SIMULATION OF SULFUR TRIOXIDE PRODUCTION IN AN ADIABATIC MULTISTAGE CATALYTIC REACTOR

ANIS SALWANI BINTI ROZMAN

UNIVERSITI SAINS MALAYSIA

2018

SIMULATION OF SULFUR TRIOXIDE PRODUCTION IN AN ADIABATIC MULTISTAGE CATALYTIC REACTOR

by

ANIS SALWANI BINTI ROZMAN

Thesis submitted as a partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

June 2018

ACKNOWLEDGEMENT

First and foremost, I would like to express my gratitude supremely to Allah s.w.t upon His blessing and permission to grant a piece of His knowledge, strength and determination for me to complete this Final Year Project. I also would like to express my eternal appreciation towards my parents, Encik Rozman bin Yahaya and Puan Noor Aini binti Ya'akop and also family members who have always been at my side giving the unconditional supports and being understanding.

My special thank is for my research supervisor, Associate Professor Dr. Norashid bin Aziz for his dedicated involvement to assist me throughout the process of my research study. His keen interest above all his overwhelming attitude to help me had been solely and mainly responsible for completing my task. His prompt inspirations, timely suggestions with kindness dynamism at every stage of my research have enabled me to achieve the objectives of this study. I owe a deep sense of gratitude to Associate Professor Ir. Dr. Zainal Ahmad and Professor Ir. Dr. Leo Choe Peng for their enthusiasm providing me necessary technical suggestions during my research pursuit.

Lastly, I am grateful to a postgraduate student named Dinie bin Muhammad and my classmates for sharing their truthful and illuminating views on a number of issues related to the project study. I thank all the people for their help directly or indirectly to accomplish my research paper.

Anis Salwani binti Rozman

June 2018.

TABLE OF CONTENTS

		Page
ACKNOWLEDGEMENT		ii
TABLE OF CONTENTS		iii
LIST OF TABLES		v
LIST OF FIGURES		vi
LIST OF SYMBOLS		vii
LIST OF ABBREVIATIONS		vii
ABSTRAK		viii
ABSTRACT		ix
CHAPTER ONE: INTRODUCTION		1
1.1	Sulfur Trioxide Production Process	1
1.2	Problem Statement	2
1.3	Research Objectives	3
1.4	Scope of Study	4
1.5	Thesis Organization	5
CHAPTER TWO: LITERATURE REVIEW		6
2.1	Manufacture of Sulfur Trioxide	6
	2.1.1 Single Contact Process	6
	2.1.2 Double Contact Process	7
	2.1.3 Wet Contact Process (WCP)	8
	2.1.4 Pressure Process	8
	2.1.5 Unsteady State Oxidation Process	9
	2.1.6 Hydrogen Peroxide (H_2O_2) Process	10
2.2	Reaction Mechanism	10
2.3	Previous Research Works on Sulfur Dioxide Conversion	11
CHAPTER THREE: MATERIALS AND METHODS		22
3.1	Overview of Research Methodology	22

3.2 Steps of Research Methodology 23
3.2.1 Data Collection 23
3.2.2 Run Simulation 29
3.2.3 Comparison of Simulation Results with Literature 30
3.2.4 Sensitivity Analysis 31

CHAPTER FOUR: RESULTS AND DISCUSSION 33
4.1 Process Validation 33
4.2 Sensitivity Analysis of Reaction Model 41
4.2.1 Case 1: Effect of reactor inlet temperature towards sulfur dioxide conversion 42
4.2.2 Case 2: Effect of reactor inlet pressure towards sulfur dioxide conversion 43

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS 44
5.1 Conclusion 44
5.2 Recommendations 46

REFERENCES 47
APPENDICES 49

LIST OF TABLES

		Page
Table 2.1	Previous study of sulfur dioxide oxidation	17
Table 3.1	Sulfur dioxide oxidation industrial reactor specifications and feed condition (Gómez-García et al., 2015)	26
Table 3.2	Properties of hollow ring shape catalyst (data supplied by the catalyst manufacturer) (Gómez-García et al., 2015)	26
Table 3.3	Approximation lengths for the four RPLUG reactor blocks (Gómez-García et al., 2015)	27
Table 3.4	Approximation inputs for the three heat exchangers (Gómez-García et al., 2015)	27
Table 3.5	Results of sulfur dioxide oxidation reactor (Gómez-García et al., 2015)	30
Table 3.6	Range of manipulating variables (MVs) for sensitivity analysis purpose	31
Table 4.1	Comparison of simulation results with literature	34

