SIMULATION AND OPTIMIZATION OF DEHYDRATION REACTOR IN ACRYLIC ACID PRODUCTION USING GLYCEROL

BELINDA ANNE XAVIER

UNIVERSITI SAINS MALAYSIA

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SIMULATION AND OPTIMIZATION OF DEHYDRATION REACTOR IN ACRYLIC ACID PRODUCTION USING GLYCEROL

by

BELINDA ANNE XAVIER

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Pre-exponential factor	kmol $kgcat^{-1}$ s^{-1} atm^{-1}
C_g	Concentration of Glycerol	wt glycerol/wt solution
COR	Catalyst to oil ratio	kg kg^{-1}
E_a	Activation Energy	$kJkmol^{-1}$
H_o	Hammett Acidity	-
K	Kinetic Constant	-
S	Selectivity	-
T	Temperature	°C
WHSV	Weight-hourly space velocity	h^{-1}
X_G	Conversion of Glycerol	-
Y	Yield	-

LIST OF ABBREVIATIONS

BTX	Benzene, Toluene, Xylene
CAGR	Cumulative Annual Growth Rate
CAGR	Cumulative Annual Growth Rate
NRTL	Non-Random Two Liquid Model
PFR	Plug Flow Reactor
RPLUG	Plug Flow Reactor
SAP	Superabsorbent Polymer
SAR	Silica to Alumina Ratio
ZSM-5	Zeolite Socony Mobil-5

SIMULASI DAN PENGOPTIMUMAN REAKTOR DEHIDRASI DALAM PENGHASILAN ACID AKRILIK YANG MENGGUNAKAN GLISEROL

ABSTRAK

Penghasilan asid akrilik dengan menggunakan gliserol perlu dikaji dan dioptimumkan supaya hasil dan kualiti asid akrilik akan terjamin sebelum pelaksanaannya dalam skala industri. Dengan kewujudan perisian simulasi seperti Aspen Plus, proses tertentu dapat disimulasi dan dioptimumkan dengan ciri-ciri produk akhir yang dikehendaki. Walau bagaimanapun, wujudnya ketidakpastian berkenaan keadaan tindak balas optimum bagi menghasilkan asid akrilik yang maksimum. Dalam kajian ini, Aspen Plus digunakan untuk mensimulasi dan mengoptimumkan reaktor dehidrasi katil tetap aliran berterusan (PFR) di mana glycerol bertindak balas atas pemangkin zeolite, ZSM-5 untuk menghasilkan akrolin serta produk sampingan seperti asetaldehid, etena, karbon monoksida, hidrogen dan kok. Keputusan simulasi dibandingkan dengan keputusan yang diperolehi dalam literatur dan didapati bahawa keputusan simulasi yang diperolehi oleh Aspen Plus boleh diterima dengan penukaran dan hasil purata kesilapan sebanyak 4.84% dan 26.25%. Seterusnya, analisis sensitiviti terhadap model reaktor RPLUG tersebut menunjukkan bahawa suhu reaktor, tekanan reaktor dan kepekatan gliserol mempunyai kesan yang jelas terhadap penukaran gliserol dan hasil akrolin. Penukaran glycerol didapati meningkat dengan suhu dan tekanan reaktor tetapi menurun dengan peningkatan WHSV dan kepekatan gliserol. Manakala, hasil acrolein pula meningkat dengan peningkatan suhu reactor sehingga 420°C, WHSV dan kepekatan gliserol sehingga 60%. Akhir sekali, pengoptimuman model reactor menunjukkan bahawa hasil acrolein maksimum yang boleh dicapai ialah 42.85% pada keadaan optimum iaitu suhu reaktor 450.78°C, tekanan 1 bar dan kepekatan gliserol 60%.

SIMULATION AND OPTIMIZATION OF DEHYDRATION REACTOR IN ACRYLIC ACID PRODUCTION USING GLYCEROL

ABSTRACT

The production of acrylic acid using glycerol feedstock is gaining importance worldwide and thus the process needs to be studied and optimized fully so that the yield and quality of acrylic acid are assured before its implementation in industrial scale. With the development of simulating software such as Aspen Plus, it is possible to simulate and optimize a process with desired end-product characteristics. However, there is no fixed idea on the optimum reaction conditions to produce maximum yield of acrylic acid. In this work, Aspen Plus was used to simulate and optimize an isothermal fixed bed plug flow dehydration reactor where glycerol was dehydrated into acrolein and side-products such as acetaldehyde, ethylene, carbon monoxide, hydrogen and coke in the presence of ZSM-5 zeolite catalyst. The simulation results obtained were first compared with that from literature. The simulated results obtained by Aspen Plus showed that it is acceptable since the simulation values obeyed that of the literature with an average conversion and yield errors of 4.84% and 26.25% respectively. Sensitivity analysis on the same RPLUG reactor model showed that reactor temperature, pressure and glycerol concentration had significant effects on glycerol conversion and acrolein yield. The glycerol conversion was found to increase with reactor temperature and pressure but decreased with WHSV and glycerol concentration. Meanwhile, acrolein yield increased with the rise in reactor temperature till 420°C, WHSV and glycerol concentration up to 60 wt%. Lastly, optimization study on the reactor model resulted in maximum acrolein yield of 42.85% which is achieved at optimum variables of 450.78°C, 1 bar and 60 wt% glycerol concentration.

