase activity coefficients. It is a model based on the UNIQUAC and its basis equations of the original UNIFAC for the activity coefficient of compound *i* are (Georgeios & Georgeios, 2010):

$$\ln\gamma_i = \ln\gamma_i^{comb} + \ln\gamma_i^{res}$$

Where the combinatorial (*comb*) and residual (*res*) contributions are given by the equations:

$$\ln\gamma_i^{comb} = \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \left(\frac{\phi_i}{x_i}\right) - \frac{Z}{2} q_i \left(\ln\frac{\phi_i}{\vartheta_i} + 1 - \frac{\phi_i}{\vartheta_i}\right)$$

$$\ln\gamma_i^{res} = \sum_k v_k^{(i)} \left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right)$$

Where,

$$\vartheta = \frac{x_i q_i}{x_i q_i + x_j q_j} = \frac{x_i q_i}{q}$$

q_i = Surface area parameter for species *i* = $\sum_k v_k^{(i)} Q_k$

$$\phi_i = \frac{x_i r_i}{x_i r_i + x_j q r_j} = \frac{x_i r_i}{r}$$

r_i = Molecular weight parameter for species *i*= $\sum_k v_k^{(i)} R_k$

Note that the combinatorial term is identical to that of UNIQUAC (Z= 10)

v_k = Number of *k* groups present in compound

$\ln\Gamma_k$ = residual contribution to the activity coefficient of group *k* in pure fluid *i*

$$\ln\Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right]$$

θ_m = Surface area fraction of group *m* in the mixture $= \frac{x_m Q_m}{\sum_n x_n Q_n}$

X_m = mole faction of the group *m* in the mixture

Besides that, UNIFAC covers larger number of functional group in the aspen databank. Zeng *et al*. (2006) have used UNIFAC model in their research to obtain the remaining thermodynamic parameters for the production of n-butyl acrylate. Komon *et al*. (2012) have checked this UNIFAC model with all the available literature data for the similar system. The obtained results were satisfactory enough to be accepted for further use.

3.5 Procedures for Simulation Study

For this research, the simulation of RDC was done by using ASPEN PLUS™ version 7. A validation model for esterification system between acrylic acid and n-butanol was first run in order to check the accuracy of the RDC model for acrylate ester production system. After obtaining the validated model, the simulation was run for the present work which is esterification of acrylic acid (AA) and 2-ethylhexanol (2EHOH) by using RDC. The effects of operating parameters were investigated. These parameters include AA concentration, reflux ratio, bottom rate, catalyst weight and column configuration of the RDC. The parameters was varied in a suitable range for the simulation. The simulation results obtained was used to check the feasibility to produce 2-ethylhexyl acrylate (2EHA) by using a reactive distillation. Figure 3.2 shows the general RADFRAC simulation methodology for the RDC.

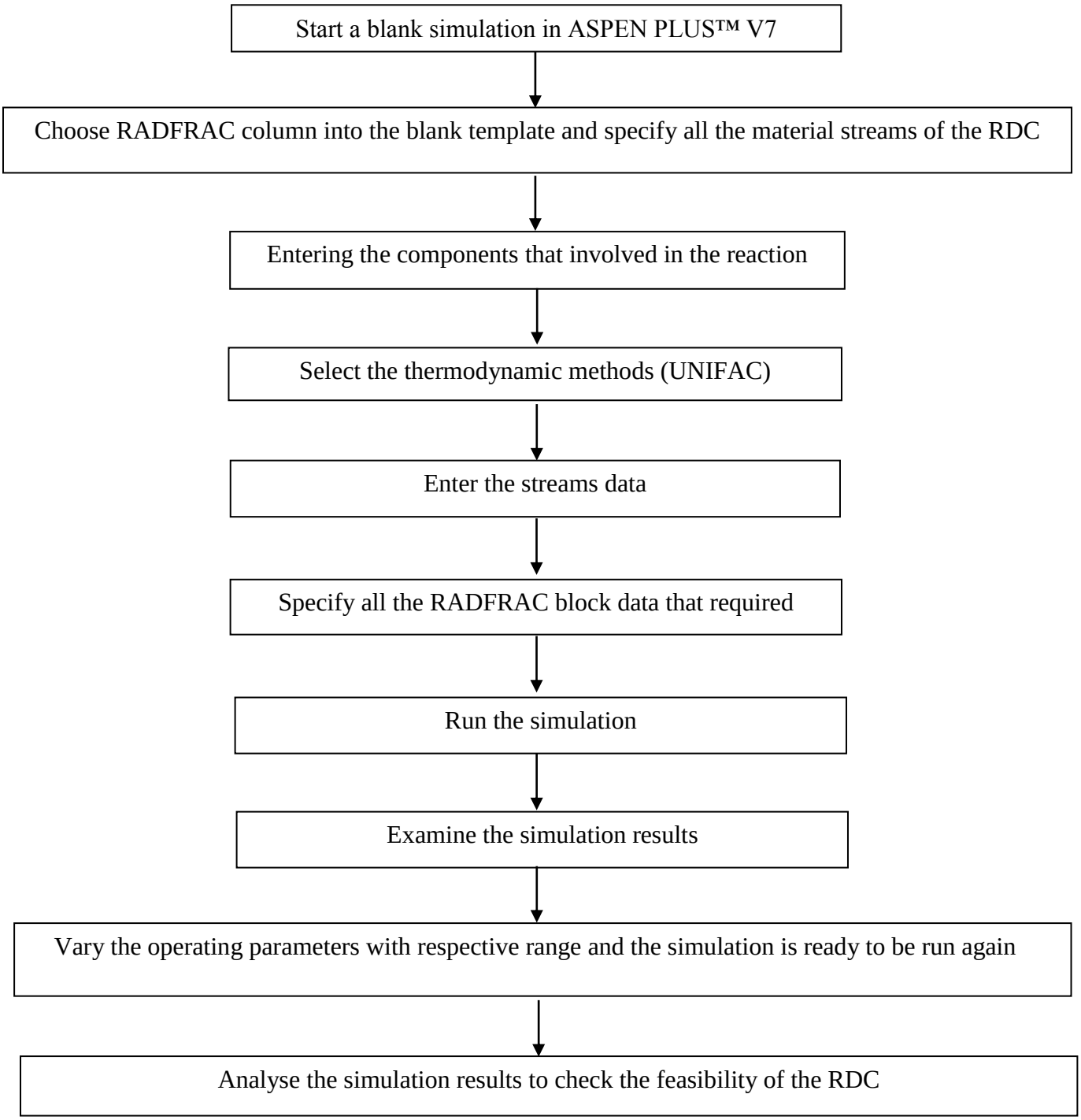


Figure 3. 2: General RADFRAC simulation methodology flowcharts for the reactive distillation process.

Figure 3.3 shows the selection of RD model into the blank flowsheet. To start the simulation, RD block was chosen from the column tab at the bottom of the Aspen Plus process flowsheet window. The RD block was moved into the blank flowsheet and clicked in. After that, the 'material stream' box which located at the bottom left corner of the window was clicked. There were two feed streams and two product streams were

connected to the RADFRAC block. Red and blue arrows were appeared at the RD block. The red arrow represents a stream that required for a design specification; blue arrow represents an optional stream. After finished for defining the flowsheet, the NEXT input button was clicked to continue with the components input.

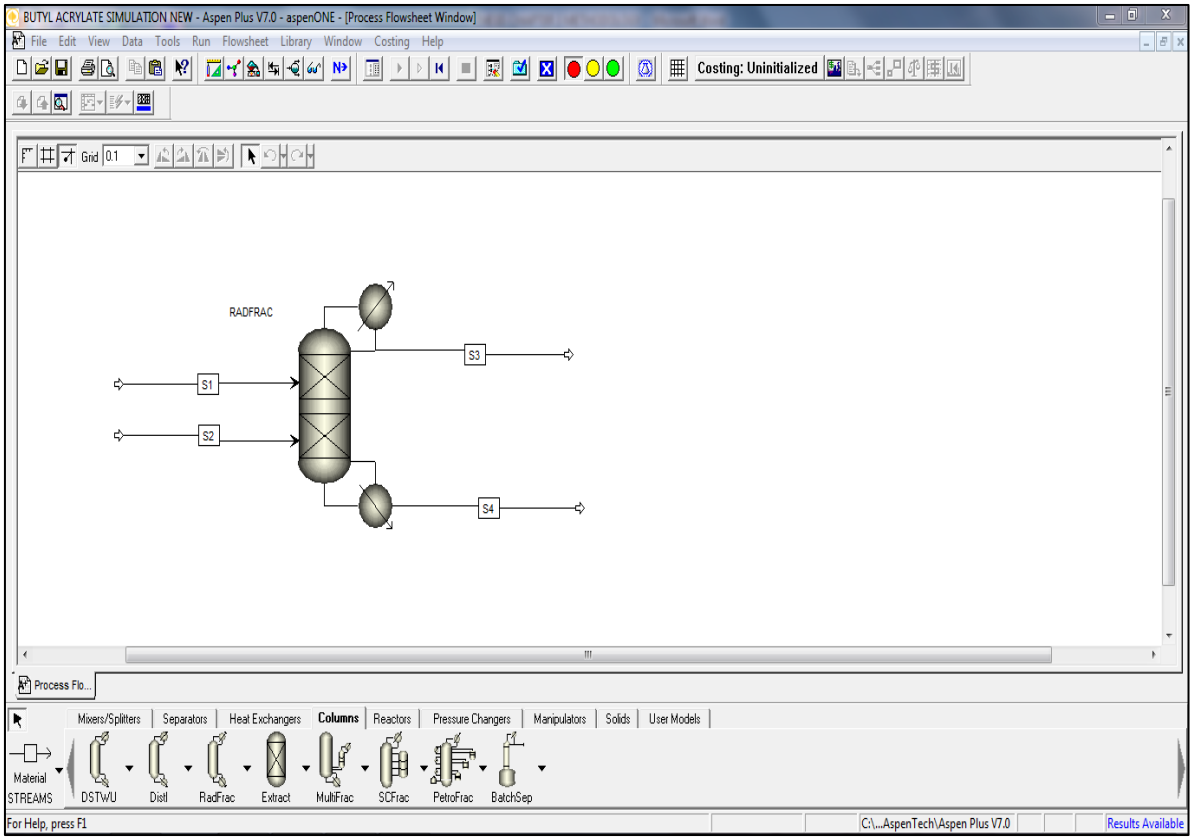


Figure 3. 3: Defining the flowsheet in Aspen Plus user interface

Figure 3.4 shows the selection of components that were involved in the esterification process in the reactive distillation column. The components involved for the process in this simulation were 2-ethyl hexanol (EHOH), acrylic acid (AA), 2-ethyl hexyl acrylate (2EHA) and water (H_2O). The selection of components was found out in the 'component specifications' in Aspen Plus. Components EHOH, AA, 2EHA, and H_2O were all available in the software databank.

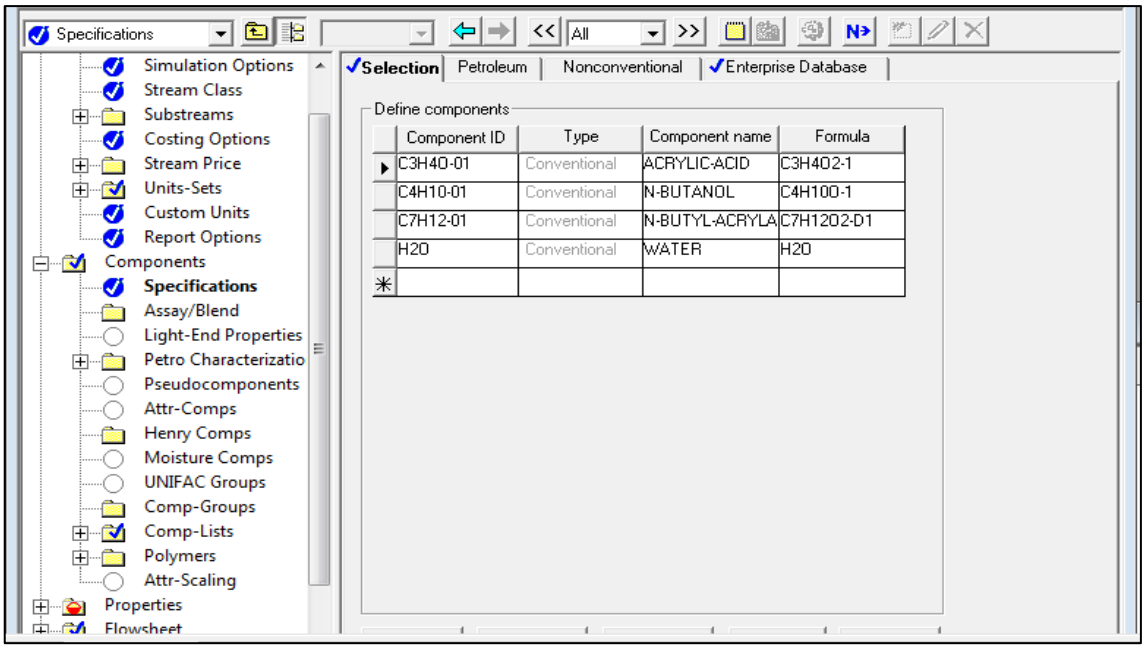


Figure 3. 4: Components| Specification| Selection sheet for entering the involved components in the process.

Figure 3.5 shows the selection of thermodynamic properties of UNIFAC for the esterification system. The selection of thermodynamic model was based on figure 3.6 and figure 3.7. The esterification process of 2-ethyl hexanol and acrylic acid was containing polar component but no electrolytes based on the figure 3.6 and continue with figure 3.7 to predict the thermodynamic property for the simulation. Activity coefficient models are used to accurately predict non-ideal liquid behavior such as vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE). In figure 3.7, simulation pressure less than 10 atm should go for Wilson, NRTL, UNIQUAC and UNIFAC to predict the activity coefficients. UNIFAC model was chosen to estimate the component interactions. UNIFAC was able to predict the activity coefficient as a function of composition and temperature. Besides that, UNIFAC can be used to predict the activity coefficient even when there is no experimental data available for the esterification process (Calson E. C., 1996).

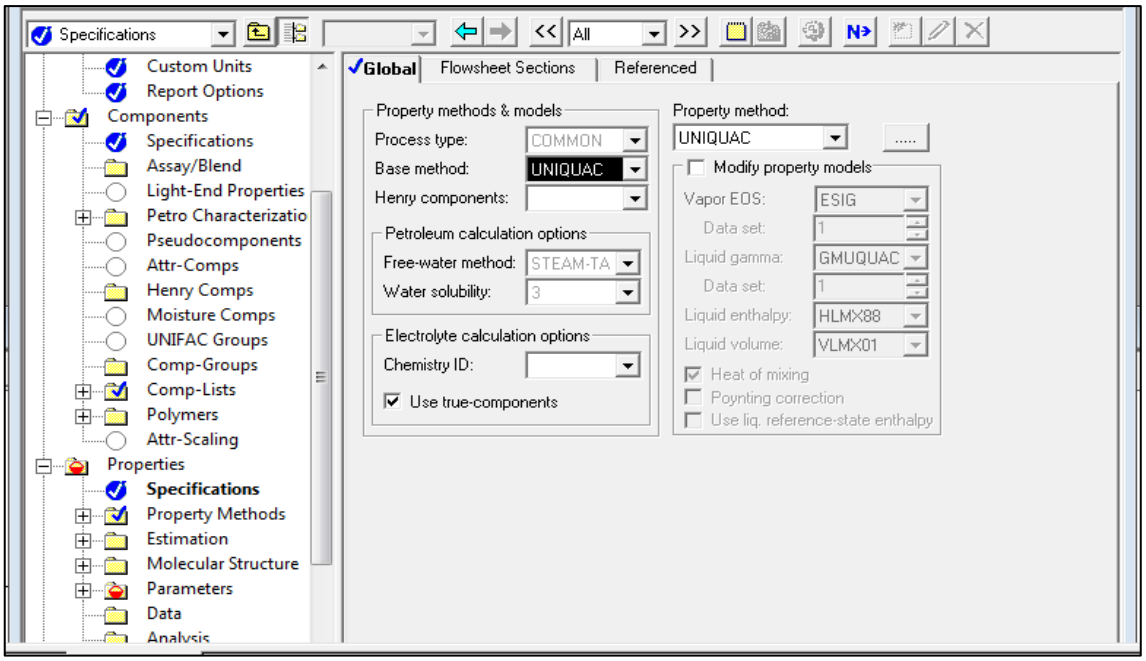


Figure 3. 5: Properties| Specifications| Global sheet for selecting the approporiate thermodynamic method.

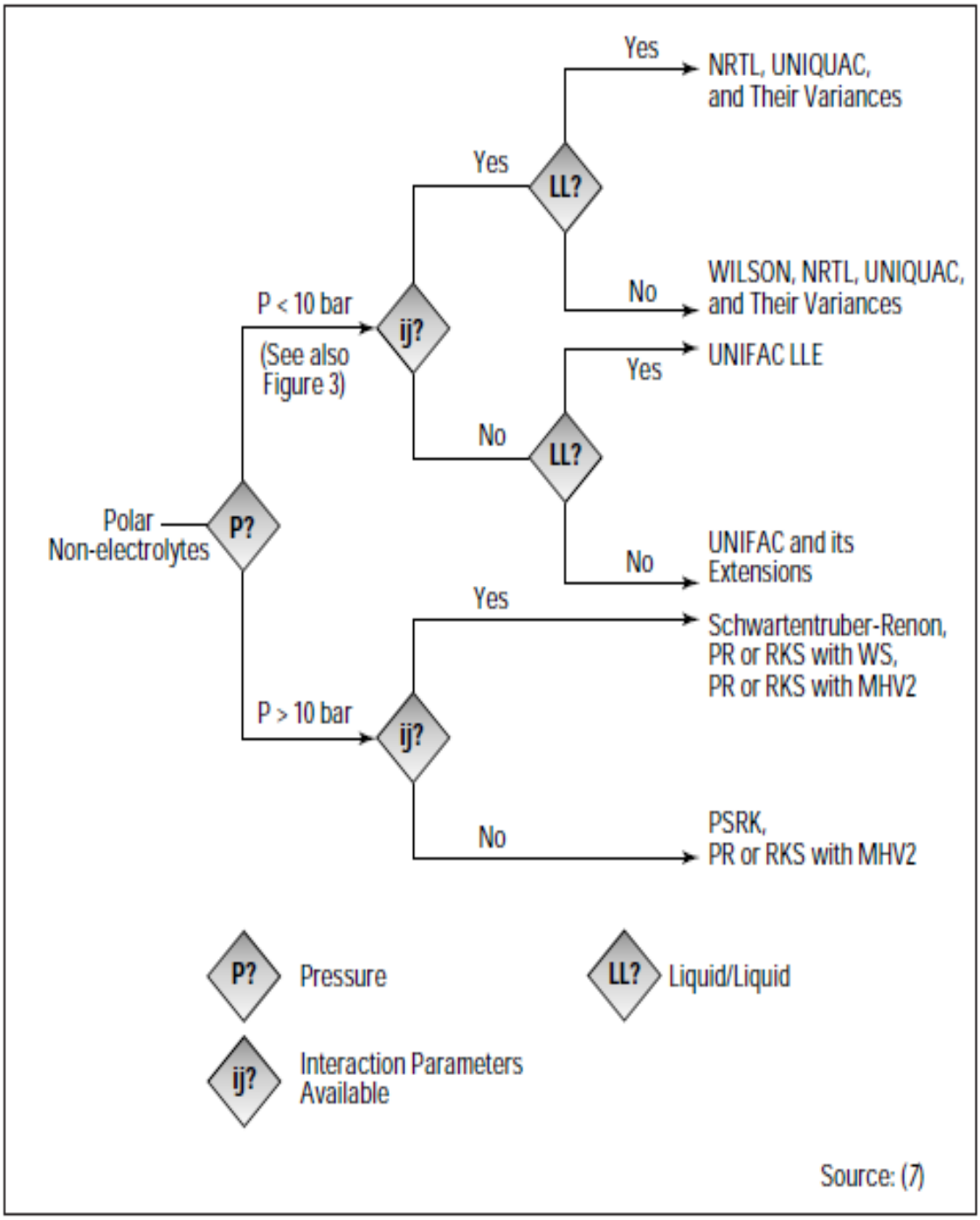


Figure 3. 6: Selection of thermodynamic method based on polar and non electrolyte components

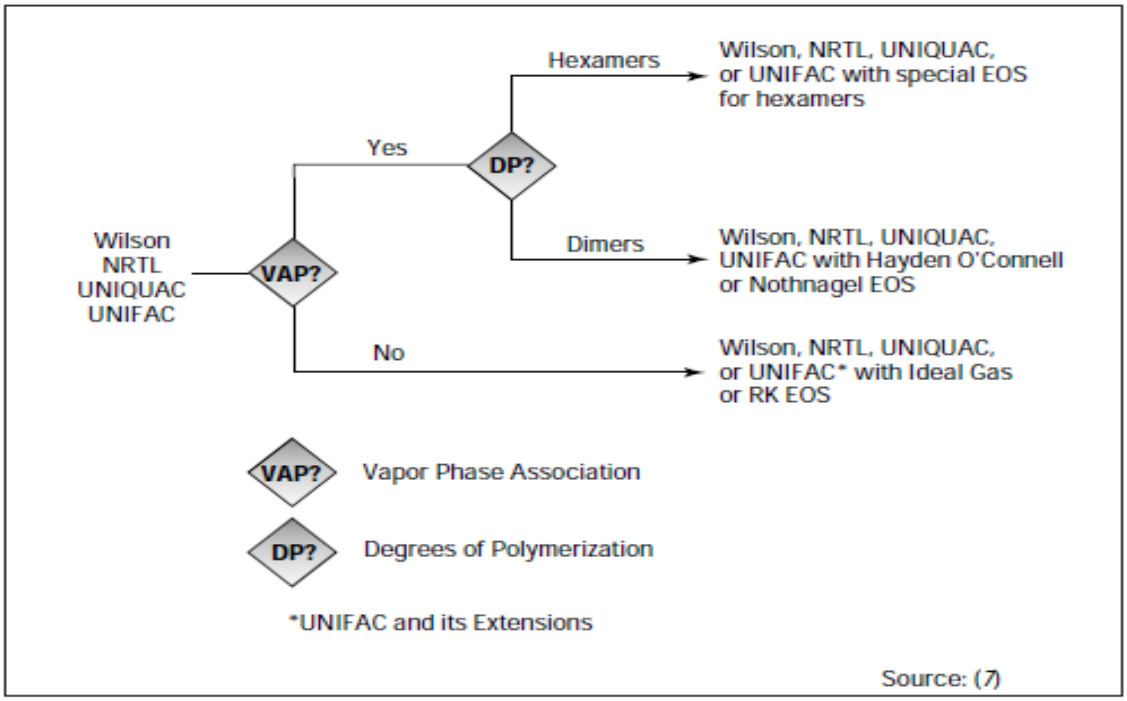


Figure 3. 7: Thermodynamic models for vapor phase activity coefficient models

Figure 3.8 and figure 3.9 show the entering of stream data in 'stream specification. The boiling point of 2-ethyl hexanol is 456K which is higher than boiling point of acrylic acid, 414K. This makes 2-ethylhexanol as a heavy boiling feed and was fed in stream 1 which is above the reactive section. On the other hand, acrylic acid as the light boiling feed was fed in stream 2 which is below the reactive section. The component flow specifications for 2-ethyl hexanol feed stream were entered to the Stream 1 input specification sheet; while the component flow specifications for acrylic acid feed stream were entered to the stream 2 input specification.