LIST OF FIGURES

		Page
Figure 3.1	Methodology flow chart	23
Figure 3.2	Reactor used in the literature (Gómez-García et al., 2015)	25
Figure 3.3	Four RPLUGs and three coolers used as a model in the simulation	25
Figure 3.4	Sensitivity analysis methodology	32
Figure 4.1	Sulfur trioxide composition profile in BED 1	35
Figure 4.2	Sulfur trioxide composition profile in BED 2	35
Figure 4.3	Sulfur trioxide composition profile in BED 3	36
Figure 4.4	Sulfur trioxide composition profile in BED 4	36
Figure 4.5	Temperature profile in BED 1	37
Figure 4.6	Temperature profile in BED 2	37
Figure 4.7	Temperature profile in BED 3	38
Figure 4.8	Temperature profile in BED 4	38
Figure 4.9	Pressure profile in BED 1	39
Figure 4.10	Pressure profile in BED 2	40
Figure 4.11	Pressure profile in BED 3	40
Figure 4.12	Pressure profile in BED 4	41
Figure 4.13	Effect of reactor temperature on sulfur trioxide composition	42
Figure 4.14	Effect of reactor pressure on sulfur trioxide composition	43

LIST OF SYMBOLS

Symbol	Description	Unit
A	Area of catalyst bed	m^2
ρ_p	Density of catalyst pellets	kg/m^3
M	Mass of catalyst bed	kg
H	Height of catalyst bed	m
ε	Bed voidage	-

LIST OF ABBREVIATIONS

WCP	Wet Contact Process
USRKIN	User Kinetic
FORTRAN	FORmula TRANslation

SIMULASI PENGHASILAN SULFUR TRIOKSIDA DI DALAM SEBUAH REAKTOR ADIABATIK DENGAN BERBILANG PERINGKAT PEMANGKIN

ABSTRAK

Penghasilan sulfur trioksida daripada gas sulfur dioksida sudah mendapat kepentingan global dan oleh itu proses ini perlu dikaji supaya penukaran sulfur dioksida terjamin semasa pelaksanaannya dalam industri kimia terutamanya dalam industri asid sulfurik. Simulasi untuk proses pengeluaran sulfur trioksida boleh dijalankan dengan menggunakan perisian simulasi yang maju seperti Aspen Plus tanpa perlu menggunakan simulasi berangka seperti kerja-kerja penyelidikan sebelumnya. Aspen Plus Versi 8.8 digunakan dalam kajian penyelidikan ini untuk mensimulasikan reaktor adiabatik yang mempunyai berbilang peringkat pemangkin untuk reaksi sulfur dioksida dioksidakan menjadi gas sulfur trioksida dengan kehadiran pemangkin vanadium pentaoksida. Keputusan simulasi yang diperoleh dibandingkan dengan jurnal untuk pengesahan. Keputusan simulasi yang diperoleh oleh Aspen Plus menjana 4% daripada ralat purata umum dari segi penukaran sulfur dioksida, suhu dan tekanan keluar. Dari analisis sensitiviti yang dijalankan, didapati bahawa komposisi molar sulfur trioksida meningkat sedikit sehingga 0.082 pada 2.5 bar tekanan masuk reaktor manakala suhu masuk reaktor menunjukkan tiada kesan yang signifikan terhadap komposisi molar sulfur trioksida yang dihasilkan.

SIMULATION OF SULFUR TRIOXIDE PRODUCTION IN AN ADIABATIC MULTISTAGE CATALYTIC REACTOR

ABSTRACT

The production of sulfur trioxide from sulfur dioxide gas is already gaining global importance and thus this process needs to be studied so that the conversion of sulfur dioxide is assured during its implementation in the chemical industry especially in sulfuric acid industry. It is possible to simulate sulfur trioxide production process with a well-developed simulation software such as Aspen Plus despite using the numerical simulation like previous research works. Aspen Plus Version 8.8 is used in this research study to simulate an adiabatic multistage catalytic reactor where sulfur dioxide gas is oxidized into sulfur trioxide gas in the presence of vanadium pentoxide catalyst. The simulation results obtained are compared with literature for validation. The simulated results obtained by Aspen Plus generate 4% of general average error in terms of the sulfur dioxide conversion, temperature and pressure outlet. From the sensitivity analysis conducted, it is found that the molar composition of sulfur trioxide increases lightly up to 0.082 at 2.5 bar of reactor inlet pressure while the reactor inlet temperature shows no significant effect on the molar composition of sulfur trioxide generated.

CHAPTER ONE

INTRODUCTION

1.1 Sulfur Trioxide Production Process

Sulfur trioxide (SO_3) is generally a colourless liquid. It can also exist as fiber-like crystals or as a gas. It is also called as sulfuric oxide and sulfuric anhydride (U.S. Department of Health and Human Services, June 1999). Sulfur trioxide is an important raw material for many processes in chemical industry as for instance, it is used for the sulfonation of organic compounds to produce detergents, for sulfuric acid production and for many other applications.