CHAPTER ONE

INTRODUCTION

1.1 Acrylic Acid Production Process

Acrylic acid belongs to the organic group of α, β-unsaturated carboxylic acids which consists of a vinyl group connected directly to a carboxylic acid terminus. This colorless liquid has a characteristic acrid or tart smell and is miscible with water, alcohols, ethers, and chloroform (CTI Reviews, 2016). It is well-known that acrylic acid manufacturing industry is a thriving and well-developed industry in many countries which contributes to its economic growth and development. The factors that are driving the growth of the market are soaring demand for superabsorbent polymers, widespread adoption of acrylic-based products in emerging economies such as Asia Pacific and growing industries such as adhesives and sealants (Clark, 2014).

The global acrylic acid market size is predicted to reach USD 13.21 billion by 2020 at a cumulative annual growth rate (CAGR) of 5.2% between 2015 and 2020. Other study also showed that global acrylic acid market demand was 5,750 kilo tons in 2014 and is expected to reach 8,750 kilo tons by 2022, growing at a CAGR of 5.6% from 2015 to 2022 which is worth USD 22.55 billion (Grand View Research, 2016). These statistics alone prove that acrylic acid has a well-established market and importance which contributes to its mass production around the world.

The current industrial production of acrylic acid worldwide adopts the utilization of propylene as its main raw material which is deemed as non-sustainable and less environmentally friendly due to high emissions of carbon dioxide and unwanted by-products. Studies have been conducted and still ongoing by various researchers on different alternative feedstock to replace and reduce dependency on fossil fuel based feedstock due to its price volatility and depleting resource. The production of acrylic acid using glycerol as its raw material has attracted attention due to the attractive pricing and abundance in glycerol availability from the growing biodiesel production around the world (Fan et al., 2010). The process is a two-step reaction that involves the dehydration of glycerol to produce acrolein as its intermediate product which is then oxidized into the desired acrylic acid product using two separate fixed bed reactors in series with the presence of catalysts (Li and Zhang, 2015).

The production of acrylic acid using renewable glycerol feedstock is gaining importance worldwide and thus the process needs to be studied and optimized fully so that the yield and quality of acrylic acid are assured before its implementation in industrial scale. With the development of computer aided simulation software such as Aspen Plus, it is possible to simulate and optimize a particular process with desired end-product characteristics. Proper optimization can significantly improve the quality and yield of the desired product as well as make the process safer with less formation of unwanted toxic by-products.

1.2 Problem Statement

The production of acrylic acid using glycerol as its raw material has attracted attention due to the increase in glycerol availability from the growing biodiesel production around the world. However, the earlier plans to commercialize acrylic acid production through dehydration of glycerol were abandoned due to lack of technology with acceptable yields and heavy coke deposits due to acidic nature of the catalyst and high reaction temperature (Knothe et al., 2010 ; Pagliaro, 2017) . With the price of glycerol decreasing, more alternatives are proposed by using bio-based feedstock in the form of glycerol instead of petroleum-based feedstock. Since the production of acrylic acid using glycerol feedstock is not yet established worldwide in an industrial scale, it is of utmost importance that the process optimization is carried out before its implementation.

In addition to that, most of the previous research works on acrylic acid production using glycerol have focused on an experimental based approach in collecting data which is time-consuming to be performed rather than software-based. Thus, this work tries to simulate the glycerol dehydration reaction by using Aspen Plus version 8.2 to achieve higher conversion of glycerol and acrolein yield. In order to maximize the yield of acrolein, it is important to understand the effect of certain operating parameters such as reactor temperature, pressure, feed concentration and others on the conversion and yield values. With Aspen Plus version 8.2, sensitivity analysis tool can be used for quick study of sensitivity of process performance (in this case, acrolein yield) to changes in the input operating variables. This enables a wide range of manipulating variables to be studied at a time, after which a set of results of the user's choice can be tabulated and plotted.

Besides that, since previous research works on this topic have been mostly experimental based, the research parameters have also been limited and their combined effect on the yield of acrolein is not thoroughly explored nor studied. Hence, this resulted in lack of optimum set of reaction conditions as inconsistency exists from one work to another. The lack of consistency of the effect of operating conditions on the yield of acrolein from the previous studies indicates that there is no standard optimization to be obeyed in the production of acrylic acid. Hence, optimization studies using Aspen Plus need to be done in order to find out the best optimum parameter conditions for the maximum yield of acrolein cumulatively.

From the market demand statistics, it is clear that the global demand and consumption for acrylic acid will continue to grow in the upcoming decades and therefore comes the importance of optimizing the acrylic acid production process to increase its yield and quality . Research must be stepped up efficiently to improve the acrylic acid production process in order to supply to the ever-increasing needs of the market as well as to ensure a high quality acrylic acid product. Thus, in this work, the Aspen Plus version 8.2 is used to study the individual and combined effects of the various manipulating variables on the yield of acrolein using sensitivity analysis followed by optimization of the dehydration reaction to maximize the yield of acrolein.

Through this study, it is hoped that industrial scale production of acrylic acid using glycerol feedstock can be established with higher yield and better quality of acrylic acid using Aspen Plus simulation software. From the industrial viewpoint, this provides a more sustainable option and helps to reduce complexity of the traditional acrylic acid plant with the potential elimination of the various separation and purification steps to remove large amount of by-products if the product yield is high enough.

1.3 Research Objectives

The objectives of this work are as follow:

1) To simulate the dehydration reaction of glycerol using the plug flow reactor (RPLUG) model.