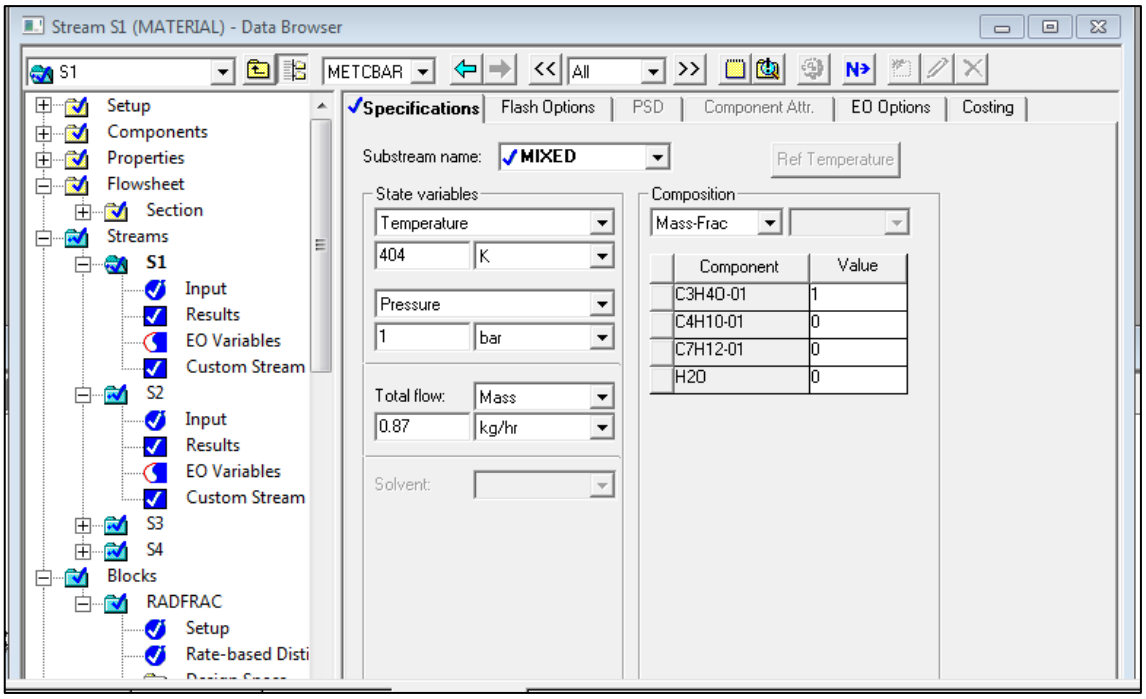


Figure 3. 8: Stream| 1| Input| Specifications sheet for entering the feed 1 (acrylic acid) stream data.

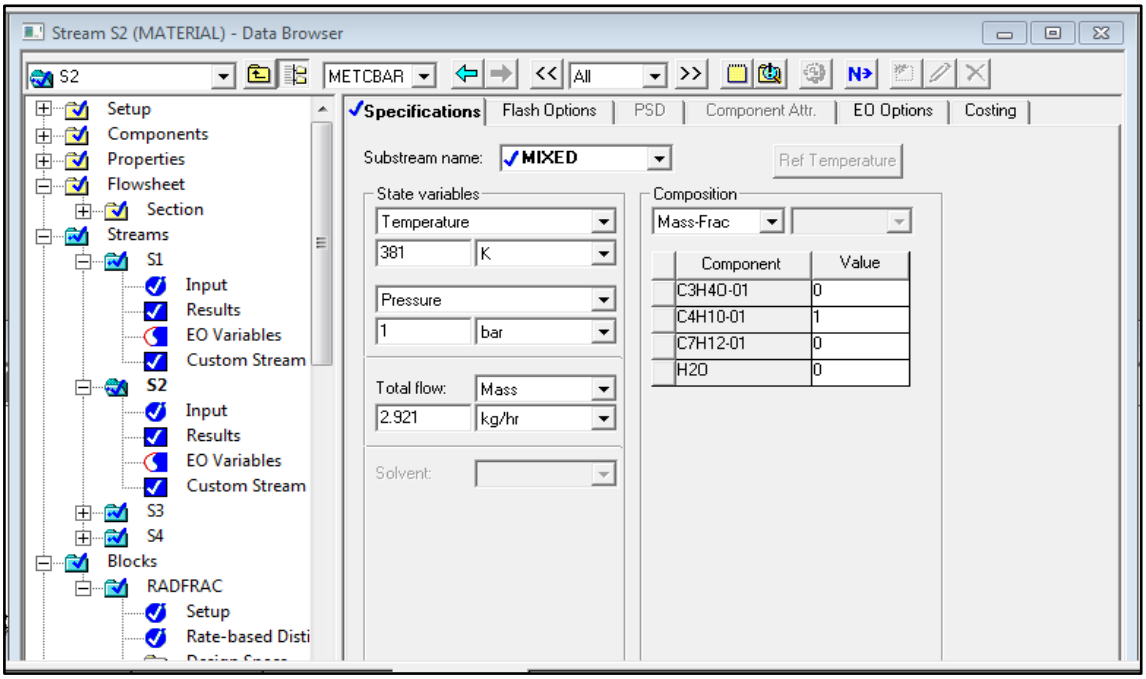


Figure 3. 9: Stream| 2| Input| Specification sheet for entering the feed 2 (n-butanol) stream data.

Figure 3.10 shows entering of RADFRAC block data. In RADFRAC block setup, the number of stages, the condenser type, reflux ratio and distillate rate have to be

entered. A total of 33 stages were present in the reactive distillation column with one condenser type total and a natural circulating reboiler. Meanwhile, the feed stages of 2-ethyl hexanol and acrylic acid were entered to the Stream sheet under Block setup was shown in figure 3.11. In the present study, the top stage pressure of 0.352 bar was entered into the Block setup for pressure sheet which shown in figure 3.12

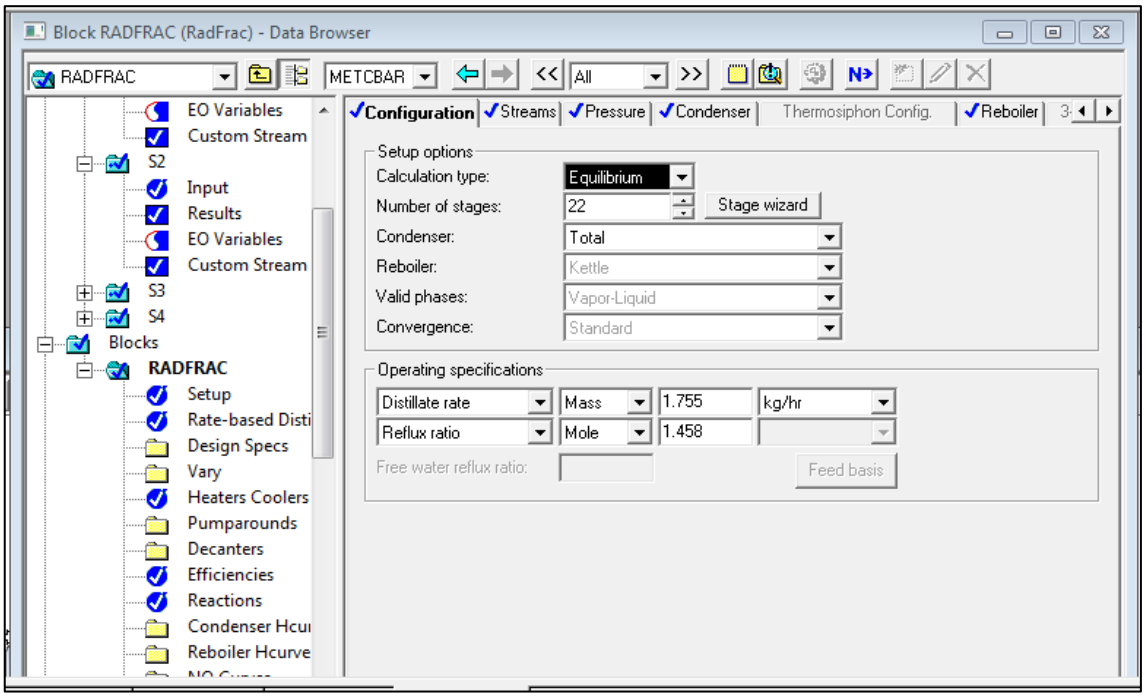


Figure 3. 10: Blocks| B1| Setup| Configuration sheet for entering the setup options and operating specifications

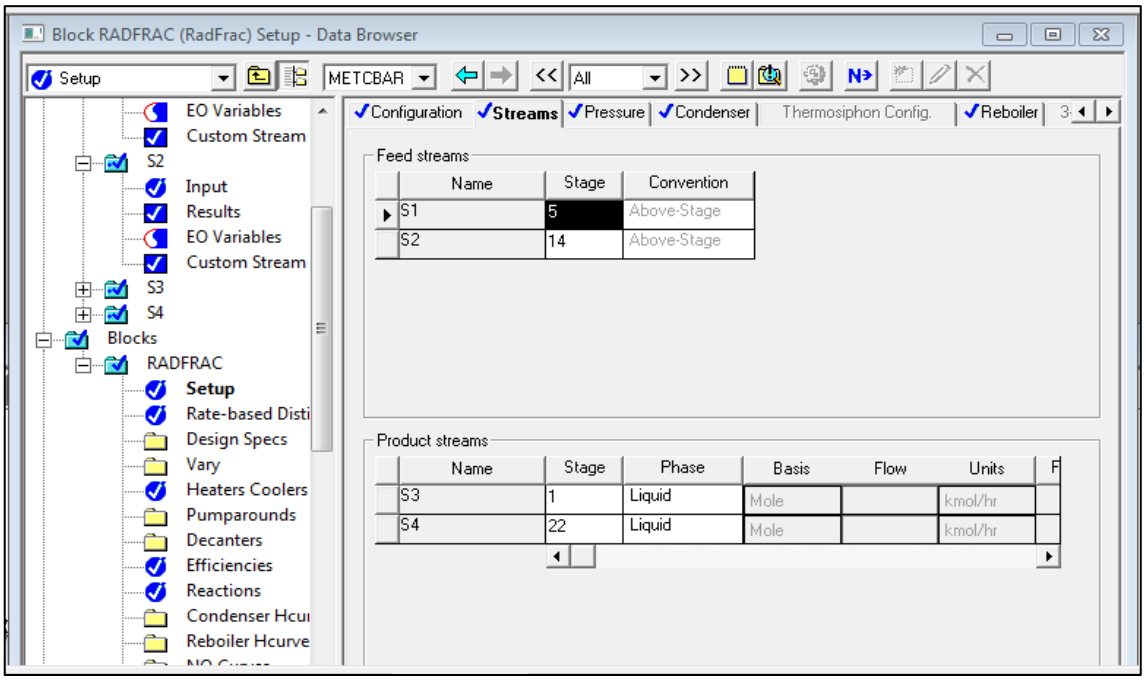


Figure 3. 11: Blocks| B1| Setup| Streams sheet for entering the feed to the column

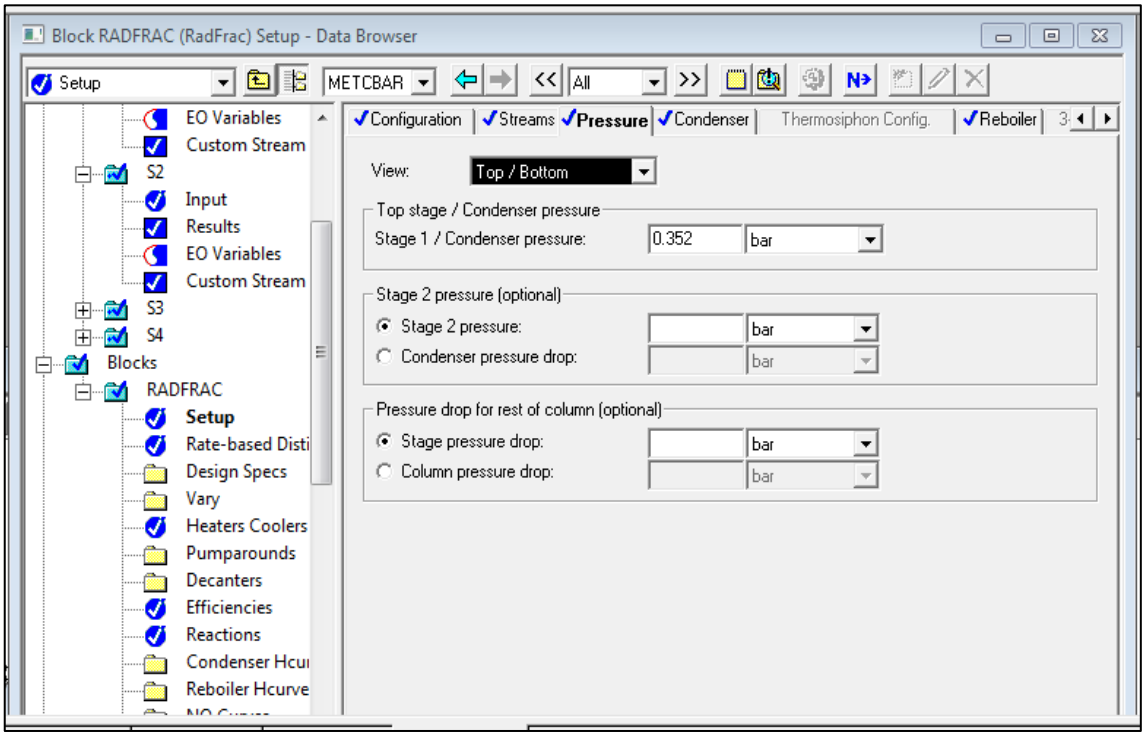


Figure 3. 12: Blocks| B1| Setup| Pressure sheet for entering the operating pressure

Figure 3.13 and figure 3.14 show the incorporation of *k* model in Aspen Plus. The kinetic model for the reaction was entered in the reaction box. The type of reaction model used is based on Power Law rather than LHHW kinetics. The important data need to insert in the reaction box are (i) Chemical reaction for esterification of 2-ethyl hexanol and acrylic acid, (ii) Pre-exponential factor (k_o)and (iii) Activation energy (E_a). The stages for the reactive section in the RDC and the holdup were entered in the Block reaction sheet. After finished, the simulation was ready to run.

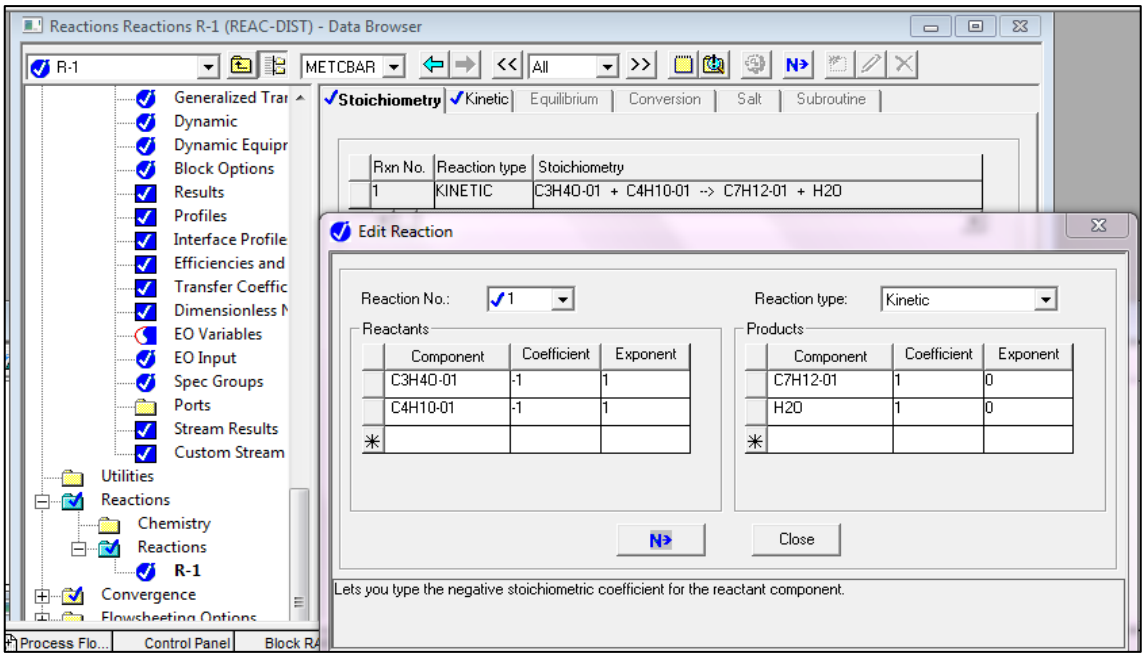


Figure 3. 13: Reactions| Reactions| R1| Stoichiometry for specifying the stoichiometry of the esterification of acrylic acid and n-butanol

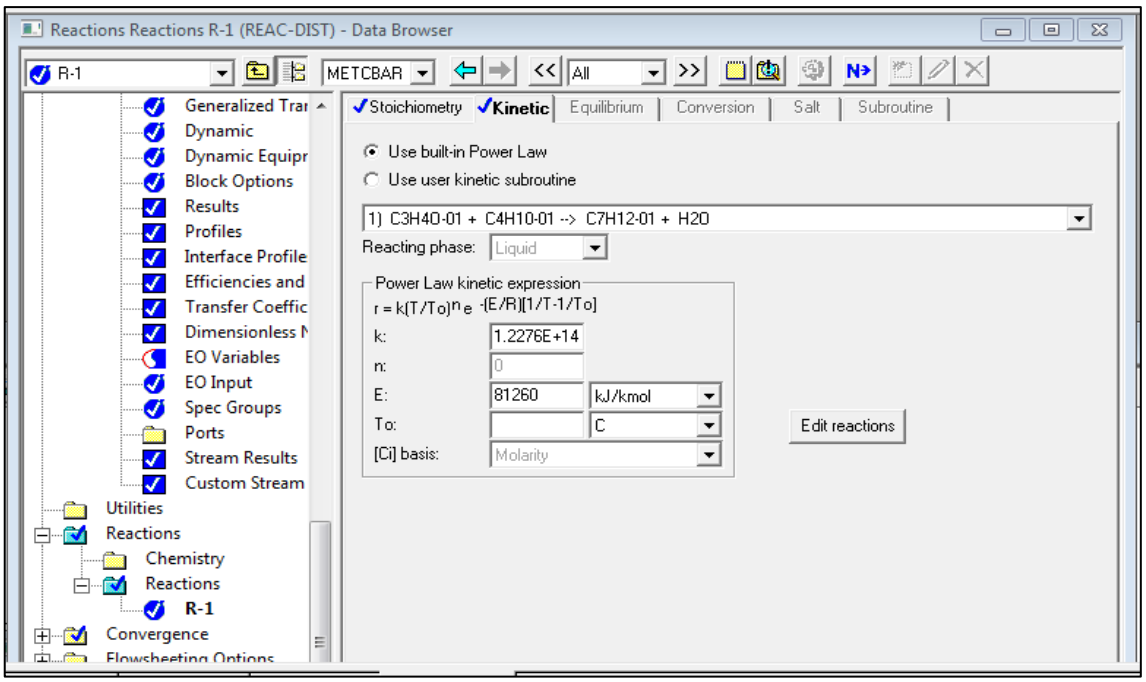


Figure 3. 14: Reactions| Reactions| R1| Kinetic for the esterification of acrylic acid and n-butanol

Figure 3.15 and Figure 3.16 show the result obtaining from the simulation. Figure 3.15 and figure 3.16 represents the liquid composition profile and temperature profile respectively. The effect of several important operating parameters such as concentration

of AA feed, reflux ratio, bottom rate, catalyst weight and column configuration were studied by varying these parameters in the respective input specification sheet. The simulation was then rerun with the changed input in order to obtain the new results.

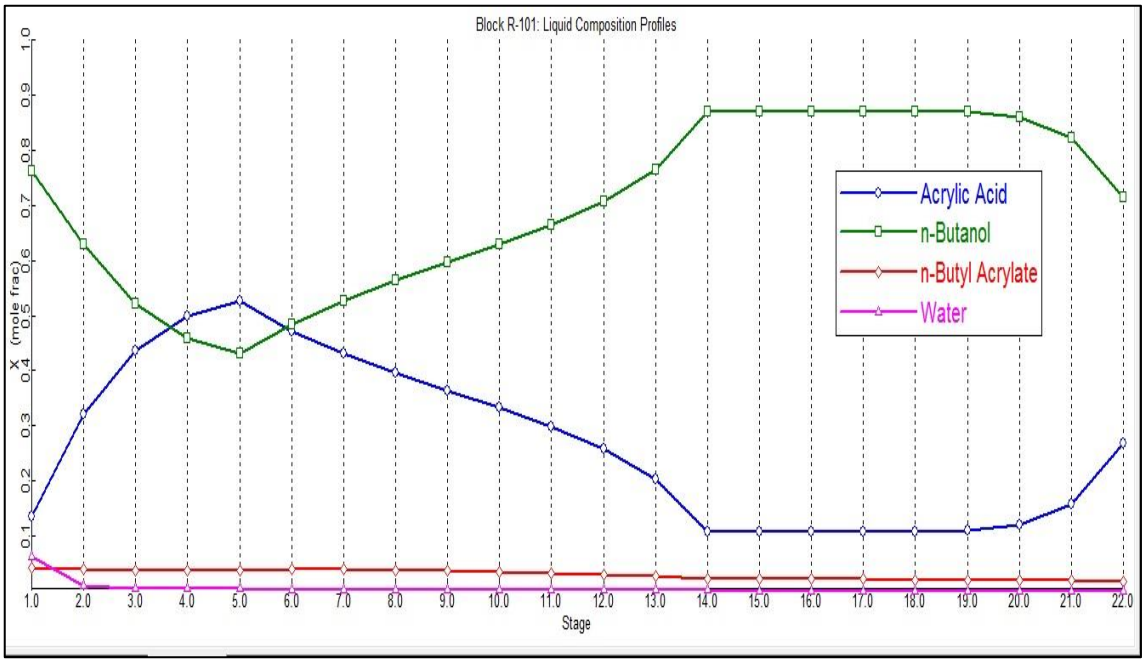


Figure 3. 15: Liquid composition profile for esterification of acrylic acid and n-butanol.