Sulfuric acid (H_2SO_4) is one of the most demanding chemicals in the world (Wegerhoff and Engell, 2013). It plays an important role in the process of almost all manufactured goods like chemical production and metal processing. Most of it is used for the production of phosphate fertilizers (Gómez-García et al., 2015). Approximately 65% of the sulfuric acid produced is used in the production of agricultural fertilizers (Amin, 2013). Since biofuels stocks like corn and sugarcane crops can be renewable and reducing the greenhouse gas emission, the production of bio-based fuel materials drive the demand for sulfuric acid in the market (Infinite Research Limited, 2017). Sulfuric acid world production in 2012 only was about 220 million tonnes (Gómez-García et al., 2015). The demand is anticipated to increase at a steady state and post a compound annual growth rate (CAGR) closed to 3% (Infinite Research Limited, 2017).

The precursor of sulfuric acid industry is sulfur trioxide, which is gained by oxidation of sulfur dioxide (SO_2) in a contact process (Wegerhoff and Engell, 2013). The contact process consists of multiple catalytic beds, inter-stage cooling and an

absorption step in the case of sulfuric acid production. The oxidation of sulfur dioxide to sulfur trioxide undergoes an exothermic conversion and equilibrium controlled reaction (Amin, 2013). In this stage of contact process, a gas mixture containing sulfur dioxide and air is passed over the catalytic beds, which oxidizes sulfur dioxide to sulfur trioxide (Suslick, 1997) and (Benzinger et al., 2011).

Since the production of sulfur trioxide holds the importance in global chemistry industry, this process needs to be studied using a dynamic simulation as if the process is disturbed, operational problems might happen at the existing plant due to production rate changes or catalyst deactivation (Amin, 2013). Such simulation for a prominent process like sulfur dioxide oxidation is able to conduct using an advanced computer aided simulation software like Aspen Plus to achieve the desired end-product characteristics. A heterogeneous simulation model of an industrial multi-bed catalytic converter in a sulfuric acid plant was developed in this project. The studied reactor comprises four continuous cylindrical vessels which act as an adiabatic fixed bed reactor with four separate beds of vanadium pentoxide catalyst.

1.2 Problem Statement

The production of sulfuric acid using sulfur trioxide as its main intermediate material has attracted attention due to the growing phosphate fertilizer production around the world regardless of the basis of raw materials used like elemental sulfur, sulfide ores or spent acid gas like hydrogen sulfide (H_2S).

The market demand statistics shows a clear uprising global consumption for sulfur trioxide in the upcoming decades and most of the previous research works on the simulation of sulfur trioxide production have focused on numerous mathematical model

approach using the industrial operating data. Therefore, this project tries to simulate the sulfuric acid production process using Aspen Plus version 8.8 to achieve the targeted industrial conversion of sulfur dioxide. The sensitivity tool in this software is used to perform an instant analysis of sensitivity performance of this process (in this process, composition of sulfur trioxide produced) by manipulating the input operating variables (temperature and pressure) on the conversion of sulfur dioxide using sensitivity analysis.

The computer software like Aspen Plus is utilized to simulate an unit operation used in an industrial sulfuric acid plant like reactor in this case study which involves high operating temperatures and requires high maintenance costs. It is important to understand the effect of certain operating parameters such as temperature and pressure of reactor inlet stream on the conversion values. The sensitivity analysis tool in this software 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.

A more sustainable view of sulfur trioxide production using Aspen Plus simulation software can be established in this work for the industrial viewpoint. This work provides a different platform to validate a proposed sequential framework of sulfur dioxide conversion to produce sulfur trioxide using this particular software.

1.3 Research Objectives

The objectives for this research are:

i) To simulate sulfur trioxide (SO_3) production in a multistage catalytic reactor by using ASPEN Plus.

ii) To study the effect of different parameters in oxidation of sulfur dioxide (SO_2) to produce sulfur trioxide in the multistage catalytic reactor.

1.4 Scope of Study

A simulation-based approach is done in this research project to simulate the production of sulfur trioxide using Aspen Plus Version 8.8. One of the main unit operation in a sulfuric acid plant, known as sulfur dioxide converter is chosen to be simulated using Aspen Plus since the oxidation of sulfur dioxide to sulfur trioxide process has already been well established in this chemical industry.

A model of four plug flow reactor (RPLUG) blocks and three heat exchanger blocks is used to develop a simulation flow sheet of sulfur dioxide oxidation process in Aspen Plus Version 8.8. The simulation results obtained are then compared with those reported in the literature. If the simulation results obtained is comparable with the literature, sensitivity analysis is then conducted on the sulfur dioxide conversion. Using the sensitivity analysis tool, the sensitivity performance of sulfur dioxide reaction based on the effect of changing operating conditions are studied.