2) To investigate the effect of reactor temperature, reactor pressure, weight hourly space velocity (WHSV) and glycerol concentration on the conversion of glycerol and yield of acrolein by using sensitivity analysis tool in Aspen Plus.

3) To optimize the production of acrylic acid by maximizing the yield of acrolein using the optimization tool in Aspen Plus.

1.4 Scope of Study

In this work, simulation-based work was done to simulate the dehydration of glycerol reaction in acrylic acid production using Aspen Plus Version 8.2. Unlike previous experimental works done by other researchers, this work focused solely on simulation-based approach rather than experimental in order to study the effects of the various operating variables on the conversion of glycerol and yield of acrolein (intermediate product). The first reactor of the process, known as dehydration reactor was chosen to be simulated using Aspen Plus since the oxidation of acrolein to acrylic acid process has already been well developed in the industrial acrylic acid process.

Firstly, Aspen Plus Version 8.2 was used to develop a simulation flow sheet for the plug flow reactor (RPLUG) model of glycerol dehydration process. The simulation results obtained were then compared with those reported in the literature. If the simulation results obtained was comparable with the literature, sensitivity analysis was then conducted on the operating variables such as reactor temperature, reactor pressure, weight hourly space velocity (WHSV) and glycerol concentration. Using the sensitivity analysis tool, the effect of various operating conditions mentioned above on the conversion of glycerol and yield of acrolein were studied in order to obtain the optimum set of operating conditions for the glycerol dehydration reaction. Lastly. the optimization of the acrylic acid production was performed using the optimization tool in Aspen Plus by maximizing the yield of acrolein. The optimum reaction conditions were essential in order to produce high glycerol conversion and acrolein yield in the production plant. The yield of acrolein in the first reactor ultimately affects the yield of desired acrylic acid as the two-stage process enables individual optimization of both steps with respect to catalyst systems and reaction conditions (Franzke, 2010).

1.5 Organization of Thesis

The following are the contents for each chapter in this study:

Chapter 1 outlines the general information about acrylic acid production process, problem statement, objectives and scope work of this research.

Chapter 2 discusses literature review regarding the manufacturing of acrylic acid that includes petroleum-based and bio based acrylic acid production process as well as the reaction mechanism of glycerol dehydration process. Previous research works and their limitations done by other researchers on factors affecting the glycerol conversion and acrolein yield are also briefly described in this chapter.

Chapter 3 covers the materials and methodology of the research. It includes steps to develop simulation flow sheet for the plug flow reactor model (RPLUG) in the glycerol dehydration reaction followed by sensitivity analysis on operating variables such as reactor temperature and pressure, weight hourly space velocity (WHSV) and glycerol concentration as well as optimization of the process using Aspen Plus Version 8.2.

Chapter 4 presents the results and discussion of the simulation results. The simulated data is first compared with those reported in the literature. The effect of reactor temperature, reactor pressure, weight hourly space velocity (WHSV) and glycerol concentration on the conversion of glycerol and yield of acrolein are also studied. Lastly, the results obtained from the optimization are also discussed in this chapter.

Chapter 5 concludes all the findings obtained in this study. Recommendation to improve the current research results are also presented in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Manufacture of Acrylic Acid

The acrylic acid industry has seen significant changes over the past decades. Although acrylic acid can be prepared from a variety of feedstocks, it was the pathway involving synthesis from propylene that became the preferred and dominant method of production for acrylic acid in the industry till today (Sood, 1995).

Currently, licensors and technology holders of two-stage propylene oxidation technology are looking to improve their processes with new catalyst formulations, modifications to reactor design, or establishing operational best-practices through newly optimized parameters (Le, 2014). However, due to the rising price of crude oil globally, manufacturers are now focusing on developing and commercializing renewable acrylic acid (Clark, 2014). Significant efforts are continuously being made around the world to move from the current fossil-based economy to a more sustainable economy based on renewable resources. Thus, in order to match the efficiency and flexibility of the petrochemical industry, the bio-based industry needs to develop a set of versatile building blocks, or platforms from which a range of products can be derived (Dishisha, 2013).

2.1.1 Petroleum-Based Acrylic Acid Production

The current industrial production of acrylic acid involves two separate gas phase oxidation stages whereby propylene is converted to acrolein in the first stage, followed by oxidation of acrolein to acrylic acid in the second stage. The two stages of oxidation are catalyzed by bismuth-molybdenum oxide catalyst and Mo-V-Te-Nb-O mixed oxide respectively. The two-step operation has enabled the individual optimization of both steps with respect to catalyst systems and reaction conditions (Franzke, 2010). This results in a more efficient utilization of raw material which explains the adoption of the two-stage process in preference to the single-stage process in commercial ventures (Sood, 1995).

The major disadvantage of this method of production is the requirement to use propylene as a reactant where it is more desirable and economic to use the less expensive and renewable raw material for acrylic acid production (O'Neill, 2008). Due to the high demand for acrylic acid coupled with volatile crude oil prices and toxic emissions of carbon dioxide from this process, alternative methods have been studied and tested as potential replacements for the process in order to reduce the dependence of acrylic acid demand on gasoline. The need for cheaper and more sustainable alternatives has grown and hence this encourages companies to look into renewable alternatives to produce acrylic acid in a more environmental friendly and economically manner (Culp et al., 2013).