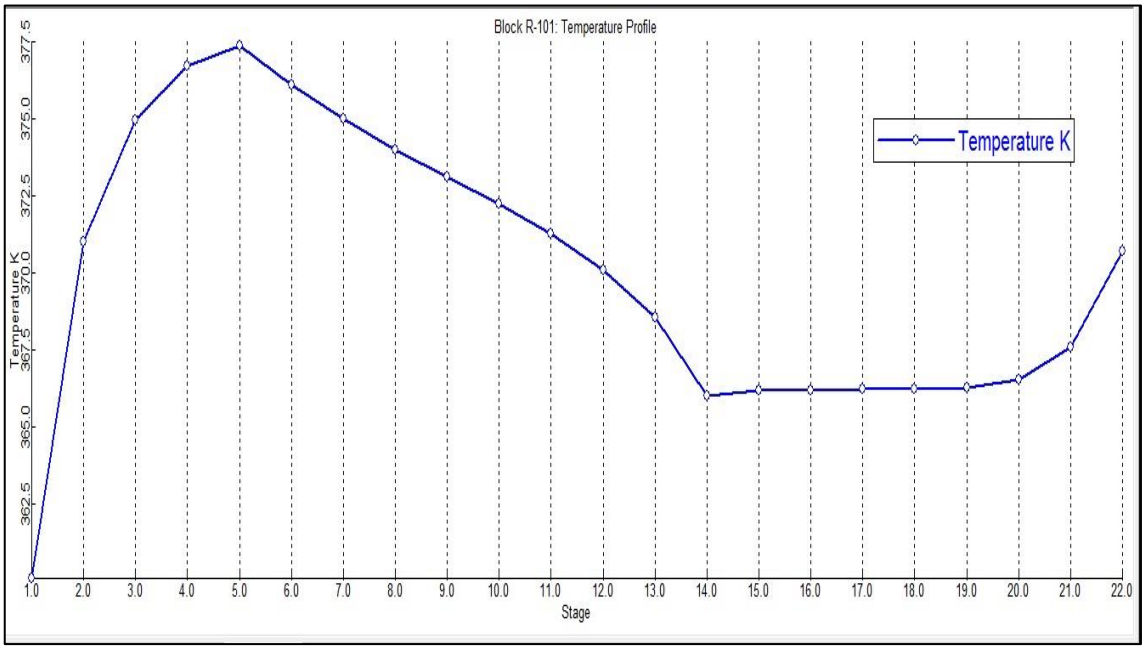


Figure 3. 16: Temperature profile for esterification of acrylic acid and n-butanol

4 RESULTS AND DISCUSSION

4.1 Overview

This chapter discusses the simulation results of the reactive distillation column (RDC) for the esterification of acrylic acid with 2-ethylhaxanol. Since RDC has yet to be applied for the production of 2-ethyl hexyl acrylate and no literature can be found on this topic, the validation model was done using the esterification of acrylic acid and other alcohols before the RDC model was used for the present simulation study. A validated RD model incorporated with appropriate thermodynamic and kinetic models was then used to simulate the esterification reaction at different operating parameters. The effect of concentration of acrylic acid, reflux ratio, bottom rate and catalyst weight are discussed in this chapter. Besides that, optimum column configuration was decided for the production of 2-ethylhexyl acrylate for this present work.

4.2 Introduction

A validation of model for esterification of acrylic acid and other alcohols was carried out in this research study as a preliminary check for the model's validity for esterification system. The esterification of acrylic acid and n-butanol in a pilot scale reactive distillation column in the literature by Niesbach *et al*. (2012) was taken into the account as a model for validation. In that literature, the past researchers were performing the esterification process in a pilot scale RD column catalyzed by heterogeneous catalyst. The column is made of glass. It has a nominal diameter of 50 mm and total height of the column is 12 m. The column is partitioned equally into six sections; each two sections for rectifying, stripping and reactive section respectively. Sulzer BX separation packings were used for the top and bottom of the column, while the two sections in the central where contained with reactive packing Sulzer Katapak SP-11with immobilized catalyst Amberlyst 46. The characteristic of pilot scale RD column was presented in the Table 4.1.

Table 4. 1: Characteristic of Pilot Scale RD Column.

Column diameter	50mm
Position of acrylic acid feed (Above the reaction section)	3.5 mm
Position of n-butanol feed (Below the reaction section)	1.3 mm
Inhibitor solution feed	Above condenser
	2.2 m
Height of rectifying section	
Height of reactive section	2.2 m
Height of stripping	1.3 m
Mass of dry catalyst per meter reactive packing	0.205 kg m^{-1}
Condenser type	Total
Reboiler type	Naturally circulating evaporator
Operating top pressure range	0.3-0.4 bar

4.3 Model Validation

The simulation for esterification of acrylic acid and n-butanol was performed using Aspen Plus version 7.0 incorporated with UNIQUAC thermodynamic model. An equilibrium stage model which also known as RADFRAC that in built in Aspen Plus V.7 was used to simulate the reactive column. To run the simulation, input data fed into Aspen Plus was based on the experimental run no. 7 from Nieshbach *et al*. (2012). The results obtained from the simulation were presented in Figure 4.1.

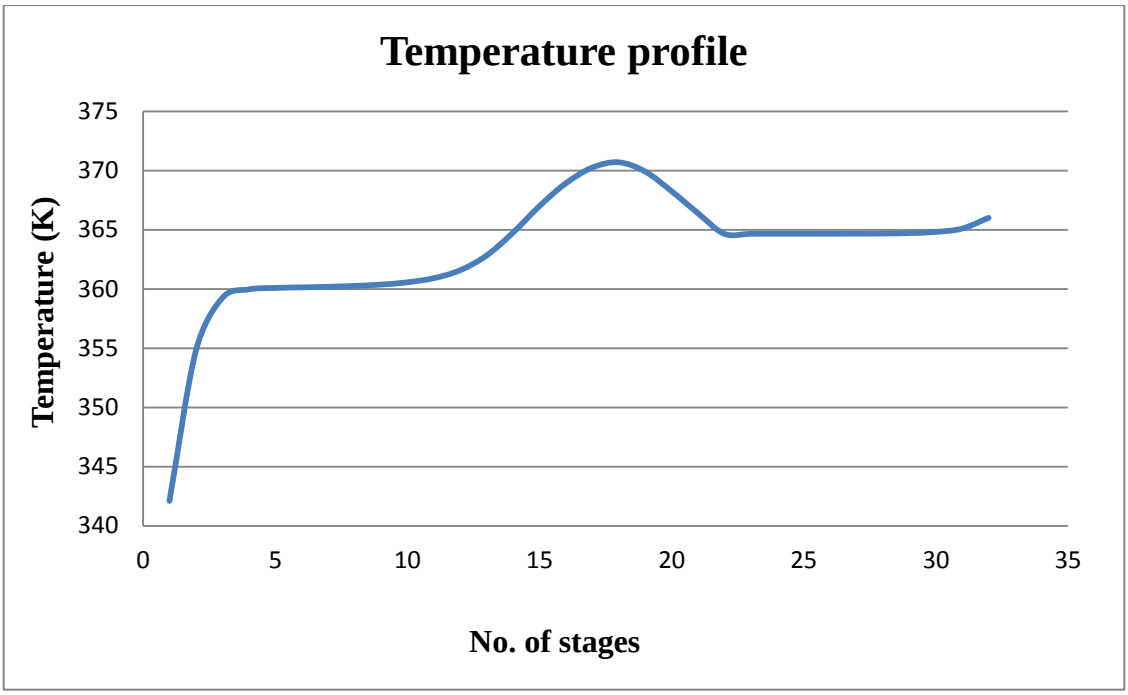


Figure 4. 1: Temperature profile for the esterification of AA with n-butanol.

Figure 4.1 shows the temperature profile for the simulation run for experimental no. 7. The validation model was carried out by comparing the experimental and the simulation results. The simulation was done based on 33 number of RDC stages which consisted of 5 reactive stages, 10 stripping stages, 16 rectifying stages and each stage of condenser and reboiler. Four points in the liquid composition profile are chosen for comparison with the experimental results. The first point was taken from the reboiler stage at 1, continue by the second and third point were taken from the reactive stage at 18th and 22nd respectively and the last point was taken from the condenser stage at 33th for comparison. Table 4.2 compared the experimental results and simulation results obtained and the errors were also calculated. The error is calculated based on the equation below:

$$\text{Error (\%)} = \frac{Predicted - Experimental}{Predicted} \times 100\%$$

Table 4. 2: Comparison of experimental and simulation results

Section	**No. of stage**	**Experimental (K)**	**Simulation (K)**	**Error (%)**
Rectifying	1 (Condenser)	357.0	342.1	4.4
Reactive	18	365.0	370.7	1.5
	22	371.0	364.7	1.7
Stripping	33 (Reboiler)	373.0	368.9	1.1

From Table 4.2, it is found that the simulation results do not deviate much form the experimental results. The temperature of the rectifying section deviates the most from the experimental data with error of 4.4%. Both points at stage no.18 and no. 22 taken from the reactive section do not deviated much with the error of 1.5 and 1.7 respectively. The temperature at the reactive section was maintained to accommodate the thermal stability of the catalyst used in the column. The catalyst used in this system is Amberlyst 45 with the thermal stability of 393.15K. The last point was taken at the last stage of the column where the reboiler located with the error of 1.1% with respect to the experimental data.

As a conclusion, the deviation of the results is observed to be small in the present study. The error mainly came from the equilibrium stage model not accounting transport phenomena. However, overall comparison of reported n-butyl acrylate pilot plant data and simulation data show a reasonable agreement. Thus, the validation model was checked to be valid for other esterification system and is suitable to run the present study of esterification with acrylic acid and 2-ethylhexanol. The simulation study was run in ASPEN PLUS V.7 to further understand the effects of other operating variables such as acrylic acid concentration, reflux ratio, bottom rate, and catalyst weight to obtain the optimized configuration of the RDC for the production of 2-ethyl hexyl acrylate.

4.4 Esterification System of 2-Ethyl Hexyl Acrylate Production

4.4.1 Effect of Acrylic Acid (AA) Concentration

According to Singh (2006), the recovery of acetic acid by esterification reaction in a RDC is effective to give a high value of ester. AA concentration was varied from 10-30% and fed to the RDC for the production of 2-ethyl hexyl acrylate to run the simulation while the other operating condition was remained. Figure 4.2 shows that the AA conversion decreases with the AA concentration in the feed. The reboiler duty required is lesser when the AA concentration increases is shown in Figure 4.3. Figure 4.4 shows the concentration of 2EHOH available in the reactive zone decreases with increasing concentration of AA. It showed that the concentration of 2EHOH at 30wt% feed of AA concentration in the reactive zone is very little. Hence, the conversion of AA in the reactive section also decreases when high concentration of AA fed into the column. The reduced reboiler duty also has resulted a drop in the temperature profile in the reactive zone as shown in Table 4.3 and hence causing low conversion. 10wt% concentration of AA was chosen for the subsequent simulation study since most of the waste water containing AA with the concentration ranged from 4-10wt%.

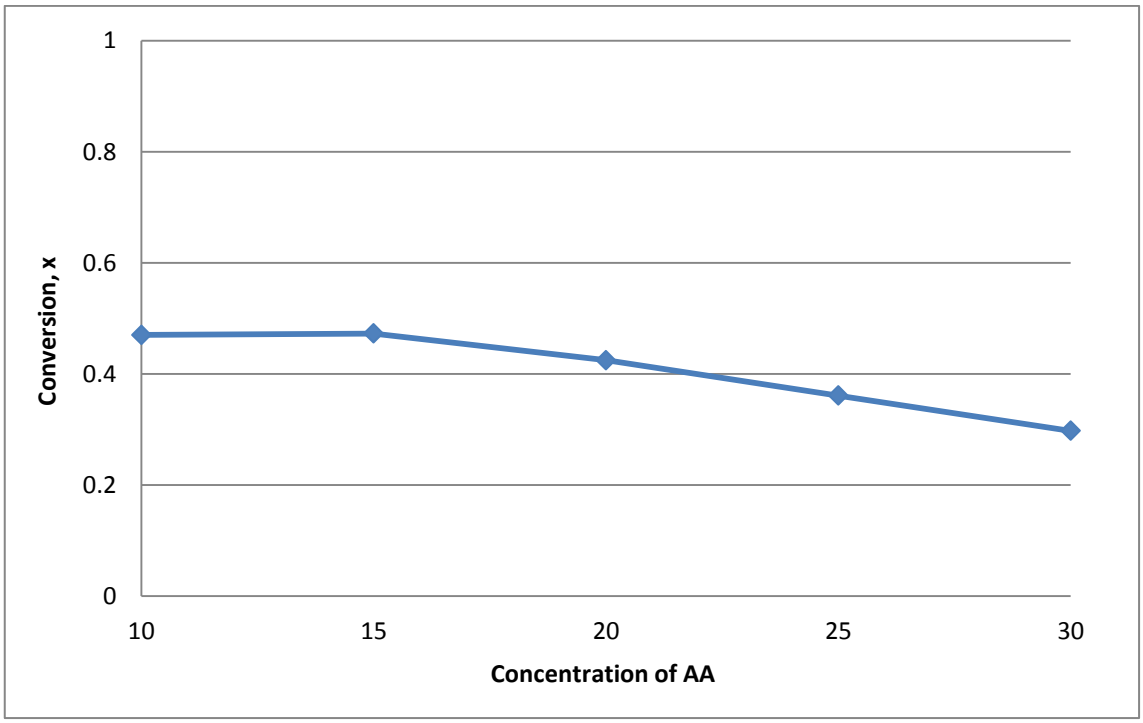


Figure 4. 2: The effect of concentration of AA on conversion of AA at 0.1 reflux molar ratio, 0.01kg/h of bottom rate and 1.5kg/m catalyst weight.

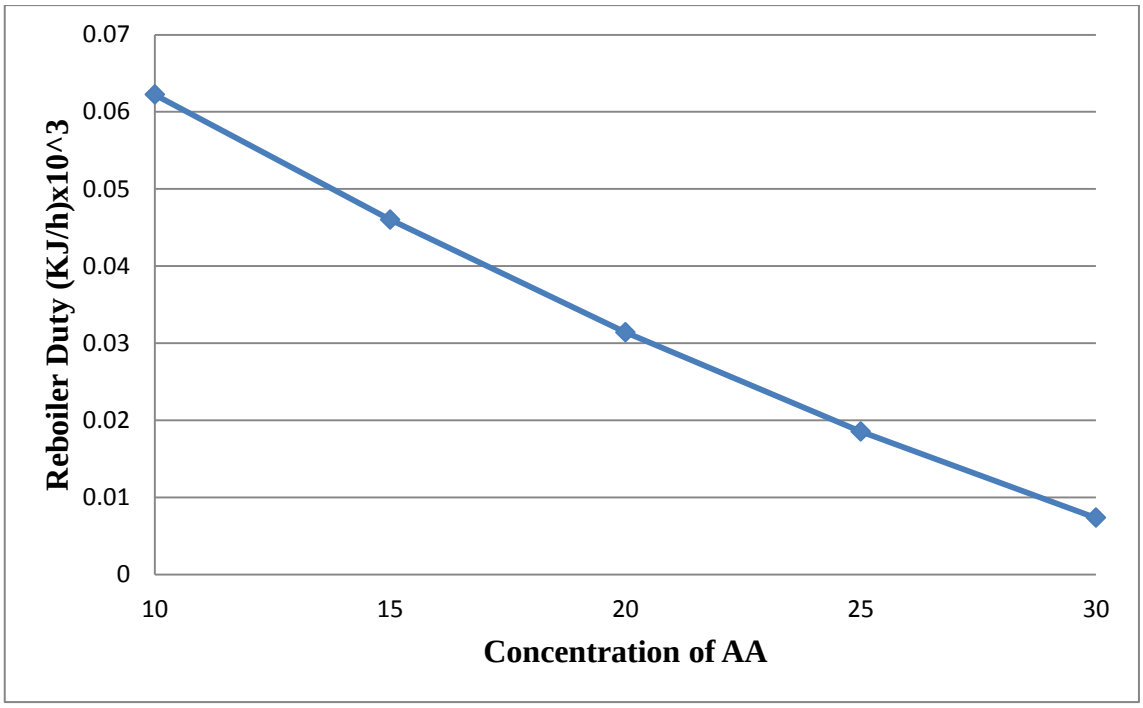


Figure 4. 3: The effect of concentration of AA on reboiler duty at 0.1 reflux molar ratio, 0.01kg/h of bottom rate and 1.5kg/m catalyst weight.

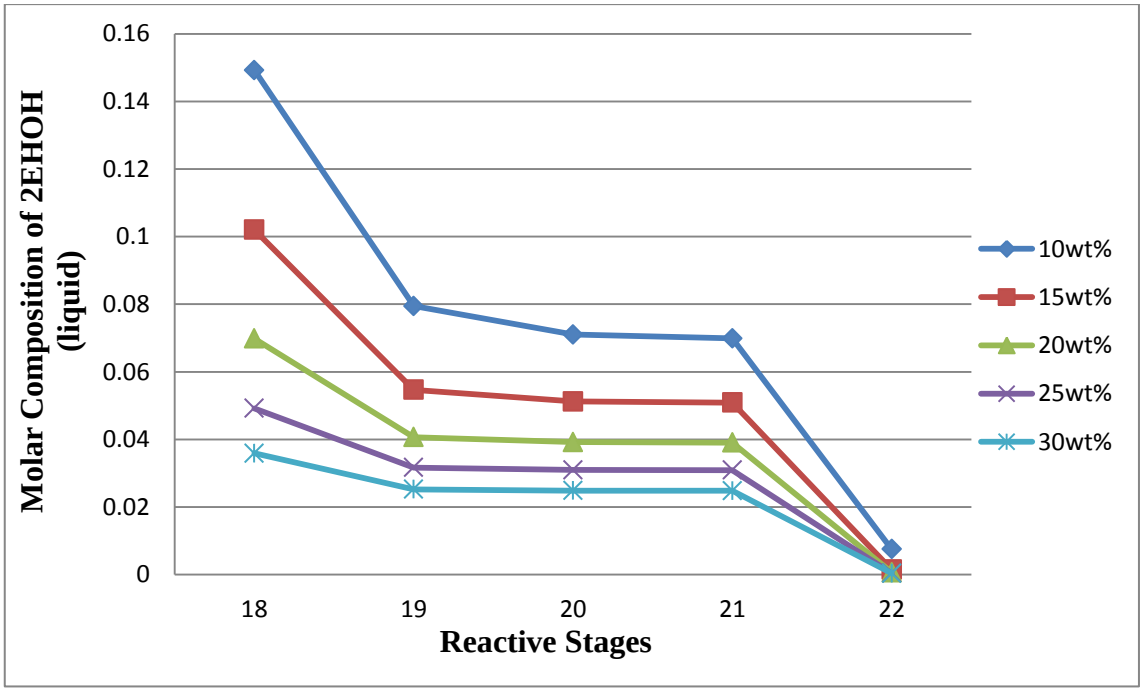


Figure 4. 4: Liquid composition of 2EHOH in the reactive stages at different concentration of AA.

Table 4. 3: Temperature profile for different concentration of AA in the reactive section.

Reactive stage	Temperature at different concentration of AA, ℃				
	10wt%	**15wt%**	**20wt%**	**25wt%**	**30wt%**
18	92.79	93.18	93.19	92.92	92.49
19	93.17	92.69	91.83	90.84	89.82
20	93.31	92.45	91.31	90.06	88.82
21	93.32	92.3	91.17	89.86	88.52
22	172.97	172.21	170.43	167.3	158.39

4.4.2 Effect of Reflux Ratio

Reflux ratio is very important in the RDC as it can help to enhance the separation of product and distillate in the column (Huang *et al*., 2010). The reflux ratio was varied from 0.1 to 0.2 with 0.025 in every increment while other operating conditions such as bottom rate at 0.01kg/h; catalyst weight of 1.5kg/m/m and total number of 33 stages in RDC were remained constant. Figure 4.5 shows that increase of reflux ratio has decreased the AA conversion. According to Schmitt *et al*. (2004), the high reflux ratio in the column has led disadvantage to the separation of the reactant, vaporizing the light component, AA to the top of the column. Hence, the amount of AA present in liquid phase available in the reactive zone is reduced. In Figure 4.6, it shows that the concentration of AA in the reactive zone is decreasing as the reflux ratio increased. When large reflux ratio present in the column, the residence time of AA in the reactive zone is not long enough (Peng *et al*., 2002).This has caused the conversion of AA in the column to drop from 0.47 to 0.28. The maximum conversion of 0.47 is achieved when small reflux ratio of 0.1 is applied to the column. Hence, the decision was made for 0.1 reflux molar ratio for the next simulation study.

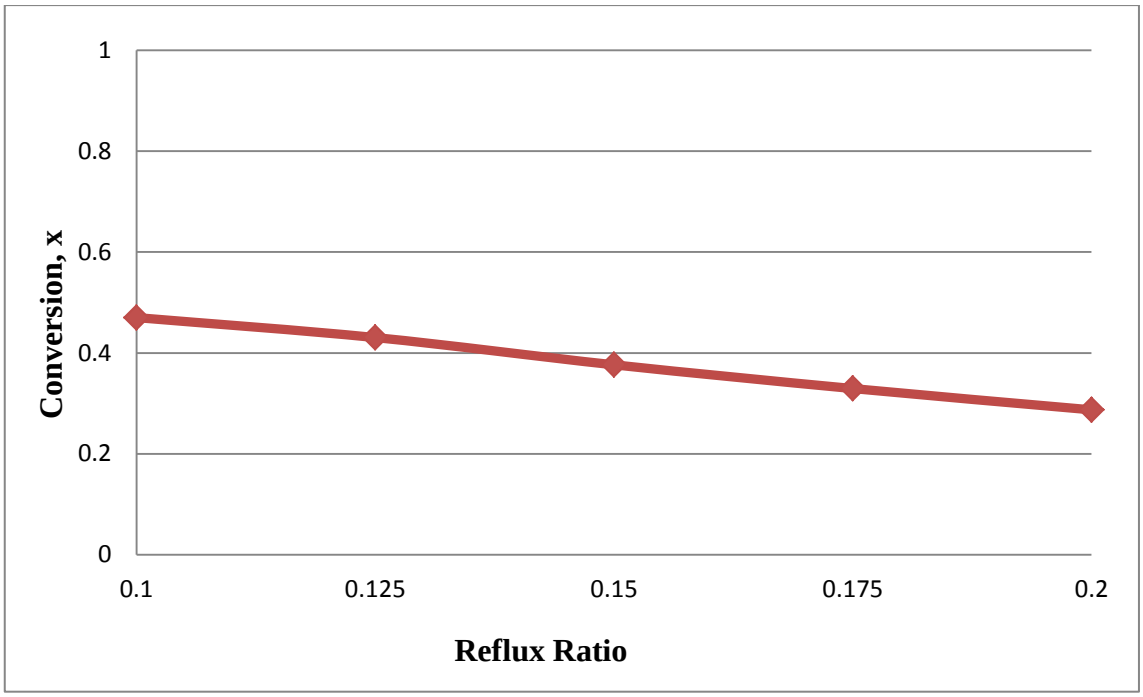


Figure 4. 5: The effect of reflux ratio on conversion of AA at 10wt% of AA concentration, 0.01kg/h bottom rate and 1.5kg/m of catalyst weight.

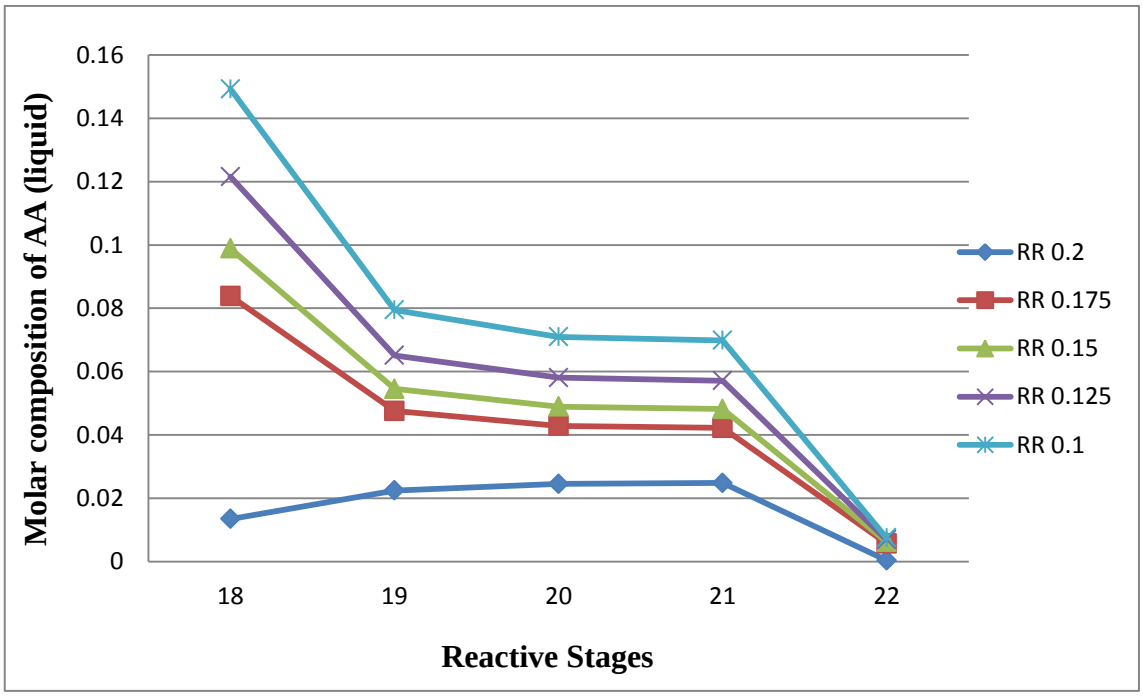


Figure 4. 6: Liquid composition of AA in reactive stages for different reflux ratio.

4.4.3 Effect of Bottom Rate

Figure 4.7 shows the effect of bottom rate on AA conversion. It can be seen that AA conversion increases with the increasing bottom rate. The high bottom rate indirectly related to the decrease in temperature of the reboiler and vice versa. If the column is operated under the low reboiler temperature, most of the liquid 2-ethyl hexanol could be retained in the reactive zone for the reaction with AA to produce 2-ethyl hexyl acrylate. Figure 4.8 has proved that the concentration of 2EHOH available in the reactive zone increases with bottom rate. Thus, the conversion of AA is shown to increase with increasing bottom rates in the column. This is inline with the study of Mueanmas *et al*. (2010) which states that at steady state, the boiling-up rate of light component, which is acrylic acid is determined by the heat load in the reboiler. Besides that, they also found that the lower reboiler temperature is favourable for better reactor performance.

2-ethylhexyl acrylate is separated from 2-ethylhexanol in the stripping section and is collected at the bottom of the RDC. Thus the bottom rate of RDC is not encouraged to set at very low range. Hence, the bottom rate is chosen at the range of 0.01kg/h to 0.13kg/h. The bottom rate of 0.13 kg/h was chosen to continue with the next simulation due to the high AA conversion achieved with the temperature of the reaction zone below the thermal stability of the catalysts used.

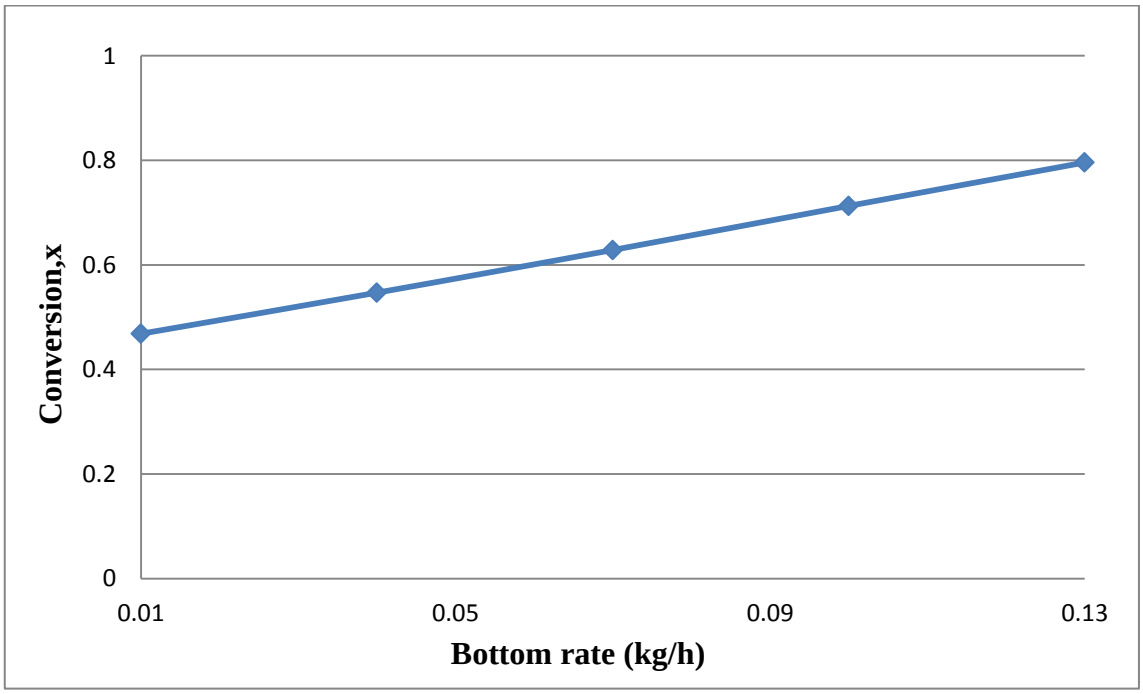


Figure 4. 7: The effect of bottom rate on conversion of AA at 10wt% of AA concentration, 0.1 reflux molar ratio and 1.5kg/m of catalyst weight.

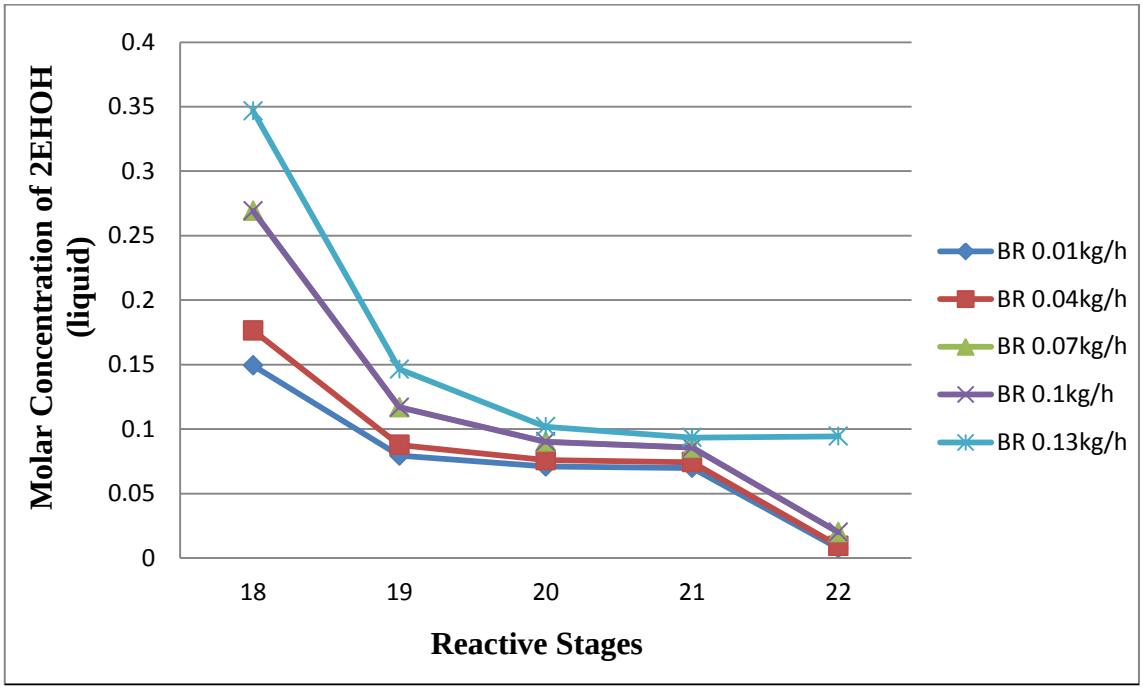


Figure 4. 8: Liquid composition of 2EHOH in the reactive stages at different bottom rate.

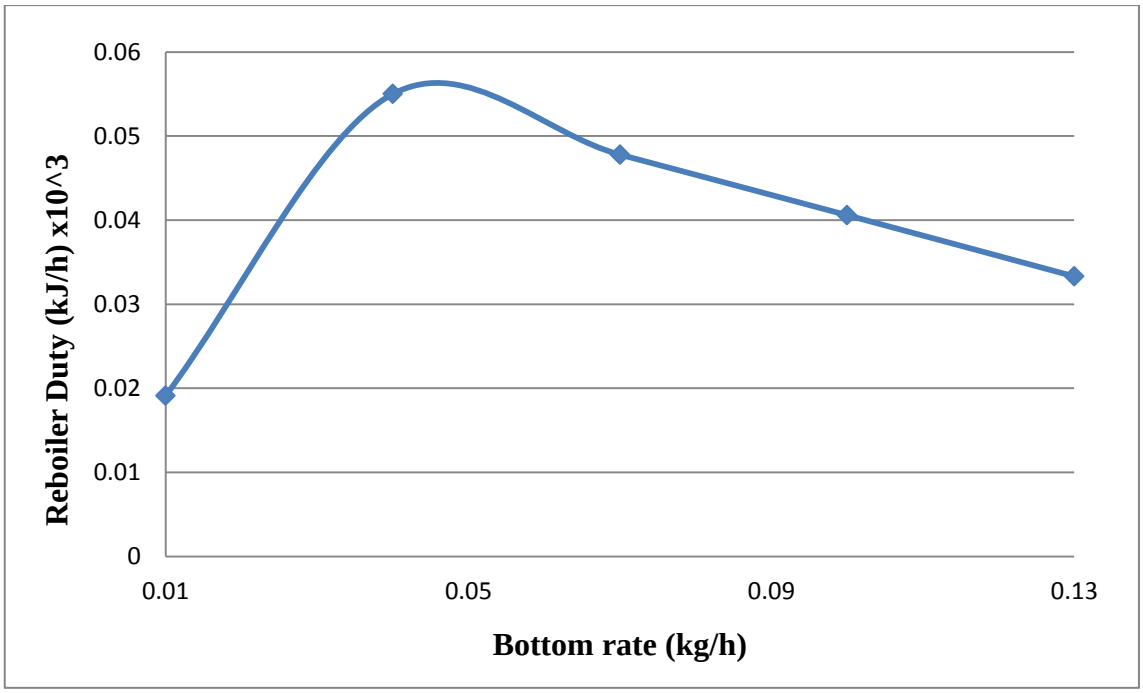


Figure 4. 9: The effect of bottom rate on the reboiler duty at 10wt% of AA concentration, 0.01kg/h bottom rate and 1.5kg/m of catalyst weight.

4.4.4 Effect of Catalyst Weight

The reaction in the RDC is controlled by the amount of catalyst weight in the reaction section. However, Figure 7 shows that there is no significant change on the catalyst weight to the conversion of AA in the column.

Even though the catalyst loading show insignificant effects on the conversion, the conversion of AA reaches the maximum when the catalyst weight is 1.5 kg/m. Figure 4.10 showed the conversion of AA increased from 0.5kg/m of catalyst weight to maximum of 1.5kg/m of catalyst weight; then it decreased when the catalyst weight are higher than 1.5kg/m. This is because the amount of catalyst to the number of active site available for the reaction has reached a saturated condition when the catalyst weight more than 1.5kg/m. Thus, the conversion starts decreasing when the catalyst weight is lower or higher than 1.5 kg/m. Thus, catalyst weight of 1.5 kg/m is used for the subsequent simulation.

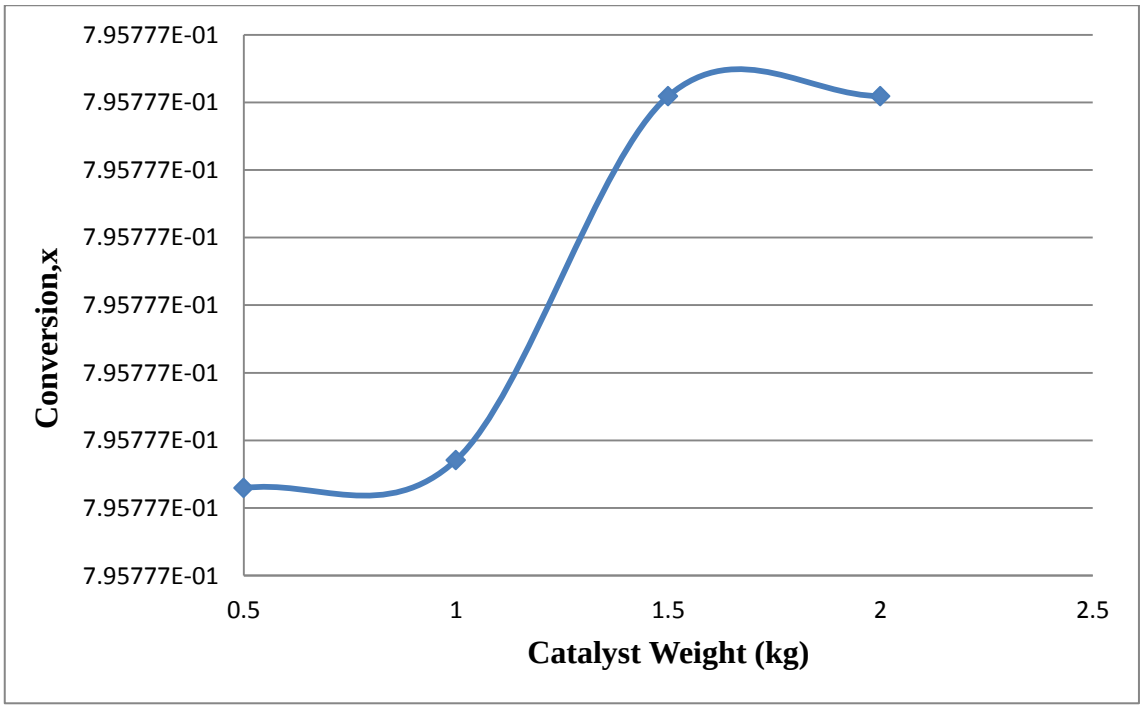


Figure 4. 10: The effect of catalysts weight on conversion of AA at 10wt% of AA concentration, 0.1 reflux molar ratio, and 0.13 kg/h bottom rate.

4.4.5 The Optimum Column Configuration

4.4.5.1 Number of Reactive Stages

In figure 4.11, it can be seen that increasing reactive stages are more favourable for the process since the conversion of AA is increasing. All other design and operating variables such as number of rectifying, stripping stages and optimized feed conditions were kept at the value of the standard condition while the number of reactive stages was adjusted to give high value of 2-ethyl hexyl acrylate. The conversion increases when there are 4 reactive stages and comes to a constant after 4 reactive stages and remain at the maximum conversion of 0.80. For equilibrium limited systems, increasing the number of reaction stages will lead to the enhancement of temperature and concentration which would favour the forward reaction for an endothermic reaction (Hui *et al*., 2012). Therefore, 4 reactive stages were chosen as the best column configuration. According to Steinigeweg and Gmehling (2003), the separation efficiency is crucial for the success of the process since the water has to be removed from the reaction section not only to shift the chemical equilibrium to higher conversions.

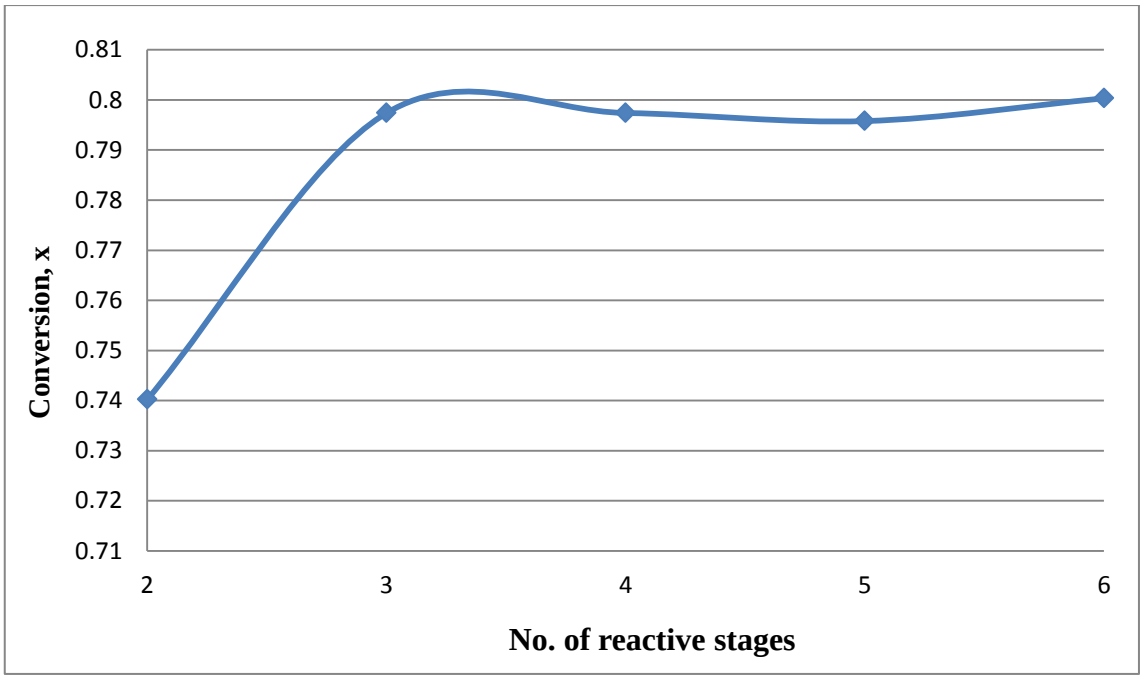


Figure 4. 11: The effect of number of reactive stages on conversion of AA at 10wt% of AA concentration, 0.1 reflux molar ratio, and 0.13 kg/h bottom rate and 1.5kg/m of catalyst weight.

4.4.5.2 Number of Stripping Stages

The purpose of stripping is to maintain favourable reaction conditioned by removing 2-ethyl hexyl acrylate from the reactive zone and purifying the product in the residue (Hui et al., 2012). In the RDC, the number of stripping stages should be adjusted to achieve a satisfactory separation. As more reactants are stripped back to the column for reaction, higher purity of the product can be obtained (Taylor & Krishna, 2000). In Figure 4.12, the number of stripping stages does not affect much on the conversion of AA in the column. However, RDC with 10 stripping stages has given the highest conversion of AA to produce higher purity of product; 2-ethyl hexyl acrylate. Increasing the number of stripping stages decreased the concentration of 2-ethyl hexyl acrylate in the reaction zone, shifting the equilibrium of the esterification forward to the product formation. Thus, it was chosen to optimize the column configuration of RDC.

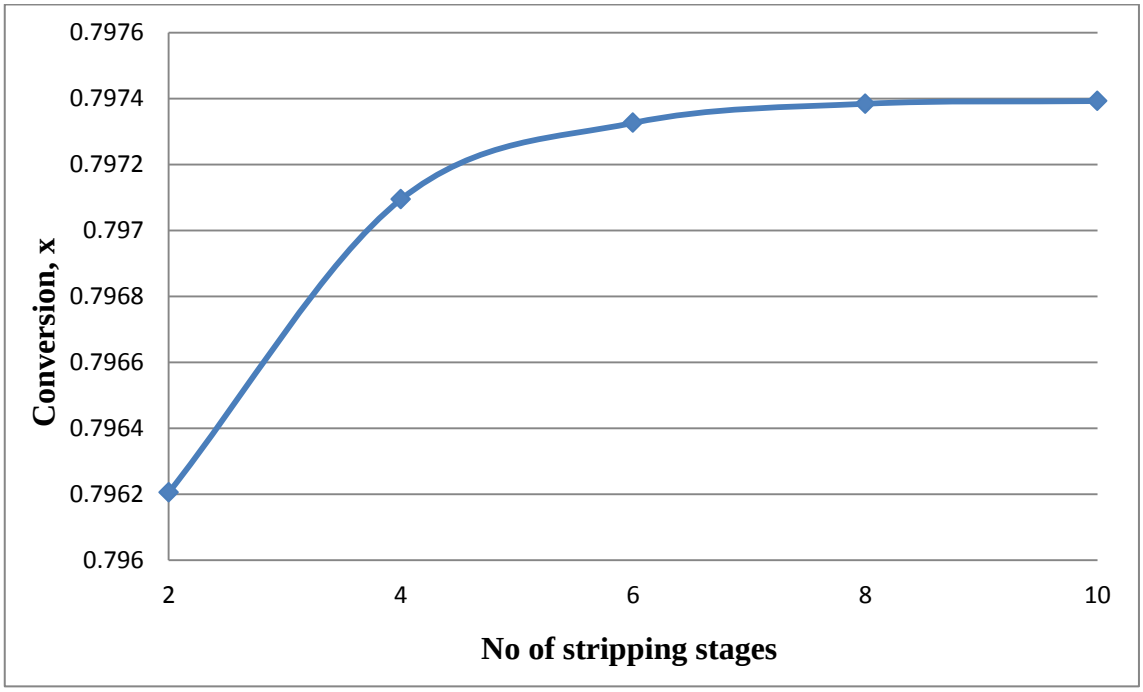


Figure 4. 12: The effect of number of stripping stages on conversion of AA at 10wt% of AA concentration, 0.1 reflux molar ratio, and 0.13 kg/h bottom rate and 1.5kg/m of catalyst weight.

4.4.5.3 Number of Rectifying Stages

The rectifying section of RDC for production of 2-ethyl hexyl acrylate should remove light components from the reactive zone, and recycle back the unreacted reactants back to the reaction section in the RDC (Hui et al., 2012). In Figure 4.13, it is observed that by decreasing the number of rectifying stages in RDC has increased the conversion of AA in the column. This is because it can recover back more 2-ethyl hexanol into the reactive zone for reaction. As an excess of alcohol is present in the column to react with AA, more 2-ethyl hexyl acrylate could be produced at the bottom of the RDC. Figure 4.14 shows the liquid composition of 2EHOH available in the reactive zone at different concentration of AA. Theoretically, with increasing rectifying stages could remove more water and light component from the reaction section (Hui et al., 2012). However, there was a present of azeotrope between water and 2-ethylhaxanol which makes it difficult to fully separate. Hence, the figure shows that 4 rectifying stages enough to achieve high conversion of 0.83.

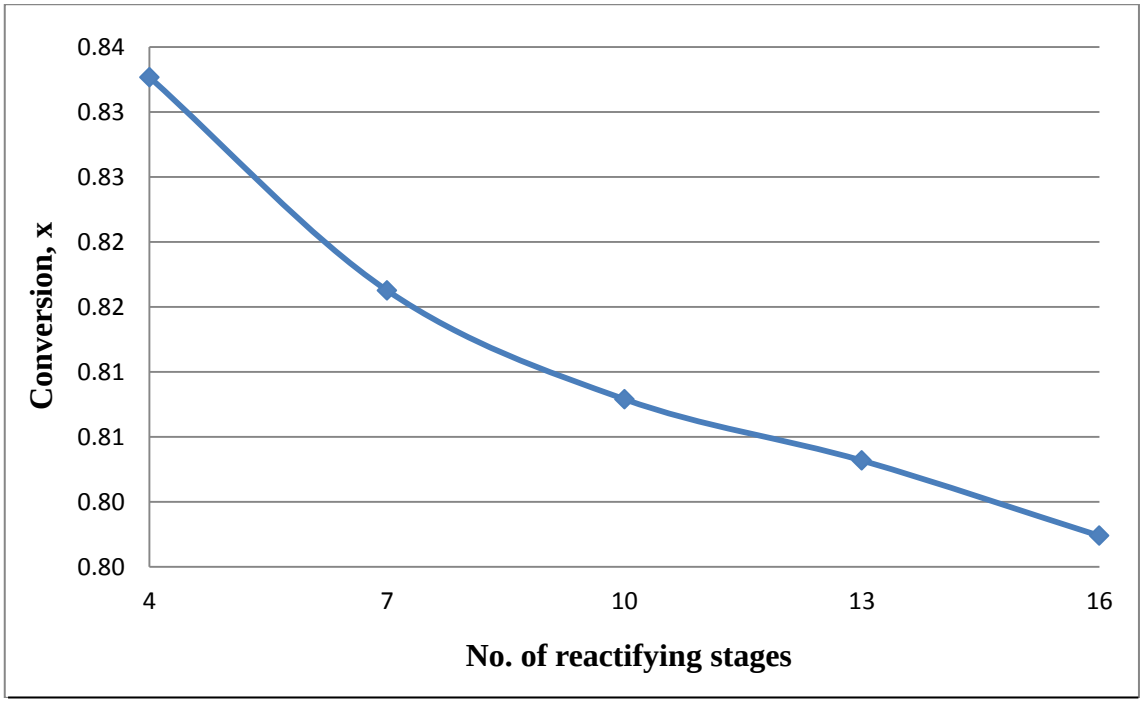


Figure 4. 13: The effect of number of rectifying stages on conversion of AA at 10wt% of AA concentration, 0.1 reflux molar ratio, and 0.13 kg/h bottom rate and 1.5kg/m of catalyst weight.