2.1.2 Bio-Based Acrylic Acid Production

The production of bio-based acrylic acid can be accomplished through dehydration of glycerol, which will be the main focus in this simulation work. Glycerol, which is generated through the trans-esterification step in the production of biodiesel, represents a promising feedstock due to its eco-friendly, sustainable properties and multifunctional structure. By using catalysts, glycerol can be transformed into a wide spectrum of hydrocarbons, aldehydes and alcohols. Among them, acrolein is considered to be one of the most essential intermediates in the chemical industry for the production of acrylic acid (Park et al., 2015).

While the development of an effective route with high yield is important, the commercial viability and success of this bio-based route depends on its competitiveness against currently implemented technologies (conventional propylene-based route). The selected raw material dictates the route's market potential in the industry especially in the bio-based industry (Le, 2014). Currently, these bio-renewable routes to produce acrylic acid cannot yet compete with their petrochemical equivalents due to the low acrylic acid yield and efficiency. However, given that most of them are still in the early stages of development, their commercial implementation is foreseen in the next two decades (Beerthius et al., 2015).

2.2 Sequential Dehydration and Oxidation of Glycerol

In this work, the production of acrylic acid is studied through a bio-based route known as the sequential dehydration and oxidation of glycerol feedstock. The best-known way to produce acrylic acid from glycerol is the two-step tandem reaction as shown in Figure 2.1. Glycerol is first dehydrated to acrolein over an acid catalyst and then oxidized to acrylic acid in the second step. Because the oxidation of acrolein to acrylic acid has already been well developed in the industrial acrylic acid process, dehydration of glycerol to acrolein in the gas phase is the main emphasis in this current simulation work (Li and Zhang., 2015).

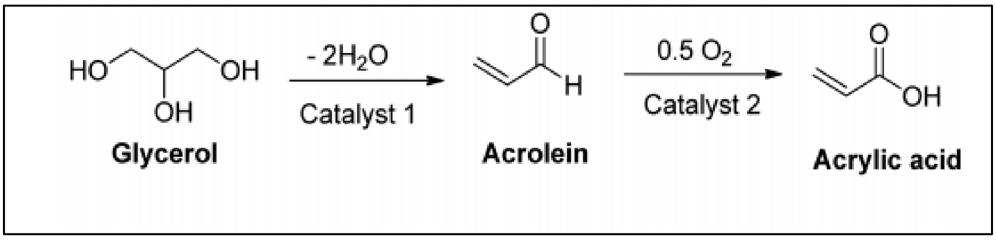

Figure 2.1: Pathway of Acrylic Acid Production from Glycerol (Li and Zhang., 2015)

2.2.1 Dehydration of Glycerol

Selective dehydration of glycerol to acrolein is an interesting catalytic process not only owing to the increasing coproduction of glycerol in the biodiesel production but also due to the emerging perspectives to provide a sustainable route for acrylic acid production (Zhang et al., 2015). In recent years, the increasing production of biodiesel has resulted in a price decline of crude glycerol which makes aqueous glycerol an attractive compound for the synthesis of fine and crude chemicals (Danov et al., 2015). The conversion of glycerol to acrolein opened a new route for the production of acrylate monomers from renewable raw materials.

According to Kraleva et al. (2011), various solid acid catalysts including sulfates, phosphates, zeolites, supported heteropolyacids have been tested for the dehydration of glycerol in the gas phase under atmospheric pressure. It was found that solid acid catalysts with a Hammett acidity (H_o) between −10 and −16 were more suitable for the dehydration of glycerol to acrolein than catalysts of lower acidity with H_o between −2 and −6 (Rao et al., 2013). Catalysts with an acidity of H_o between −3 and −10 can be chosen from natural or synthetic siliceous materials, from acidic zeolites and from mineral supports (TiO_2, Al_2O_3 and ZrO_2) impregnated with acidic functions such as sulphate, phosphate, tungstate, molybdate or alternatively heteropolyacids.

Glycerol dehydration in gas-phase is more popular due to its simplicity and advantages over liquid-phase reaction. The reaction may even occur in a regular set-up with minimal adjustments. Since usually the reaction is operated under atmospheric pressure, there is no need for pressure controlling system which reduces the process costs. Also, the effect of corrosion is minimized in this case. Additionally, packed-bed reactors (PBR) and heterogeneous catalysts are utilized for the gas-phase dehydration of glycerol. Hence, the issue of the acid catalyst separation in reactor downstream is no longer considered (Dalil, 2015).

2.2.2 Oxidation of Acrolein

The second stage of the process involves the oxidation of acrolein to produce acrylic acid in the presence of metal mixed oxides catalyst. Gas-phase catalytic oxidation of acrolein to acrylic acid has been given attention since late 1960s due to the development of the two-step process for production of acrylic acid from propene via acrolein as an intermediate. Out of the catalysts suggested, the most efficient systems for the formation of acrylic acid involve oxide systems that are based on Mo-V, Mo-Co, V-Sb and heteropolyacids. At present, it is known that the oxidation of acrolein proceeds favourably with a stoichiometric excess of oxygen, it is accelerated by the presence of steam, and the reaction temperature should not exceed 573 K. This is because the catalytic oxidation is accompanied by an undesirable radical reaction in the gas-phase volume at higher temperatures (Tichy, 1997).

Mo-V-W mixed oxide catalysts are industrially used for the oxidation of acrolein to acrylic acid. It is one of the most selective and active oxide catalyst systems. Its selectivity to acrylic acid exceeds 90% at an acrolein conversion above 90%. Moreover, Mo-V-W oxide catalysts are stable at the optimum reaction conditions and operate for years in industry without the need for regeneration (Ovsitser et al., 2002).