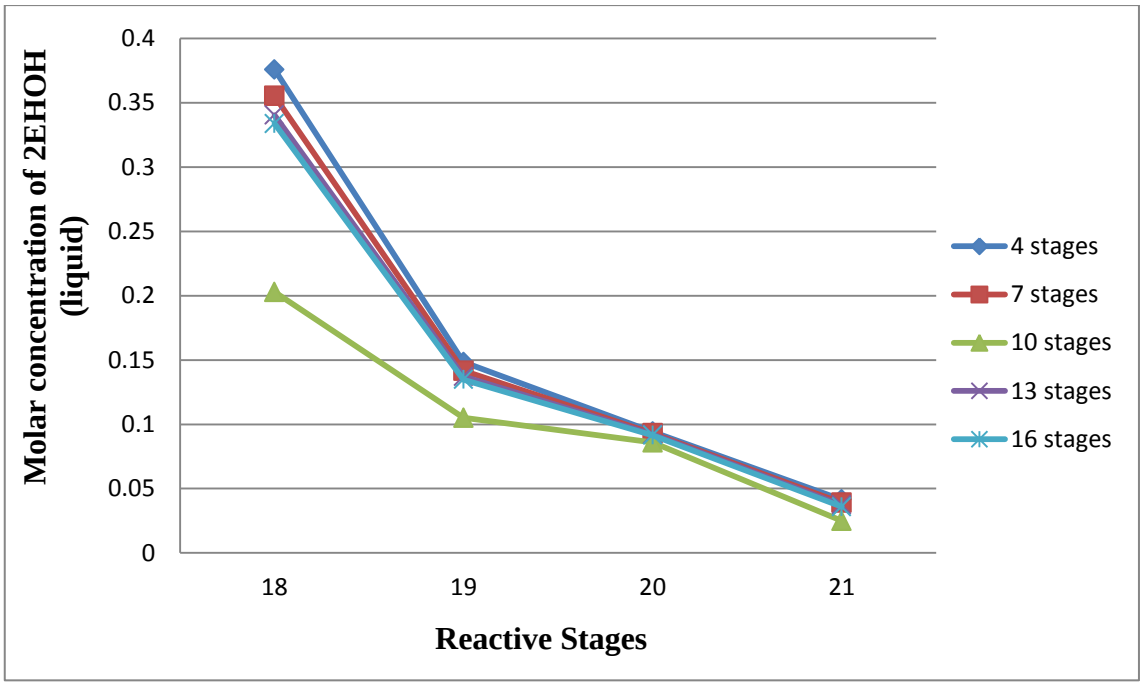


Figure 4. 14: Liquid composition of 2EHOH in the reactive stages at different concentration of AA.

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The reactive distillation column (RDC) is a promising alternative way to recover acrylic acid (AA) from wastewater. The recovery of AA for esterification via a RDC not only can reduce the environment problems but also can produce high value of ester.

The present study shows that the RD process is feasible to be recovered via esterification in a RDC. The study of different effects such as concentration of acrylic acid, reflux ratio, bottom rate and catalyst weight on the RDC for production of 2-ethyl hexyl acrylate were carried out. 10wt% concentration of acrylic acid was chosen for the simulation studies and the reaction was kinetically controlled over the range of operating parameters such as reflux ratio, bottom rate and catalyst weight. Change in bottom rate gives the most effect to the conversion of AA in the column. The conversion of AA increased from 0.47 to 0.79 in the column. The best column configuration of RDC with total of 18 numbers of stages with each stage of condenser and reboiler has yielded the maximum conversion of 83%. It consists of 4 reactive stages, 10 stripping stages and 4 rectifying stages. The maximum conversion of was achieved at a reflux molar ratio of 0.1, bottom rate of 0.13kg/h and catalyst weight of 1.5kg/m.

5.2 Recommendation

The other parameters such as feed location and reactants molar ratio can be studied to maximize the conversion. Further developments also can be done by improving the reactive distillation model by taking adsorption as well as mass transfer into the account of simulating a more realistic RDC. The simulation of RDC suggested to run for non equilibrium RDC model as it could give a more accurate results. Besides that, experimental study on pilot plant for production of 2-ethylhexyl acrylate is recommended so that the simulation results can be validated.

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7 APPENDICES

7.1 The effect of concentration of AA

7.1.1 30wt% of AA concentration

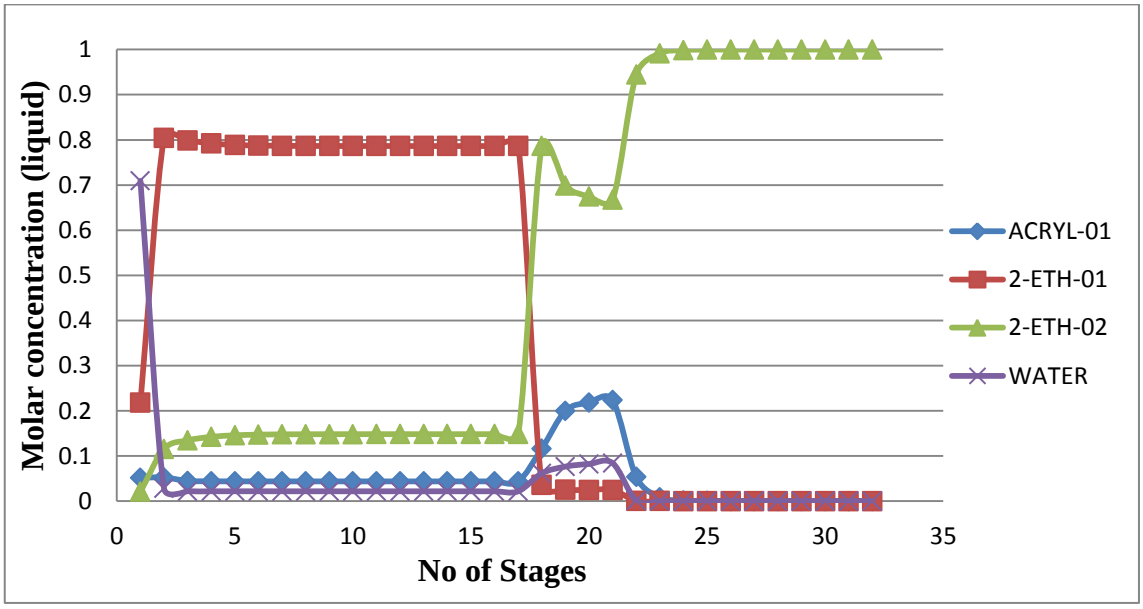

Figure 7. 1: The liquid composition profile for 30wt% of AA concentration

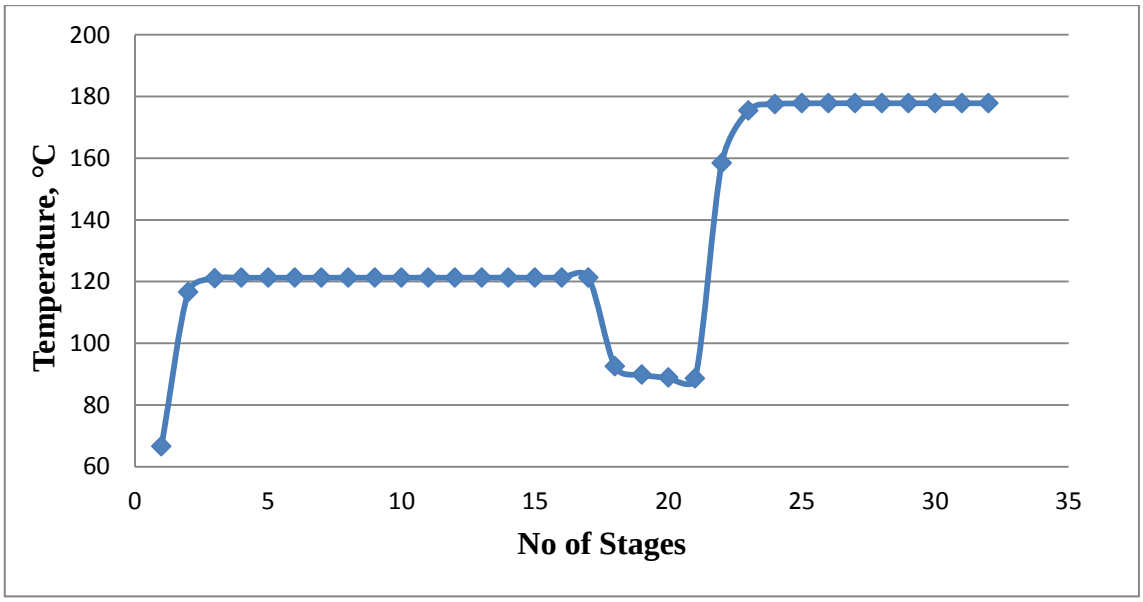

Figure 7. 2: Temperature Profile for 30wt% of AA concentration

7.1.2 25% of AA concentration

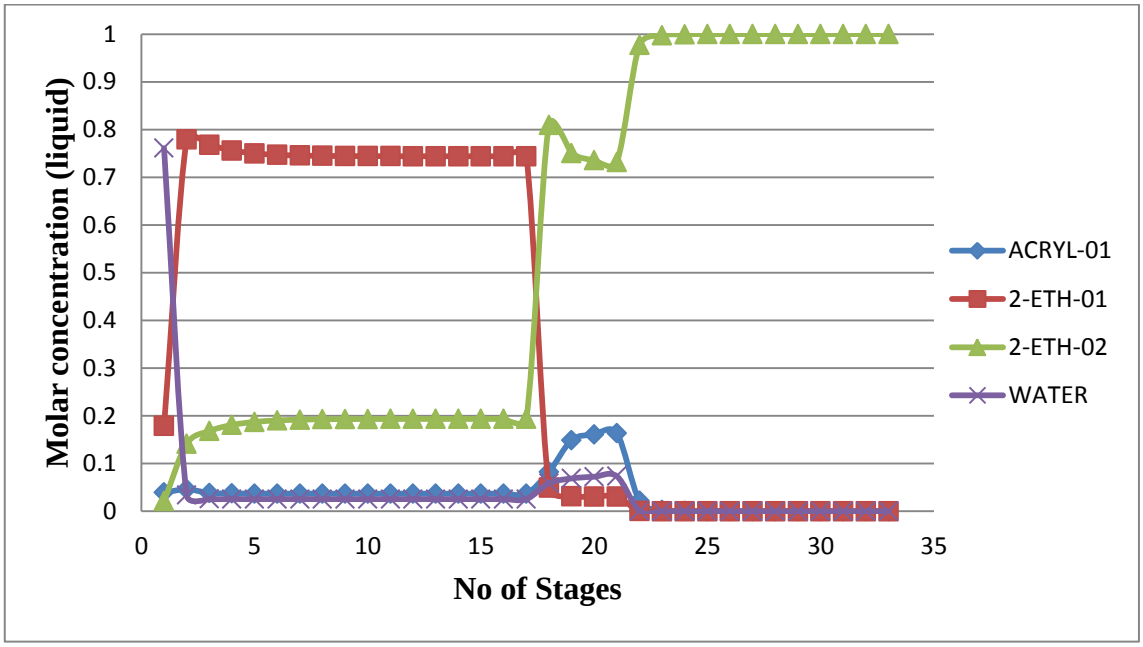

Figure 7. 3: The liquid concentration profile at 25wt% of AA concentration

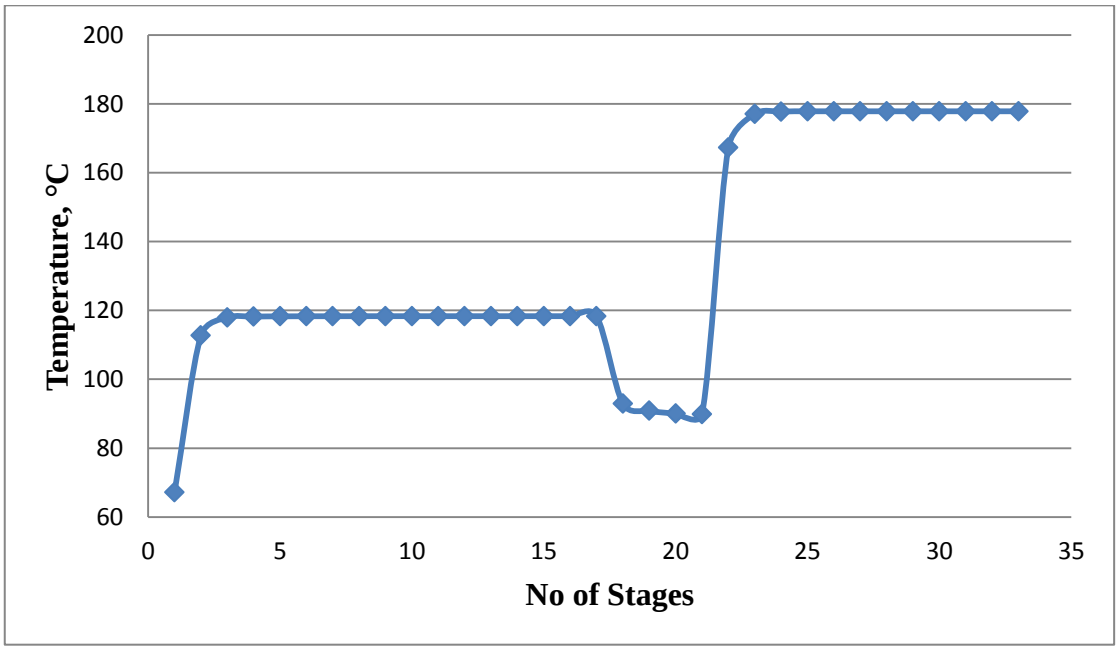

Figure 7. 4: Temperature Profile for 25wt% of AA concentration

7.1.3 20wt % of AA Concentration

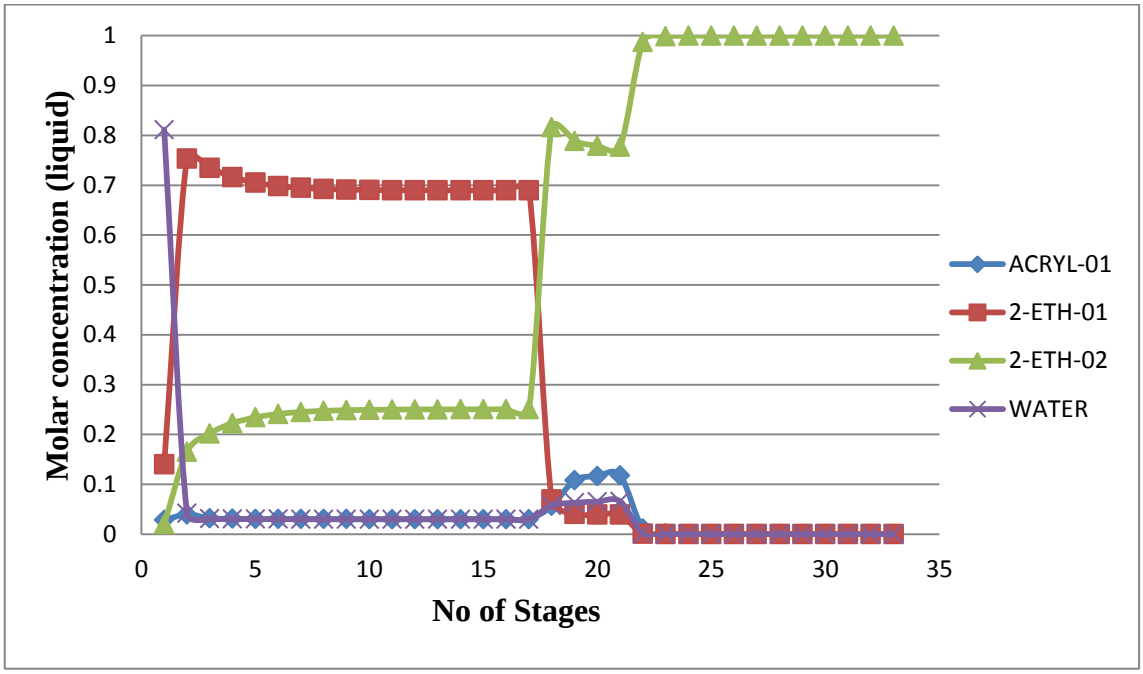

Figure 7. 5: The liquid concentration profile at 20wt% of AA concentration

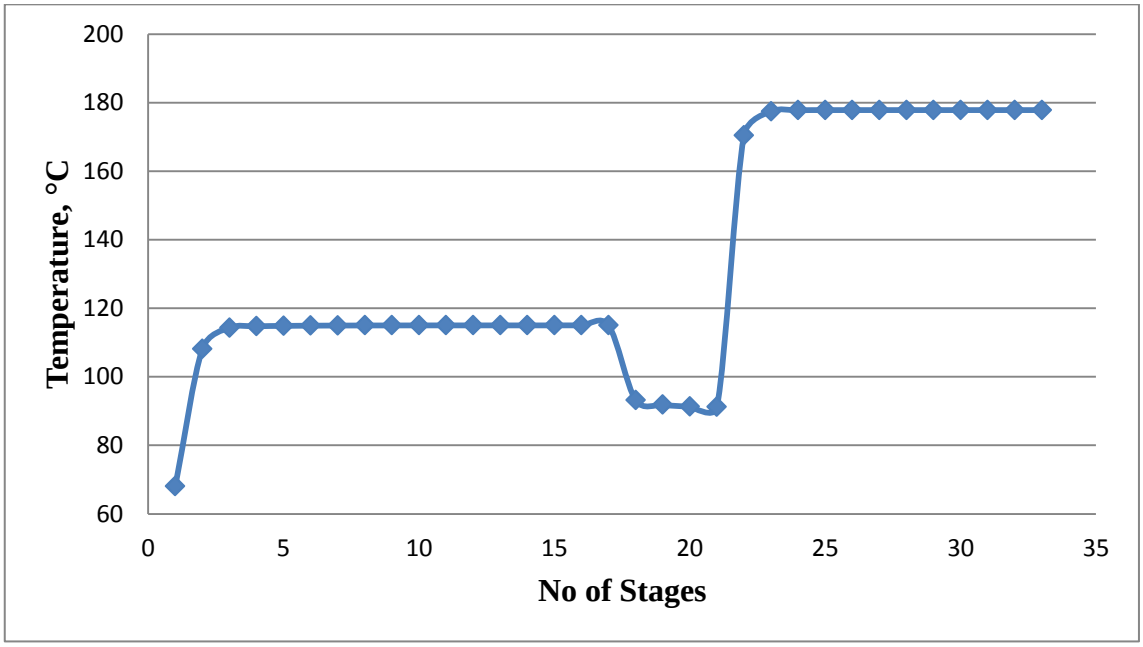

Figure 7. 6: Temperature Profile for 20wt% of AA concentration

7.1.4 15wt % of AA Concentration

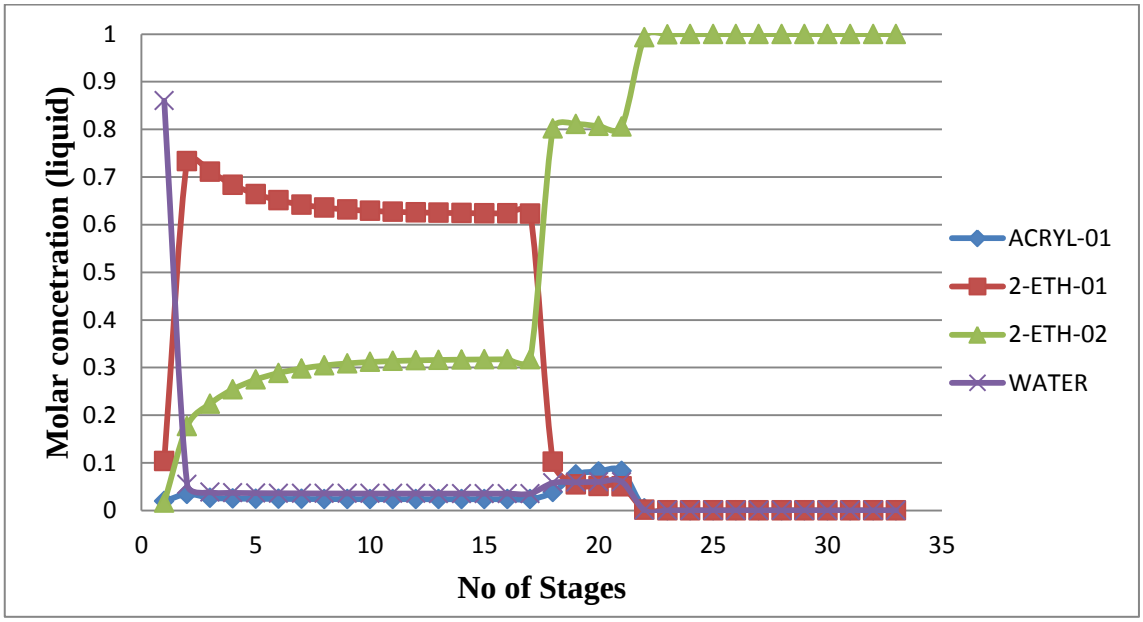

Figure 7. 7: The liquid concentration profile at 15wt% of AA concentration

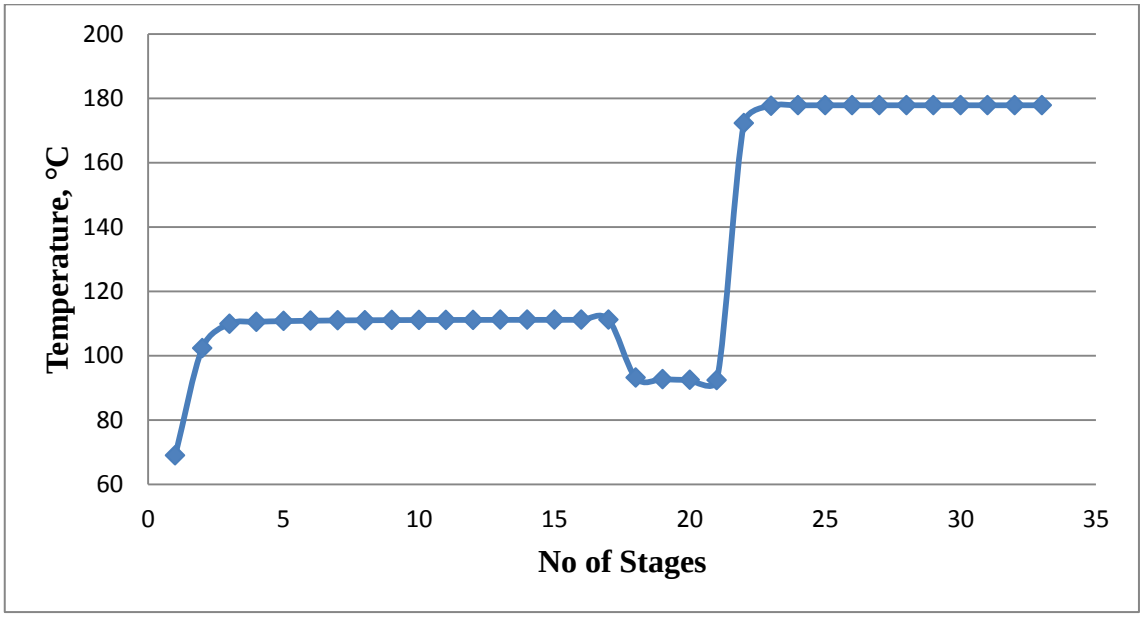

Figure 7. 8: Temperature Profile for 15wt% of AA concentration

7.1.5 10wt % of AA Concentration

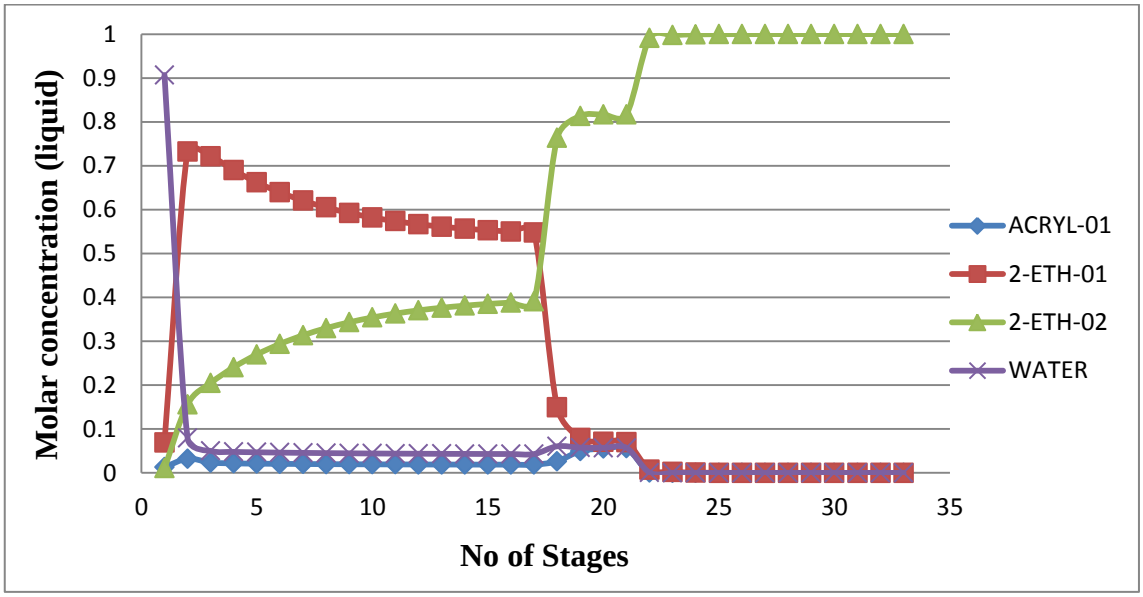

Figure 7. 9: The liquid concentration profile at 10wt% of AA concentration

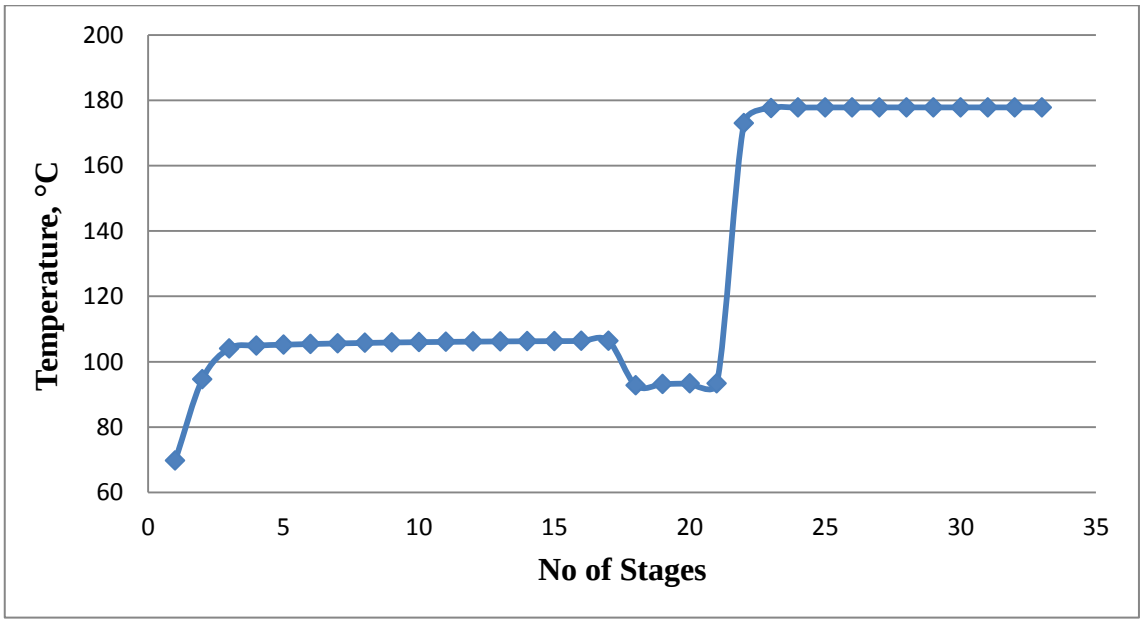

Figure 7. 10: Temperature Profile for 10wt% of AA concentration

7.2 The Effect of Reflux Ratio

7.2.1 Reflux molar ratio of 0.2

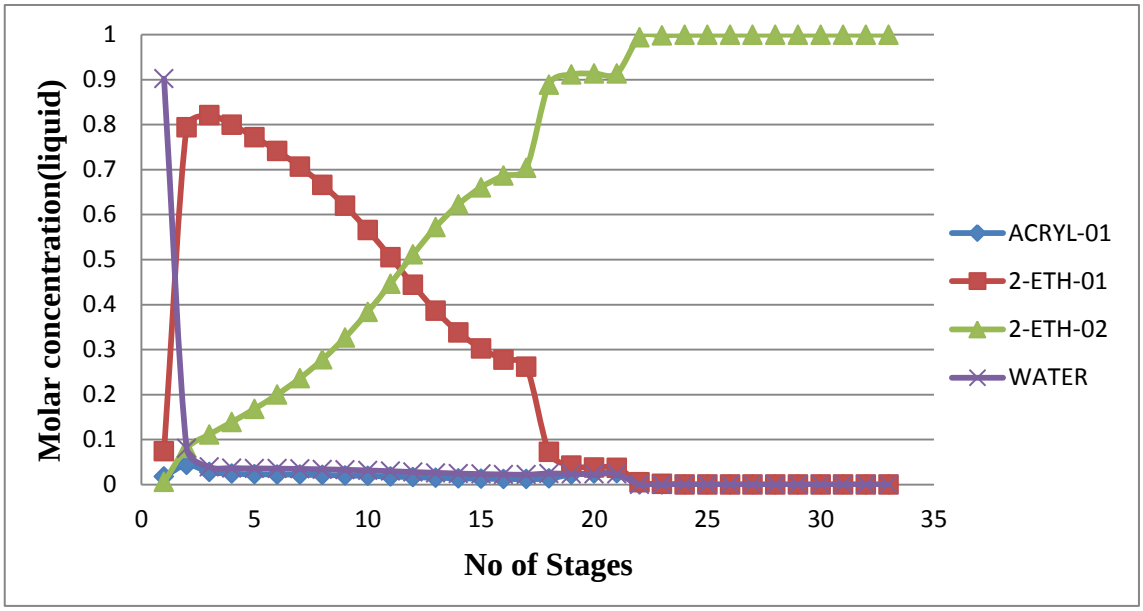

Figure 7. 11: The liquid concentration profile at 10wt% of AA concentration, 0.2 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

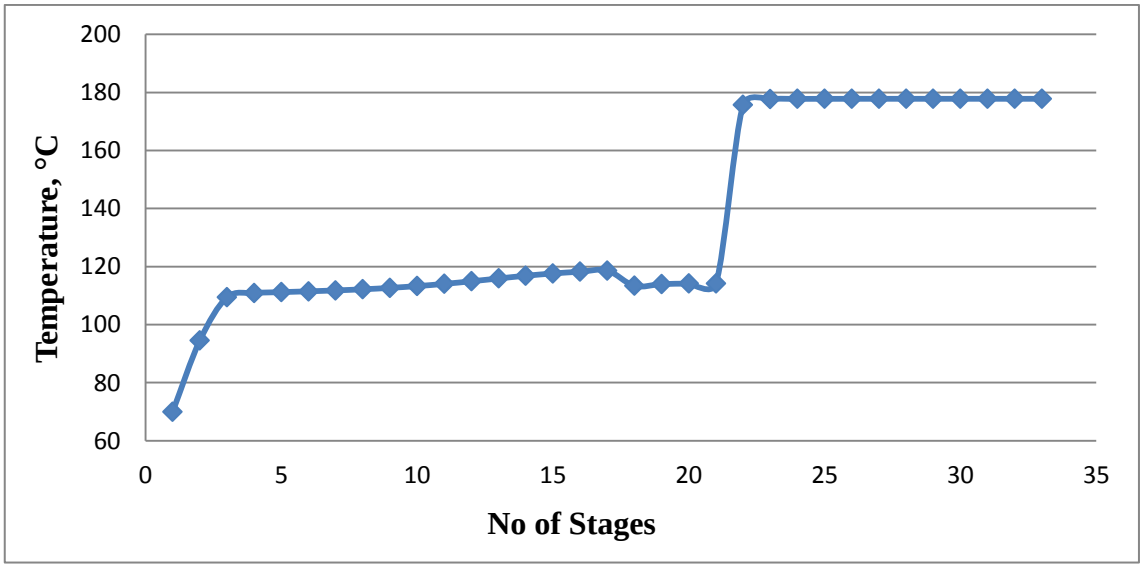

Figure 7. 12: Temperature Profile for 10wt% of AA concentration, 0.2 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

7.2.2 Reflux molar ratio of 0.175

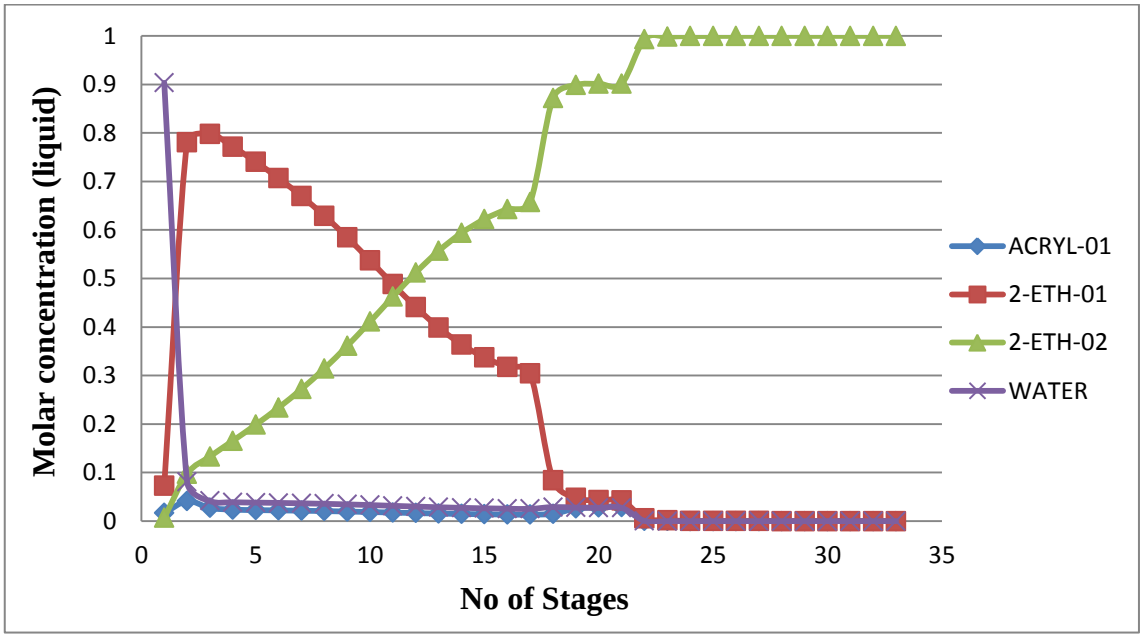

Figure 7. 13: The liquid concentration profile at 10wt% of AA concentration, 0.175 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

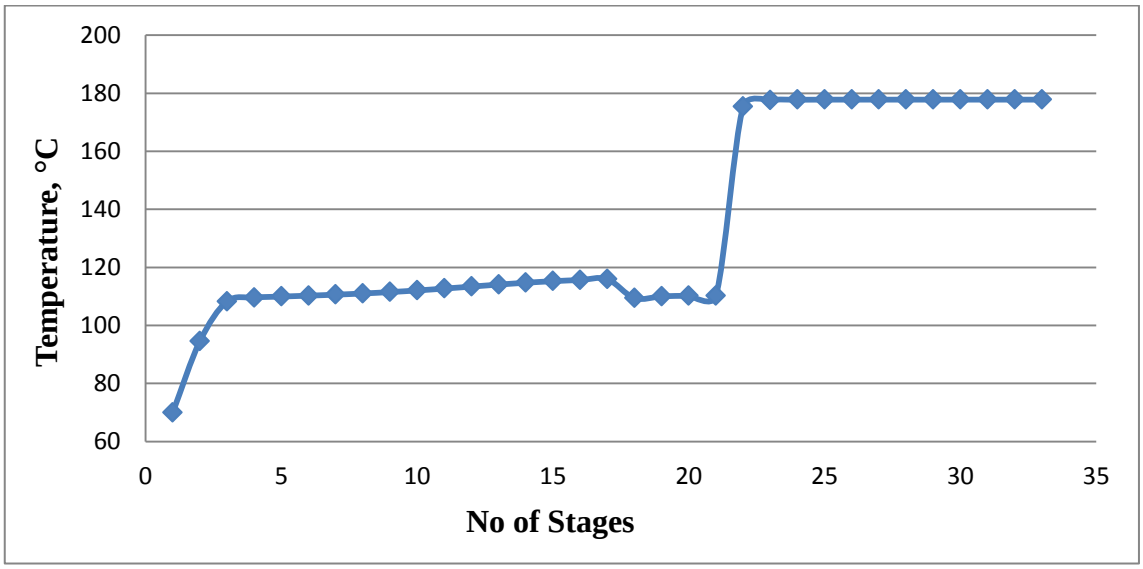

Figure 7. 14: Temperature Profile for 10wt% of AA concentration, 0.175 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

7.2.3 Reflux molar ratio of 0.150

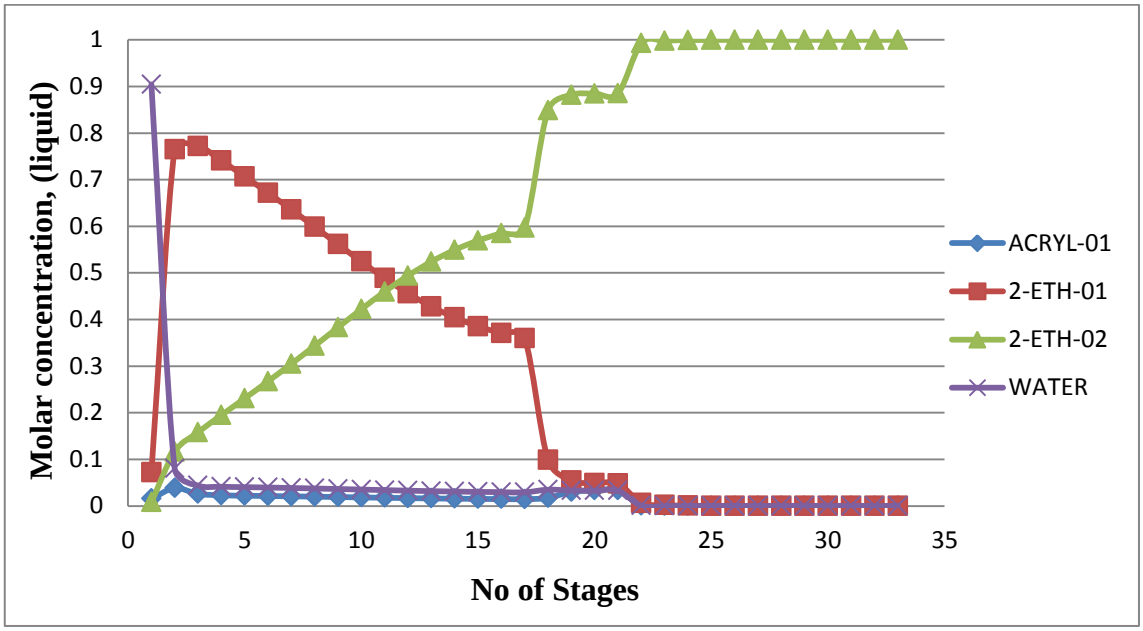

Figure 7. 15: The liquid concentration profile at 10wt% of AA concentration, 0.150 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

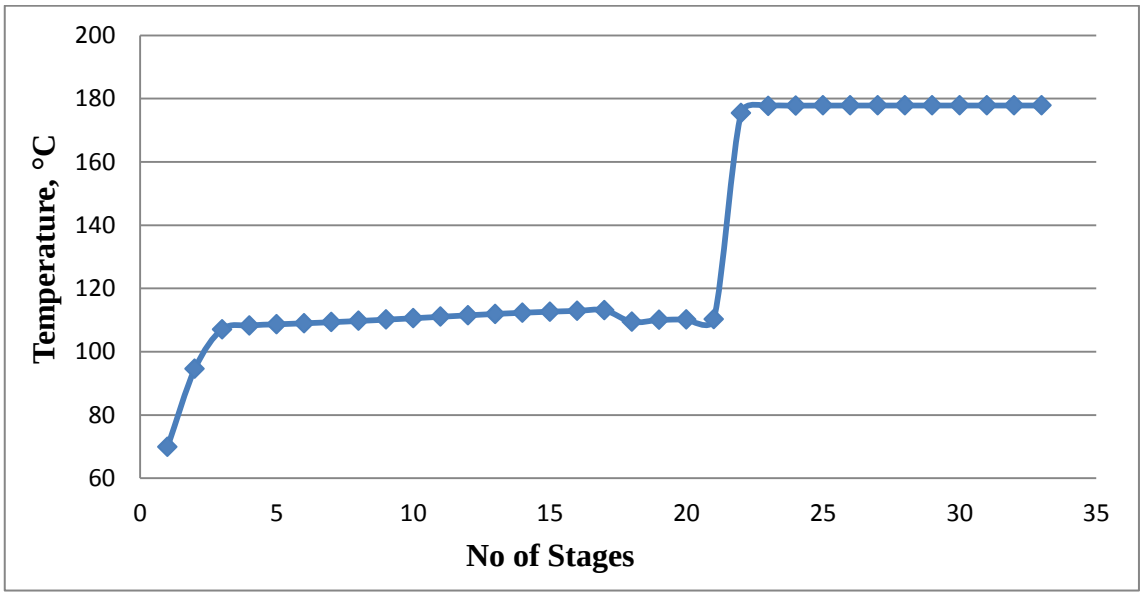

Figure 7. 16: Figure 7. 14: Temperature Profile for 10wt% of AA concentration, 0.150 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

7.2.4 Reflux molar ratio of 0.125

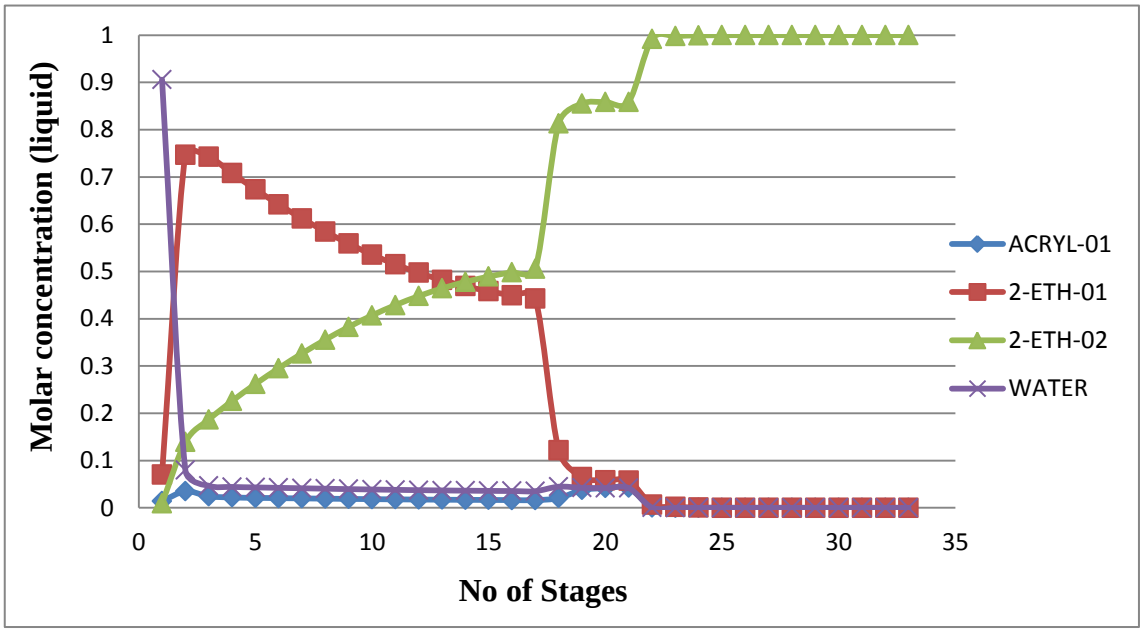

Figure 7. 17: The liquid concentration profile at 10wt% of AA concentration, 0.125 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

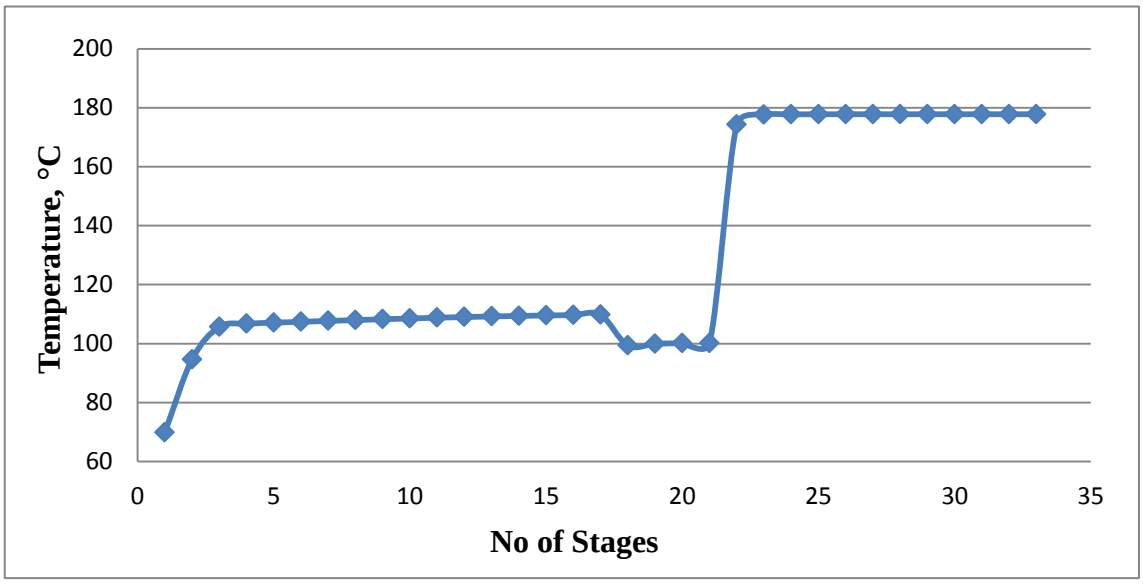

Figure 7. 18: Temperature Profile for 10wt% of AA concentration, 0.125 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