2.3 Reaction Mechanism

The study of the detailed processes of reaction mechanisms is important for many reasons which includes the help it gives in understanding and controlling chemical reactions. As most reactions of great commercial importance can proceed by more than one reaction path, knowledge of the reaction mechanisms involved may make it possible to choose reaction conditions favouring one path over another, thereby giving maximum amounts of desired products and minimum amounts of undesired products (de La Mare., 2008).

In the glycerol dehydration, two reaction routes exist in the first dehydration step depending on the type of acid sites, which produce different enols by elimination of either the primary or the second hydroxyl group, as shown in Figure 2.2. Based on Figure 2.2, glycerol is mainly dehydrated to 3-hydroxypropionaldehyde (3-HPA, R_1) and acetol (hydroxyacetone, R_2). It has been reasonably proposed that the central hydroxyl group of glycerol is protonated on a Brønsted acid site and the former reaction begins. The protonated intermediate is converted through the liberation of a hydronium ion (H_3O^+) and undergoes rearrangement to 3-HPA.

On the other hand, the latter reaction (R_2) is initiated through a different mechanism. As a glycerol molecule approaches a Lewis acid site, the terminal hydroxyl group of glycerol interacts with the Lewis acid site. This consequently leads to the formation of an enol intermediate that rapidly rearranges to give acetol. 3-HPA is sufficiently reactive and readily converted into acrolein through a second dehydration step (R_1) with high selectivity. On the other hand, acetol can be transformed into acetaldehyde (R_2) through C-C cleavage. Acetaldehyde can be also derived from glycerol through consecutive dehydrogenation and dehydration (R_3) reactions. Due to the variety of products in the glycerol dehydration reaction, the minor byproducts were grouped into a lump and the route involved in the conversion of glycerol to minor by-products are denoted as R_4 (Park et al., 2015).

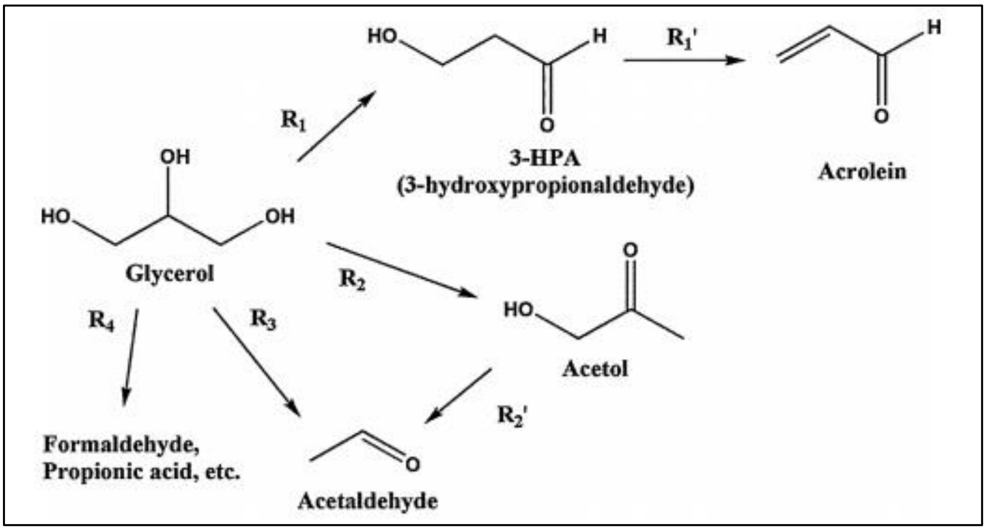

Figure 2.2: Reaction Pathway of the Dehydration of Glycerol over Solid Acid Catalysts (Park et al., 2015)

2.4 Previous Research Works on Factors Affecting Glycerol Conversion and Acrolein Yield

Much research in recent years have shown the correlation of factors such as reaction temperature and pressure, glycerol feed flowrate and concentration, oxygen concentration and Si/Al ratios on zeolite catalysts on the glycerol conversion, selectivity and yield of acrolein using glycerol feedstock. As production of acrylic acid using glycerol is still limited to laboratory scale, simulation and optimization of dehydration reactor using Aspen Plus was not explored by many researchers and experimental-based approach was more preferred (Banu et al., 2015). Since Aspen Plus simulation based researches were very limited to none, this section will discuss mainly on a few experimental literatures done on the factors affecting glycerol conversion and acrolein yield based on zeolite catalysts.

In a patent published by Neher et al. (1993), a lab-scale glycerol dehydration reaction was carried out which involves a glycerol-water mixture with a glycerol content of 10 to 40 wt% that reacts with an acidic solid catalyst with a Hammett acidity of less than +2. The reaction can either takes place in liquid phase at a temperature range of between 180°C to 340°C, or in the gaseous phase at temperatures of 250°C to 340°C. According to the patent, it was found that acrolein yields were lower in the liquid phase than in the gas phase, with the highest liquid phase yield being 36%. In addition, the selectivity of the reaction and service life of the catalyst were significantly reduced when a glycerol content above 40 wt.% and temperature above 340°C were used. This is because temperature above 340°C brings about a marked decrease in selectivity of the desired product (Neher et al., 1993).