7.2.5 Reflux molar ratio of 0.100

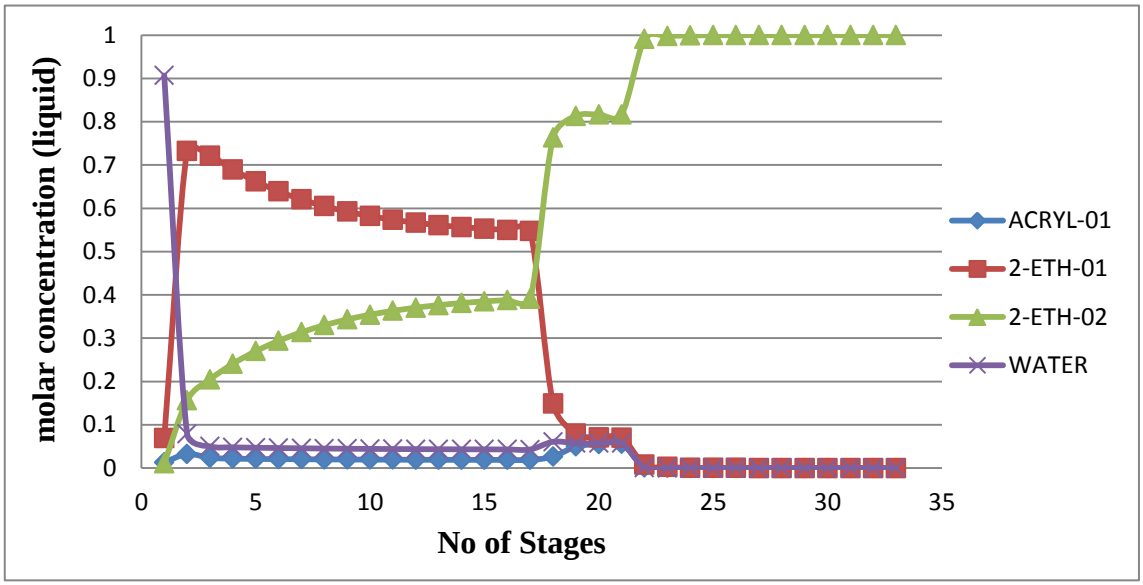

Figure 7. 19: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

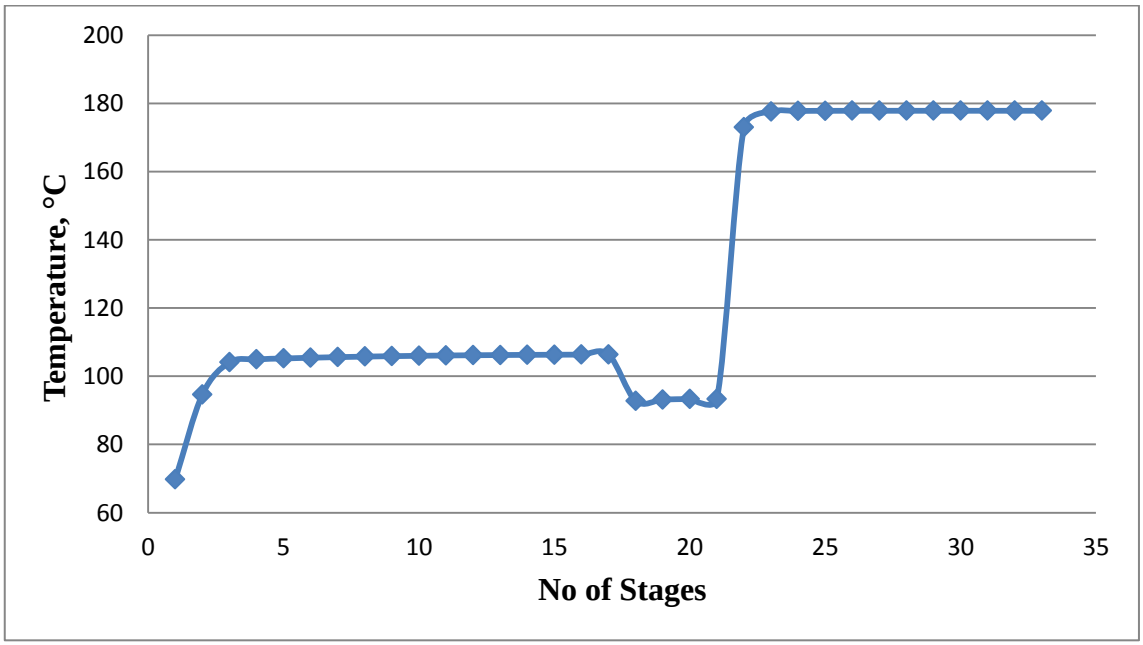

Figure 7. 20: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

7.3 The Effect of Bottom rate

7.3.1 Bottom Rate of 0.01kg/h

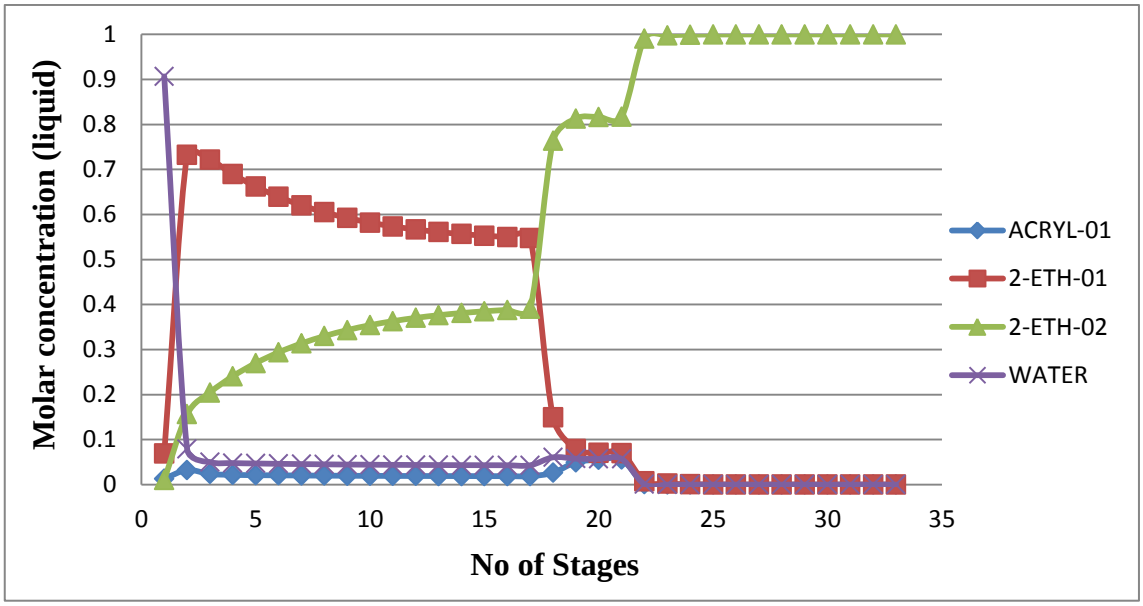

Figure 7. 21: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

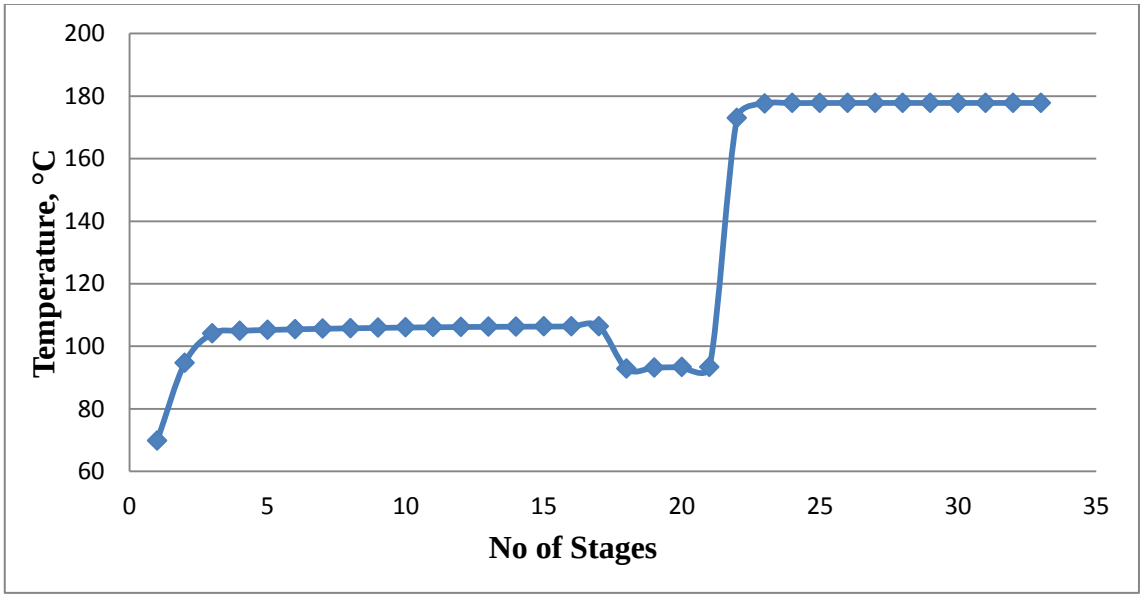

Figure 7. 22: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.01kg/h bottom rate and 1.5kg/m catalyst weight

7.3.2 Bottom Rate of 0.04 kg/h

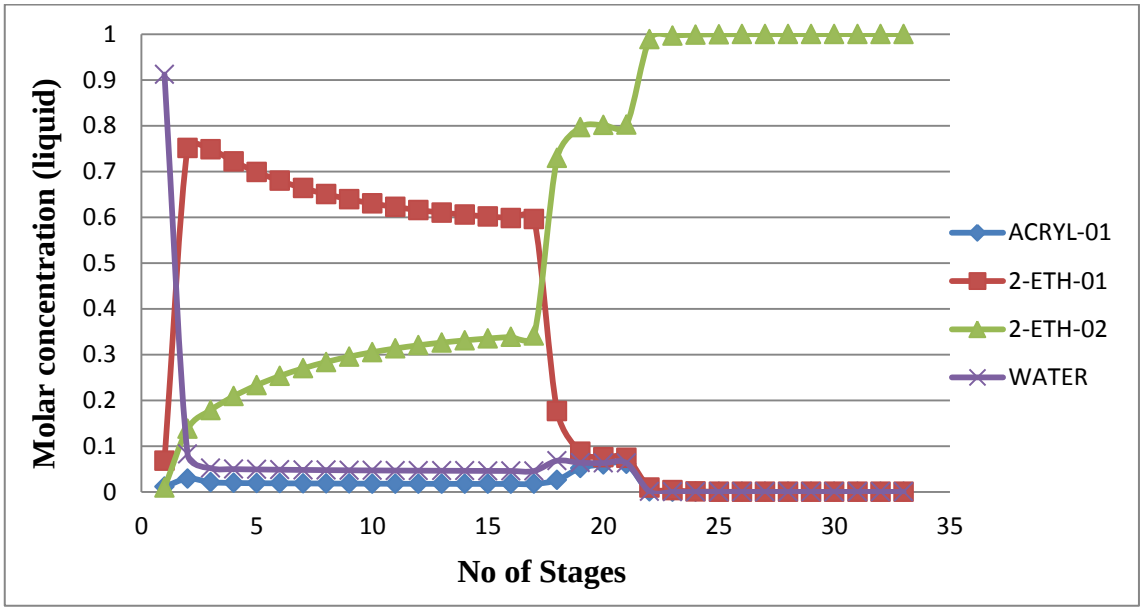

Figure 7. 23: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.04kg/h bottom rate and 1.5kg/m catalyst weight

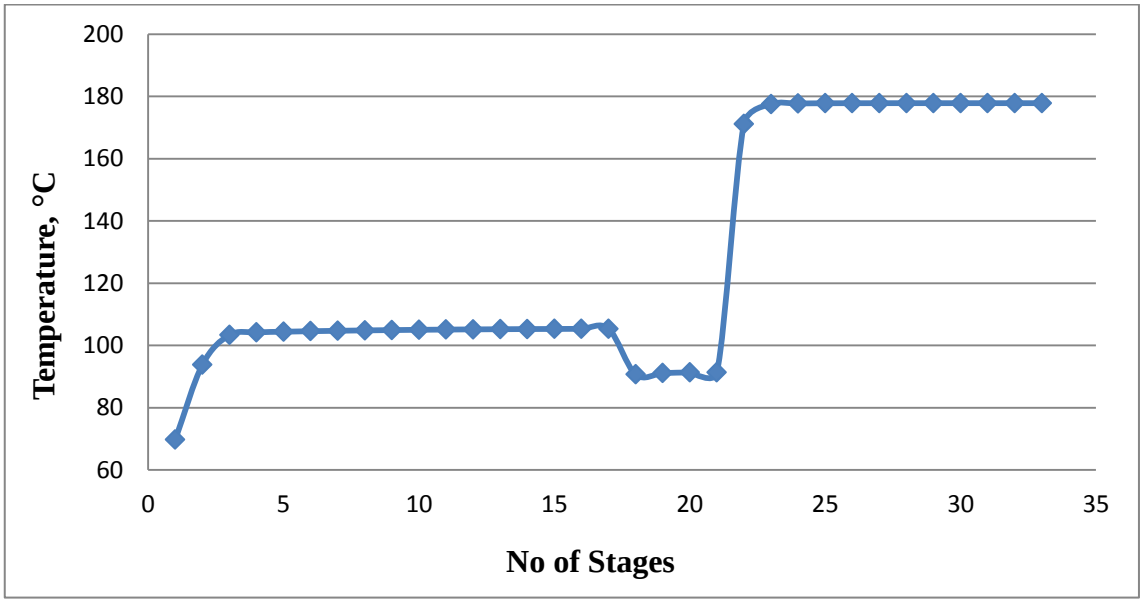

Figure 7. 24: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.04kg/h bottom rate and 1.5kg/m catalyst weight

7.3.3 Bottom Rate of 0.07 kg/h

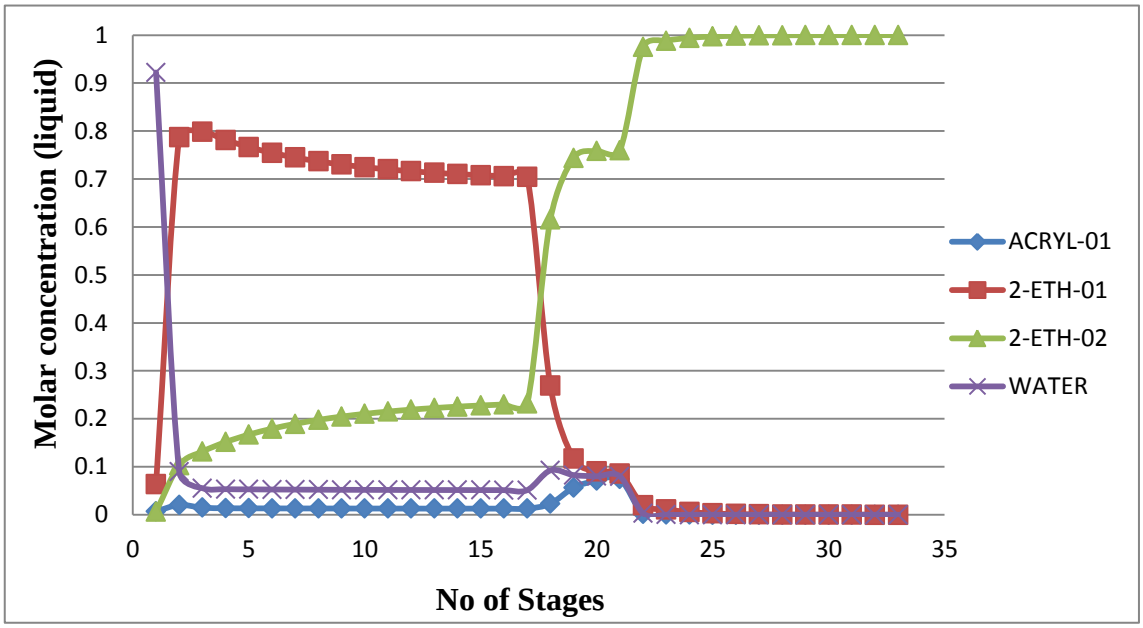

Figure 7. 25: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.07kg/h bottom rate and 1.5kg/m catalyst weight

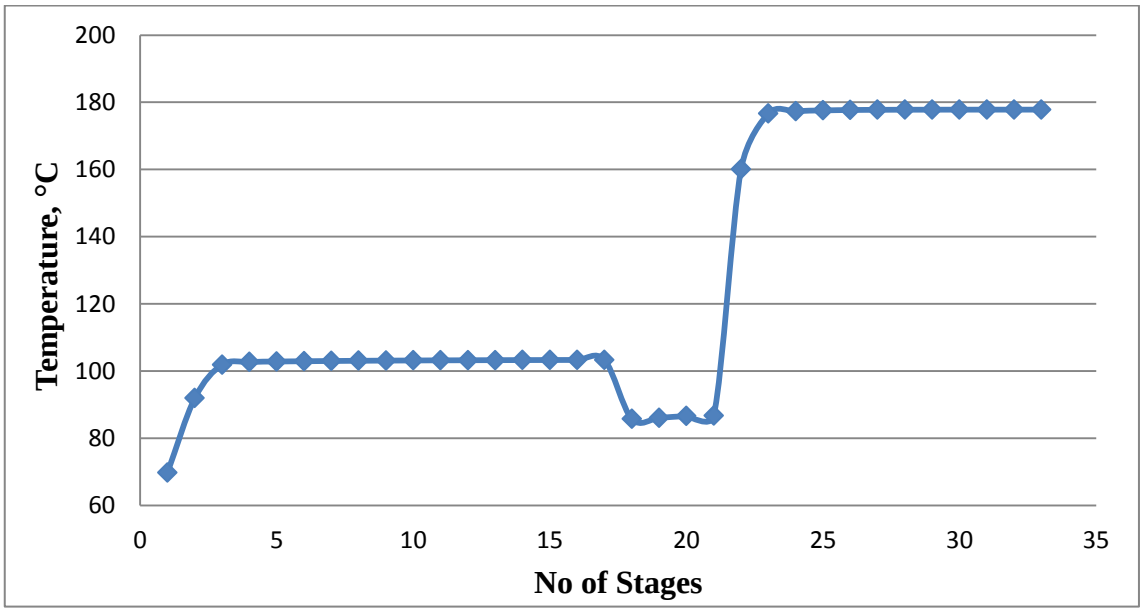

Figure 7. 26: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.07kg/h bottom rate and 1.5kg/m catalyst weight

7.3.4 Bottom Rate of 0.10 kg/h

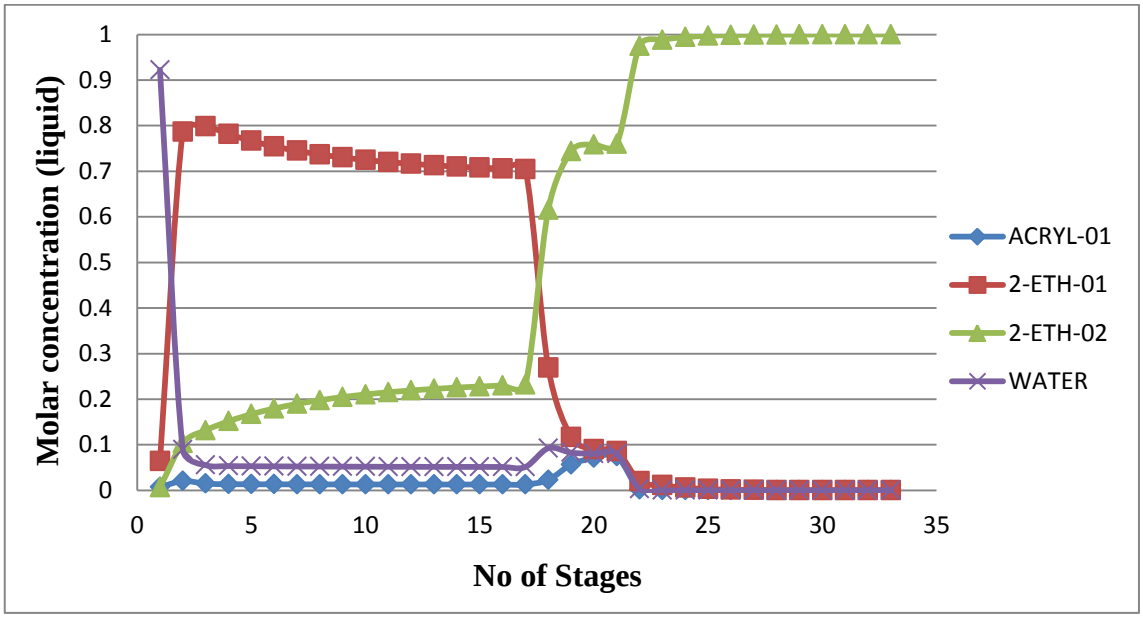

Figure 7. 27: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.10kg/h bottom rate and 1.5kg/m catalyst weight

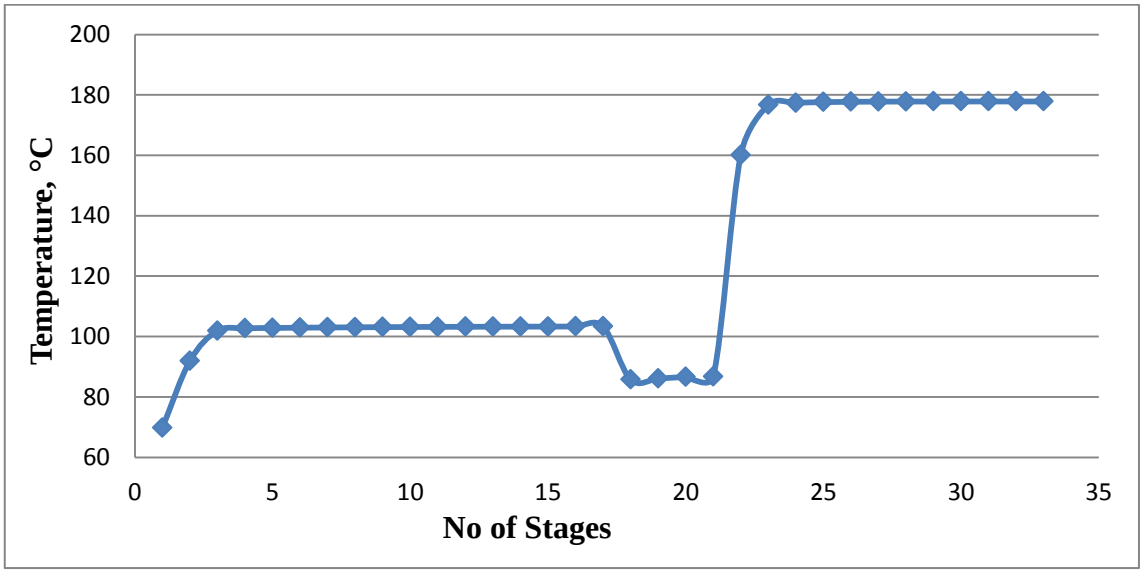

Figure 7. 28: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.10kg/h bottom rate and 1.5kg/m catalyst weight