In a similar patent published by Dubois et al. (2006), the experimental conditions of the dehydration reaction which was carried out in a fixed bed reactor, were preferably at temperature of between 250°C and 350°C and a pressure of between 1 and 5 bar using various acidic catalyst including zeolite catalysts. It was found that lower temperature led to a reduction of the glycerol conversion yield, but, at the same time, the selectivity towards acrolein was increased. It was also important to limit the residence time in the reactor to prevent side reactions and the formation of unwanted products. However, when a lower reaction temperature was used, it was desirable to increase the contact time of the reagents in the region of the catalyst in order to compensate for the decrease in the degree of conversion (Dubois et al., 2006). Since there was no simulation work involved in these two patents, the experimental-based approach limited the number of parameters studied on the glycerol conversion and acrolein selectivity which resulted in one parameter being studied at a time.

In a separate study done by Corma et al. (2008), it was reported that glycerol in water can be converted to acrolein, olefins and acetaldehyde by reactions with zeolites in a continuous fluidized-bed reactor. According to this study, this reaction system allows better heat and mass transfer than the regular fixed-bed reactors, along with the possibility of performing continuous regeneration if needed. The reaction was basically conducted using a moving-bed reactor (Microdowner reactor) and a fixed-bed reactor (Microactivity test reactor) to test an equilibrated FCC catalyst (ECat) and a ZSM5-based catalyst at different temperatures between 290°C to 650°C in various catalyst to feed ratio (CTF ratio).

The process was based on standard FCC technology in which the Microdowner (MD) reactor simulated the industrial fluid catalytic cracking process. The highest yield of acrolein between 51% to 61% was obtained at 350°C with the ZSM-5 zeolite-based catalyst, at low catalyst-to-oil ratios (6–11) and contact times of 0.5–2 s, which corresponded to weight hourly space velocities of 300 to 1300 h^{-1}. It was found that water did not significantly influence the yield of acrolein but high yields of acrolein between 55% to 62% were achieved with aqueous glycerol solutions ranging from 20 to 85 wt% glycerol. The advantage of using a moving-bed reactor is that the catalysts can be continuously separated and regenerated while producing the energy to keep the reaction (Corma et al., 2008). Overall, this experimental-based literature work was able to focus on few parameters cumulatively that affected the glycerol conversion and acrolein selectivity. However, the wide range of optimum reaction temperature, CTF ratio and glycerol concentration obtained from the experiment represent less accurate results as it was not specific to a particular value. Unlike experiments, a simulation-based approach using Aspen Plus Version 8.2 will be able to give a more specific optimum parameter value.

Besides that, Kim et al. (2010) also carried out lab scale dehydration of glycerol in a continuous fixed-bed reactor to analyze the effect of SiO_2/Al_2O_3 (SAR) ratios in ZSM-5 on the reaction using two types of zeolites with various SiO_2/Al_2O_3 ratios including Na-ZSM-5 and H-ZSM-5. The study indicated that H-ZSM-5 with a SiO_2/Al_2O_3 ratio of 150 showed the highest glycerol dehydration activity at 315°C among the various ZSM-5 catalysts tested. Although Aspen simulation was not adopted in this research work, other characterization techniques such as X-ray diffraction (XRD), temperature-programmed desorption of ammonia or water (NH_3-TPD, H_2O-TPD) with mass spectroscopy, temperature-programmed oxidation (TPO) with mass spectroscopy, infrared spectroscopy (FT-IR) after pyridine adsorption and CHNS analysis were employed. These characterization techniques played an important role in determining surface acidity of the catalyst as well as coke deposition which was vital for glycerol conversion and acrolein yield. Based on temperature-programmed desorption of ammonia (NH_3-TPD) with mass spectroscopy and infrared spectroscopy (FT-IR) after pyridine adsorption, it was found that amount of acid sites and the acid strength decreased with increasing SiO_2/Al_2O_3 in the case of HZSM-5. From the study, it was concluded that the production of acrolein was proportional to the concentration of the Bronsted acid sites, whereas the by-products were produced in the proportion of Lewis acid sites. Although surface acidity of a catalyst played a vital role in the glycerol dehydration activity, it is also mentioned that other factors such as process parameters were also controlling the catalytic activity for this reaction.

It was found that glycerol conversion and acrolein selectivity significantly increased with increasing temperature till 315°C but severe deactivation was observed at high temperatures. On the other hand, there was no noticeable difference in the glycerol conversion but the acrolein yield increased with increasing fraction of water in glycerol feed (Kim et al., 2010). Overall, this research work was able to study catalyst parameters such as SiO_2/Al_2O_3 ratio which was not offered or specified in Aspen Plus. Similar to other experimental works, the effect of operating parameter on the glycerol conversion and acrolein yield were limited to one parameter at a time in this study. In addition, other reaction parameters such as reaction pressure and weight-hourly space velocity (WHSV) were not thoroughly studied and only limited to certain type of catalyst in this research work.

From the above studies, it can be noticed that the research works have been inconsistent to one another and focused on one manipulating parameter/ variable at a time as shown in Table 2.1, instead of the cumulative effect of all relevant factors combined to maximize the yield of acrolein in the production of acrylic acid. Table 2.1 shows the summary of the literature works discussed above and the limitations faced in their respective experimental approach. With experimental approach, research work is time-consuming and tedious whereas software yield fast results and are less prone to human error. To overcome these limitations, Aspen Plus version 8.2 has been chosen to simulate and optimize the glycerol dehydration reaction in the presence of ZSM-5 catalyst.

Table 2.1: Previous experimental works on parameters affecting acrolein yield in the dehydration of glycerol based on ZSM-5 catalyst and their limitations

No	Author	Year	Parameter Studied	Limitation
1.	Dubois et al.	2006	• Reaction temperature • Pressure	Experimental approach limits the number of parameters studied on the glycerol conversion and acrolein yield which results in one parameter being studied at a time.
2.	Neher at al.	1993	• Reaction temperature • Glycerol concentration	
3.	Corma et al.	2008	• Reaction temperature, • Catalyst to feed ratio (CTF) • Glycerol concentration	Wide range of optimum reaction temperature, catalyst to feed ratio and glycerol concentration obtained from the experiment represent less accurate results as it is not specific to a particular value.
4.	Kim et al.	2010	• SiO_2/ Al_2O_3 ratios in H-ZSM-5 catalyst, • Reaction temperature • Glycerol concentration	Operating parameters such as reaction pressure and weight-hourly space velocity (WHSV) was not thoroughly studied and only limited to certain type of catalyst

Aspen Plus version 8.2 is a computer-aided software which uses underlying physical relationships including material and energy balances, thermodynamic equilibrium and rate equations to accurately and efficiently predict process behavior (Eden, 2012). Furthermore, the software also explores flexibility through the Aspen Plus Model Sensitivity Tool which quickly studies the sensitivity of process performance (in this case, acrolein yield) to changes in the key operating and design variables. As a result, a wide range of operating parameters can be studied at a time which is advantageous compared to previous experimental-based research works. Using a base set of initial condition from sensitivity analysis, Aspen Plus Optimization Tool uses its algorithm to determine a local maxima in the objective function (acrolein yield). Thus, the production of acrylic acid could be optimized by maximizing the yield of acrolein product.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Overview of Research Methodology

In order to achieve the research objectives as mentioned in Chapter One, a process model for the dehydration of glycerol to acrolein was developed using the Aspen Plus V8.2 simulator. The process model created was then used to study the relationship of reactor temperature, pressure, weight-hourly space velocity (WHSV) and glycerol concentration towards the conversion of glycerol and yield of acrolein.

Firstly, a suitable reactor block in Aspen Plus was chosen to simulate the data obtained from the literature. Suitable information and assumptions were taken into account for the reactor block. The experimental data from literature was used to validate the model in order to determine whether the model is comparable with the experimental data. If the validation succeeded, operating variables such as reactor temperature, pressure, weight hourly space velocity (WHSV) and glycerol concentration were manipulated using the Sensitivity Analysis Tool in Aspen Plus. Lastly, the optimization of the glycerol dehydration reaction was done by maximizing the yield of acrolein by using optimization tool in Aspen Plus. A general flow of the methodology is shown in Figure 3.1.

3.2 Research Methodology Steps

Figure 3.1 shows the summary of methodology steps involved in this research work.