7.3.5 Bottom Rate of 0.013 kg/h

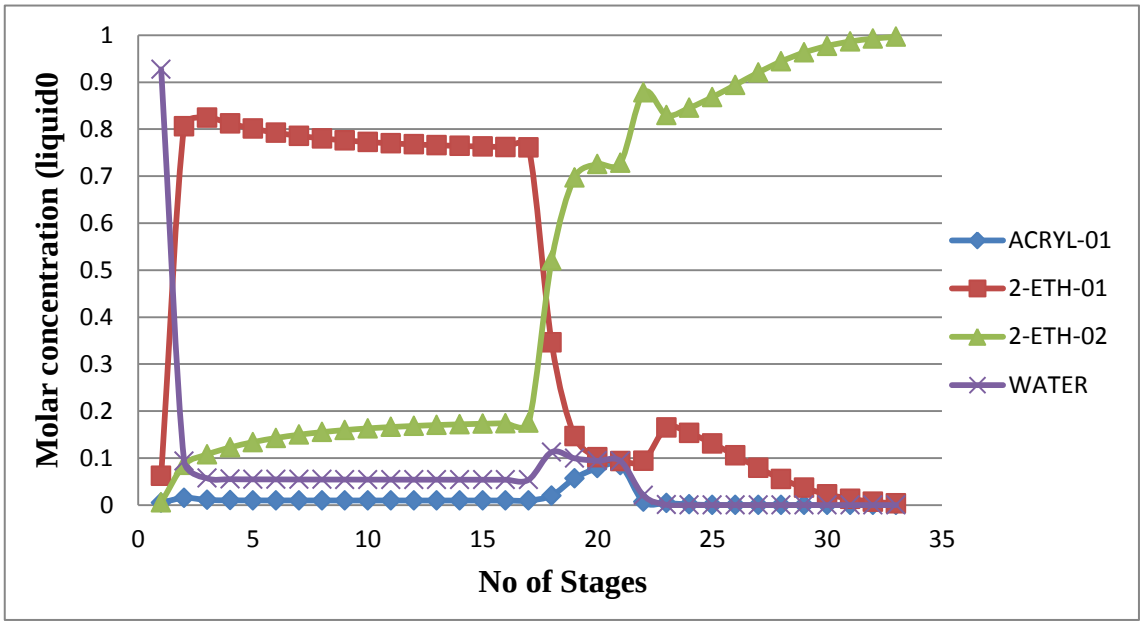

Figure 7. 29: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 1.5kg/m catalyst weight

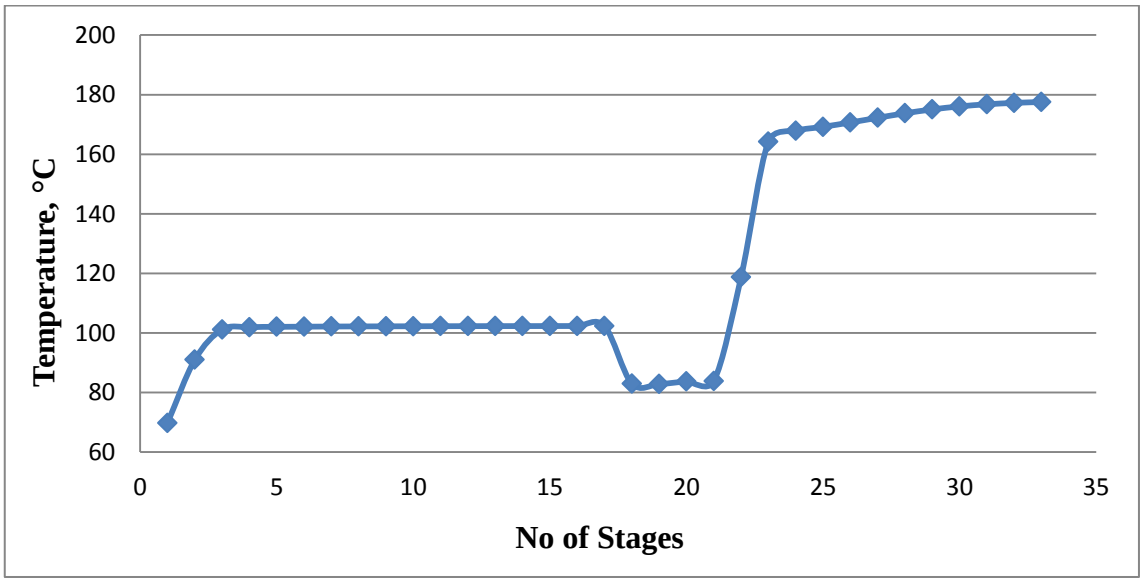

Figure 7. 30: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 1.5kg/m catalyst weight

7.4 The Effect of Catalyst Weight

7.4.1 Catalyst Weight of 0.5kg/m

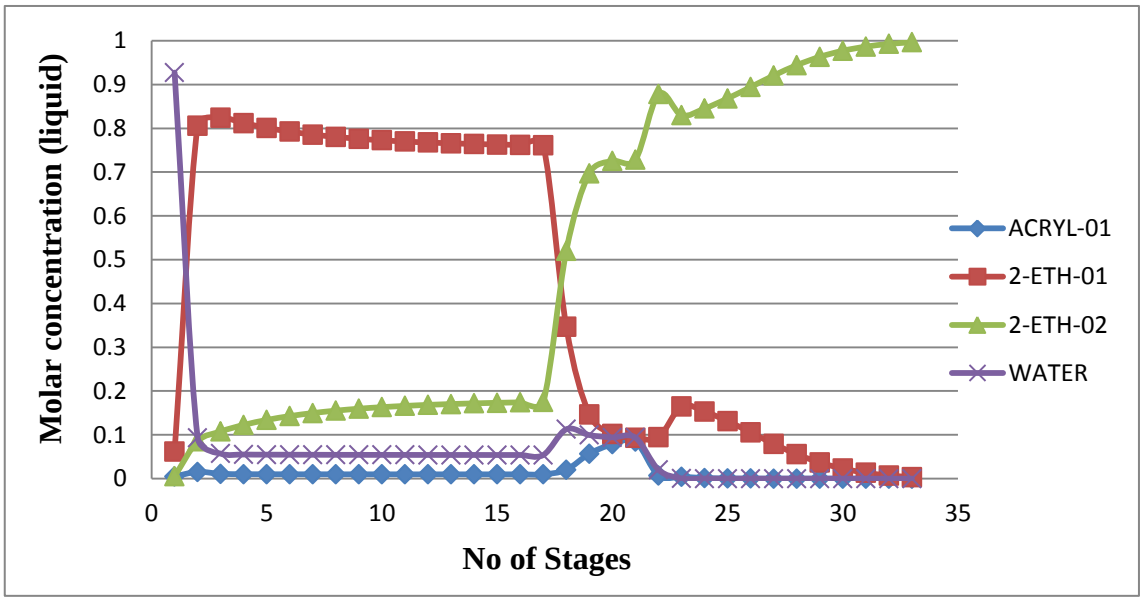

Figure 7. 31: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 0.5kg/m catalyst weight

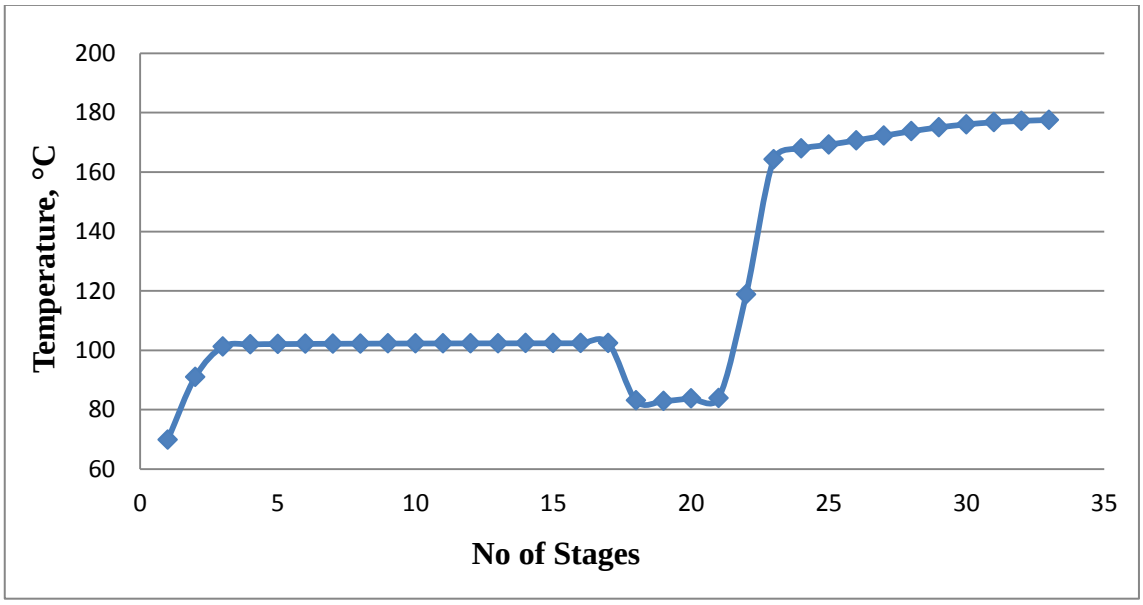

Figure 7. 32: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 0.5 kg/m catalyst weight

7.4.2 Catalyst Weight of 1.0kg/m

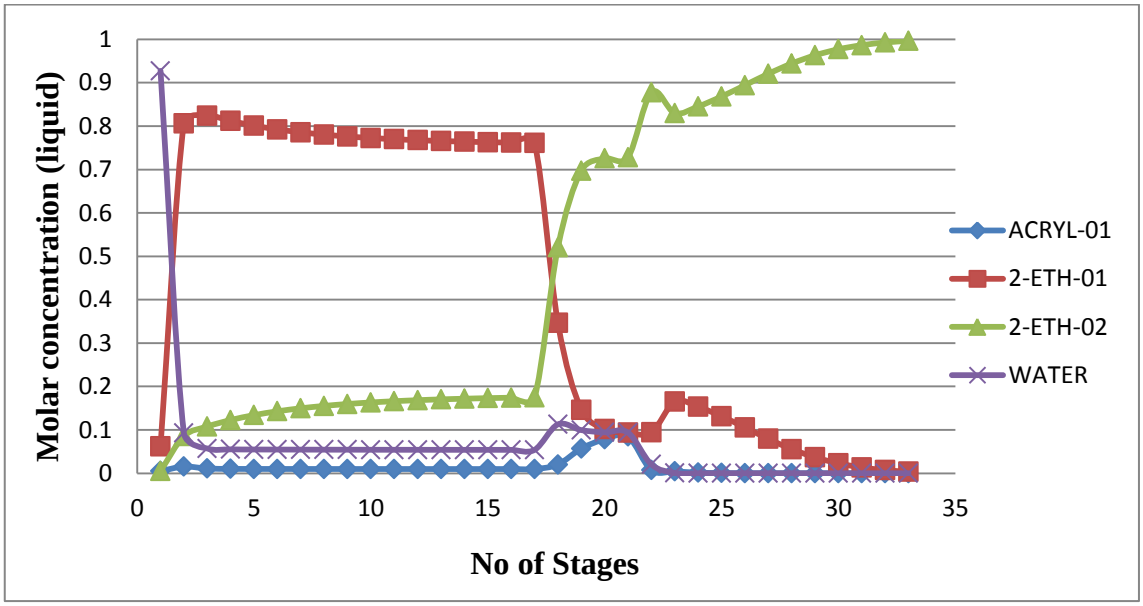

Figure 7. 33: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 1.0 kg/m catalyst weight

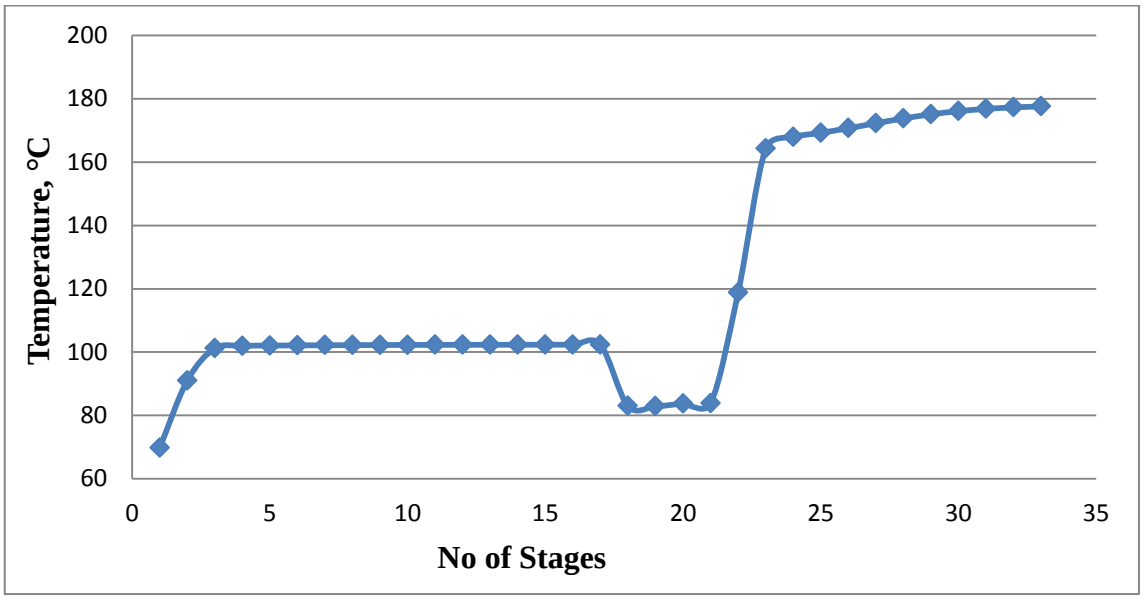

Figure 7. 34: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 1.0 kg/m catalyst weight

7.4.3 Catalyst Weight of 1.5kg/m

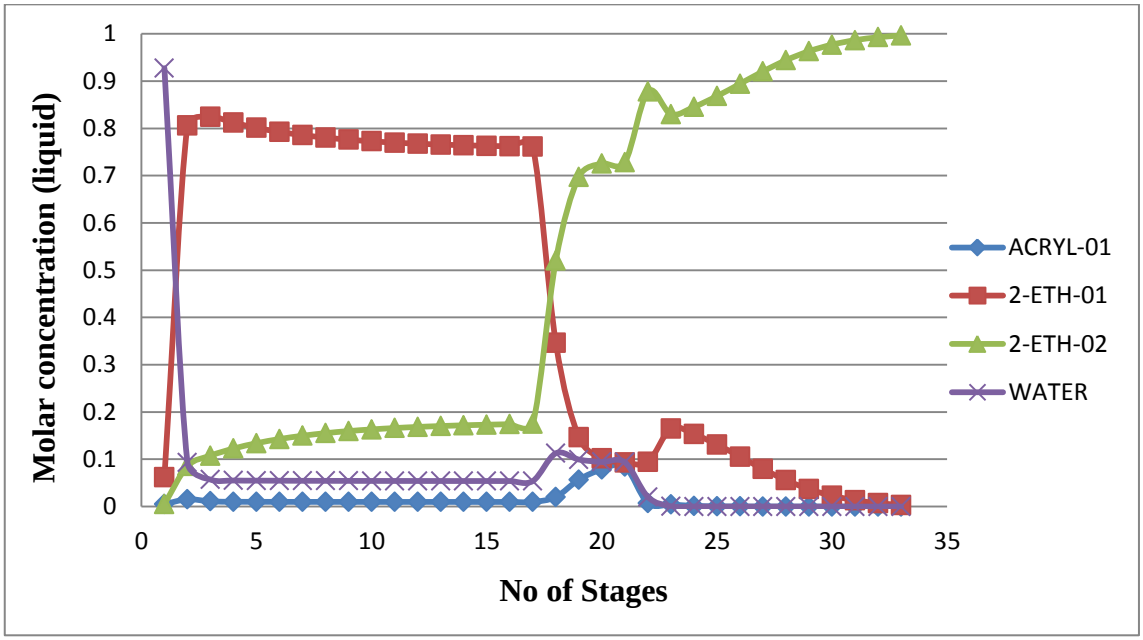

Figure 7. 35: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 1.5 kg/m catalyst weight

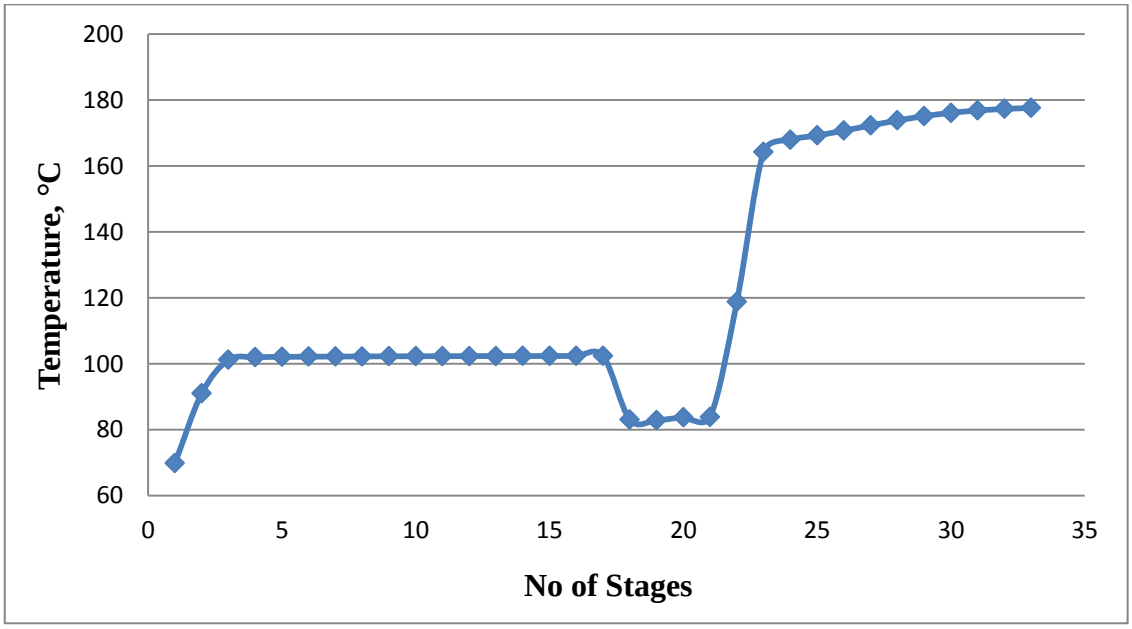

Figure 7. 36: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 1.5 kg/m catalyst weight

7.4.4 Catalyst Weight of 2.0kg/m

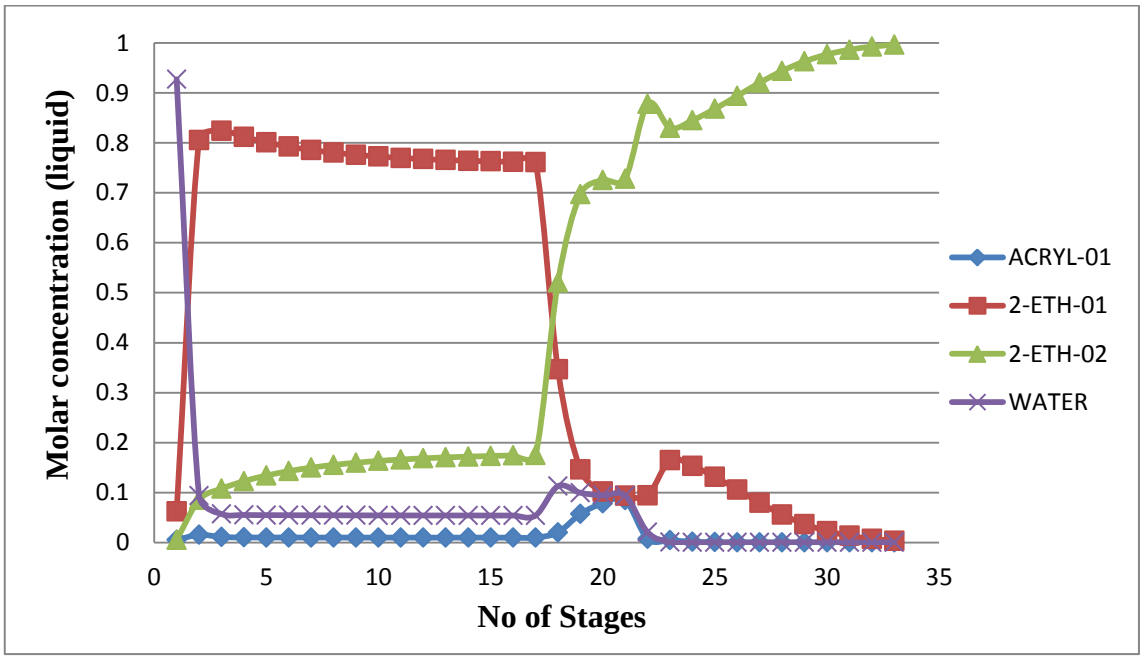

Figure 7. 37: The liquid concentration profile at 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 2.0 kg/m catalyst weight

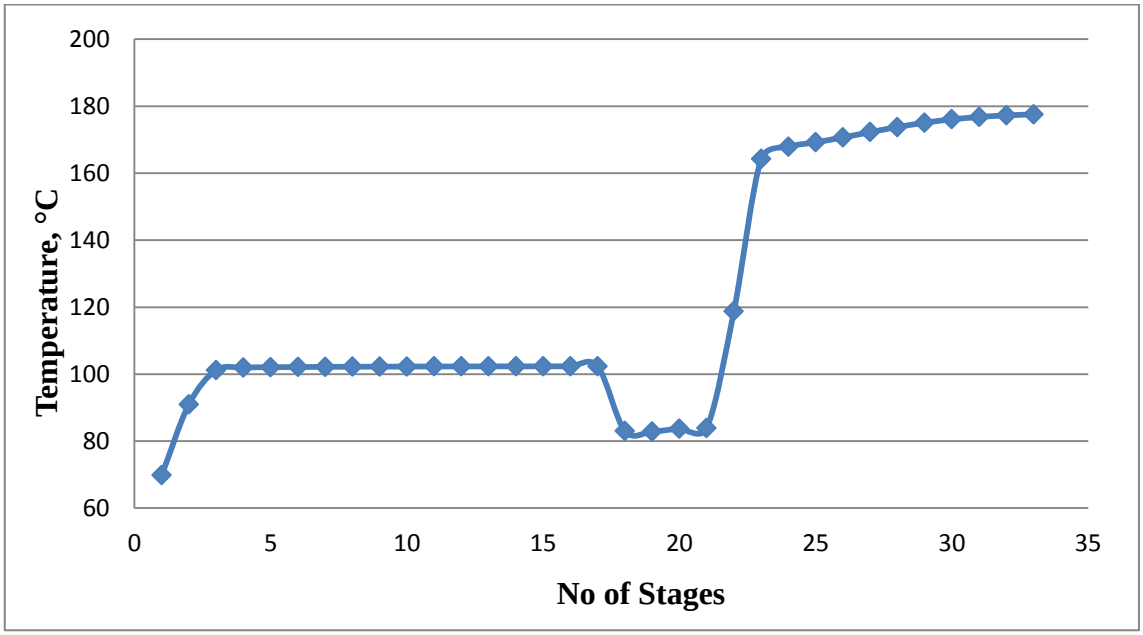

Figure 7. 38: Temperature Profile for 10wt% of AA concentration, 0.100 reflux molar ratio, 0.13kg/h bottom rate and 2.0 kg/m catalyst weight