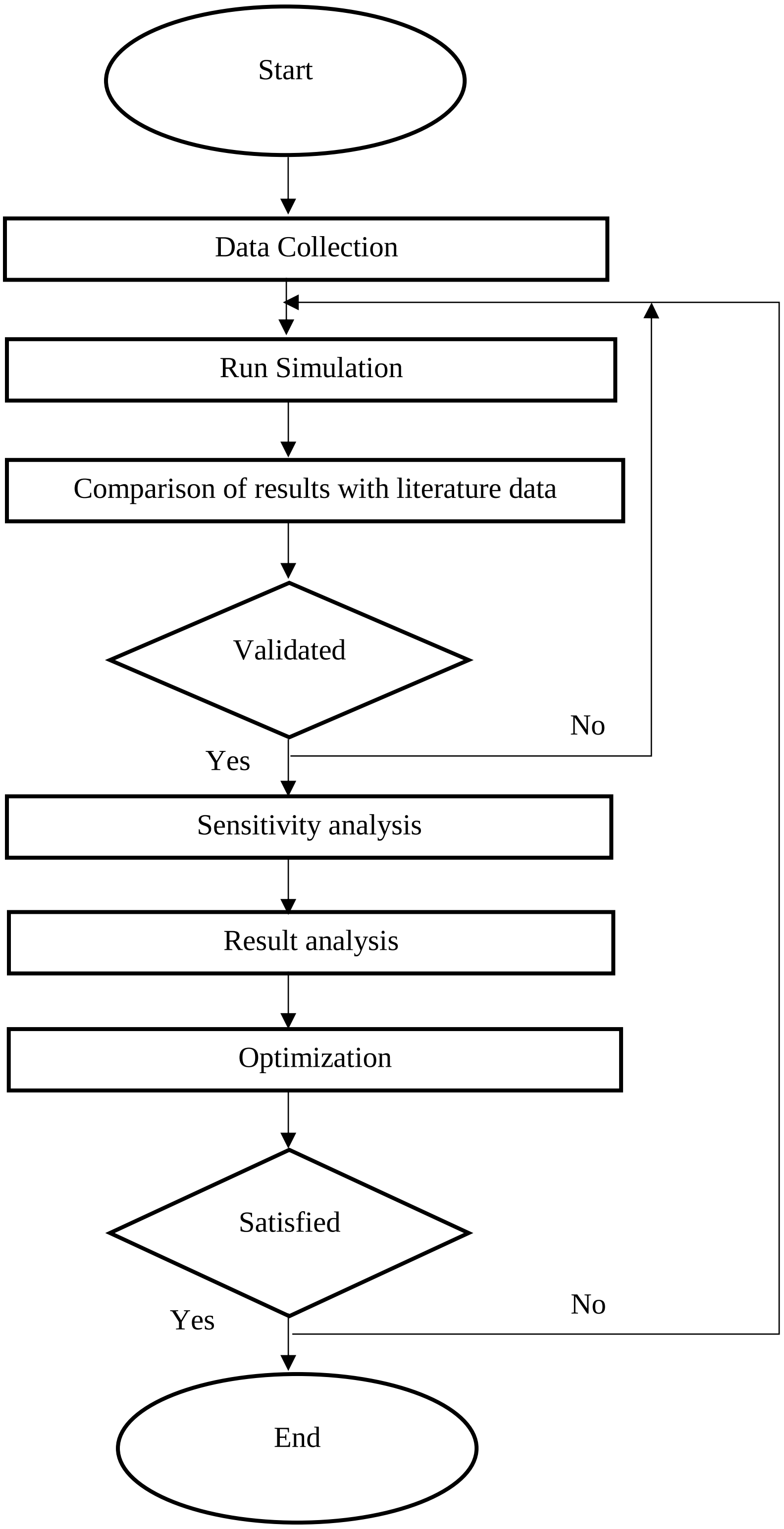

Figure 3.1: Methodology Flow Chart

3.2.1 Data Collection

The system considered in this simulation and optimization work was the dehydration reactor in the acrylic acid production plant. It is the reaction where the gaseous glycerol feed is dehydrated into acrolein which is an intermediate product to produce the desired acrylic acid in the presence of ZSM-5 zeolite catalyst. The equations below show the main reaction and side reactions that takes place in the dehydration reactor (Banu et al., 2015).

(i) Main dehydration reaction towards intermediate product acrolein:

$$\underset{\text{glycerol}}{C_3H_8O_3} \rightarrow \underset{\text{acrolein}}{C_3H_4O} + \underset{\text{water}}{2H_2O} \tag{3.1}$$

(ii) Side dehydration reaction towards side product such as acetaldehyde, carbon monoxide, hydrogen and water.

$$\underset{\text{glycerol}}{C_3H_8O_3} \rightarrow \underset{\text{acetaldehyde}}{C_2H_4O} + \underset{\text{hydrogen}}{H_2} + \underset{\text{water}}{H_2O} + \underset{\text{carbon monoxide}}{CO} \tag{3.2}$$

(iii) Side dehydration reaction towards side products such as ethylene and carbon monoxide.

$$\underset{\text{acrolein}}{C_3H_4O} \rightarrow \underset{\text{carbon monoxide}}{CO} + \underset{\text{ethylene}}{C_2H_4} \tag{3.3}$$

(iv) Side dehydration reaction towards side products such as carbon, hydrogen and water.

$$\underset{\text{acrolein}}{C_3H_4O} \rightarrow \underset{\text{carbon}}{3C} + \underset{\text{hydrogen}}{H_2} + \underset{\text{water}}{H_2O} \tag{3.4}$$

The reactor that was used in the literature is a moving or circulating bed reactor which consists of a riser reactor regenerator which is similar to Fluid Catalytic Cracking (FCC) type reactor as shown in Figure 3.2. The reactor continuously regenerates catalyst by burning off the coke to generate heat back into the reactor (Corma et al., 2008). Due to unavailability of this type of reactor in Aspen Plus Version 8.2 database, isothermal plug flow reactor (RPLUG) model was chosen to model and simulate the glycerol dehydration reaction as shown in Figure 3.3.

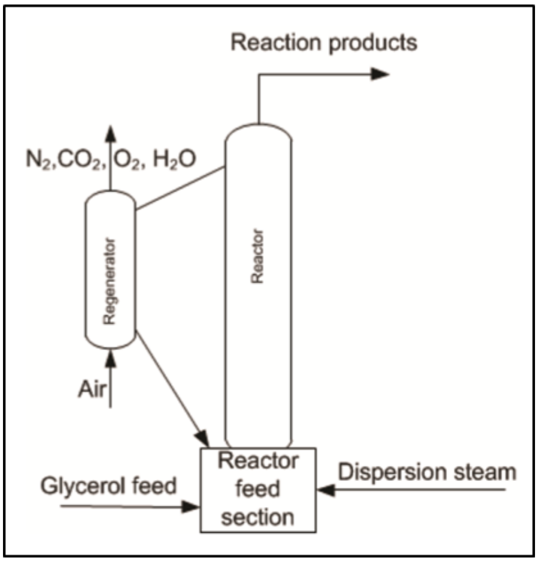

Figure 3.2: Reactor used in the literature (Banu et al., 2015)

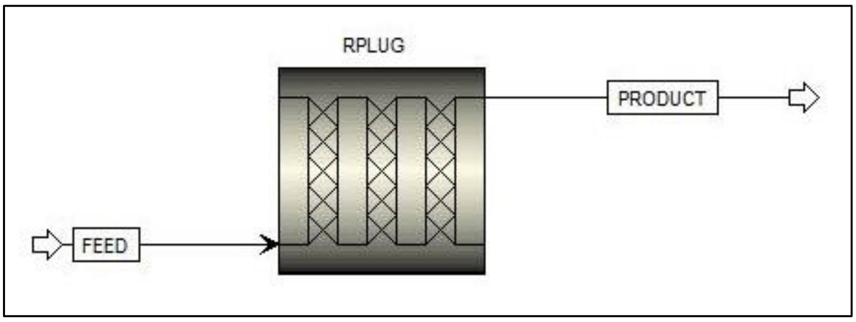

Figure 3.3: RPLUG reactor model used in the simulation