The temperature of feeding gas to the converter reactor must be high enough to initiate the catalytic oxidation reaction activate the catalyst and next to guarantee a high reaction rate. The exothermic reaction proceeds and the gas temperature rises as the gases pass through the reactor. The oxidation rate depends on activity of the catalyst and approach to equilibrium. The reaction extent is dependent on the oxidation rate and the residence time of the process gases in contact with the catalyst in the reactor (Gómez-García et al., 2015).

1.5 Thesis Organization

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

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

Chapter 2 discusses literature review regarding the manufacturing of sulfur trioxide that includes the reaction mechanism of sulfur dioxide oxidation process. Previous research works and their limitations done by other researchers on factors affecting the sulfur dioxide conversion and sulfur trioxide 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 sulfur dioxide oxidation reaction followed by sensitivity analysis on operating variables such as reactor temperature and pressure drop, and sulfur dioxide conversion as well as optimization of the process using Aspen Plus Version 8.8.

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 drop and conversion of sulfur dioxide 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 Sulfur Trioxide

In a typical sulfuric acid plant, the manufaturing process includes three important steps: (1) the formation of sulfur dioxide (SO_2), (2) its catalytic oxidation to sulfur trioxide, SO_3 (a reversible and highly exothermic reaction) and (3) the reaction of sulfur trioxide with water, H_2O in absorption towers (Gómez-García et al., 2015).

There are six new routes that have been introduced and used conventionally to manufact sulfur trioxide in new sulfuric acid plants since the traditional plant use lead chamber process. The process rotes are single contact process (single absorption), double contact process (double absorption), wet contact process (WCP), pressure process, unsteady state oxidation process and hydrogen peroxide (H_2O_2) process (Ashar, 2013). The following section provides an overview of those applicable techniques to sulfur trioxide production in sulfuric acid industry by Ashar (2013) which refers to the existing plants.

2.1.1 Single Contact Process

Sulfur dioxide gas which have been carefully cleaned and dried, is oxidized to sulfur trioxide in the presence of catalysts containing alkali and vanadium oxides. The sulfur trioxide is absorbed by concentrated sulfuric acid in an absorption tower. The single contact process is generally used with 6-10% sulfur dioxide content of inlet gases; in new plants, the conversion efficiency is about 98.5% as a daily average and

can be upgraded to 99.1% by a good design. In the existing single conversion single absorption plants, it is actually difficult to obtain better than 98.0% conversion of sulfur dioxide. However, a conversion efficiency of 98.5% can be achieved in some existing plants with a large catalyst loading in the last bed and operating at a low temperature as possible (410–415 °C) (Ashar, 2013).

2.1.2 Double Contact Process

In the double contact process, about 99.5% conversion can be obtained, depending on the arrangement of the contact beds and of contact time preceding the intermediate absorber. After cooling the gases to approximately 160–190 °C in a heat exchanger, the sulfur trioxide formed is absorbed in the intermediate absorber in a 98.5–99.5 wt% of sulfuric acid. The absorption of the sulfur trioxide brings about a considerable shift in the reaction equilibrium towards the formation of sulfur trioxide, resulting in considerably higher overall conversion efficiencies when the residual gas is passed through one or two secondary contact beds. The sulfur trioxide formed in the secondary stage is absorbed in the final absorber. In general, feed gases containing up to 12 vol.% of sulfur dioxide are used for this process. In new plants that undergo sulfur burning process can reach the conversion efficiency about 99.6% as a daily average. In this double absorption process, the candle type demister developed by Monsanto (USA) was the major breakthrough. This prevents 99.99% of mist amount is above 1 μm as any mist carryover would affect the heat exchangers as well the catalyst activity in the following passes of converter (Ashar, 2013).

2.1.3 Wet Contact Process (WCP)

In earlier stage of WCP, this process was used to treat lean hydrogen sulfide gases. It has been used to treat off-gas from a molybdenum smelter as well as being installed in two desulfurization plants (one in a flue gas desulfurization system, the other on an industrial boiler) which are currently under construction. WCP is one kind of process that is not sensitive to the water balance. Sulfurous components in the gas feeds are converted to sulfuric acid without drying the gas first. Roaster gases that are cleaned by a combination of cyclones, bag filters, electrostatic precipitators, venture scrubber, etc.; cleaned gases (containing sulfur dioxide) are brought up to a conversion temperature prior to admission to the converter.

Sulfur dioxide is converted to sulfur trioxide by the catalyst and the hot gases passing through the converter exit are cooled by heat exchange with the incoming cold feed gas. Sulfur trioxide combines with water vapor present in the gases to form sulfuric acid. Then, it is condensed by a specially designed condensers that minimized acid mist formation. In addition to the usual utilities required for a sulfuric acid plant, an additional fuel (e.g., for oil/gas fired burners) might be needed for heating the process gas to a suitable conversion temperatures if the gas strength is low (less than 3.5–4.0% of sulfur dioxide) since autothermal operation is difficult at such low strengths (Ashar, 2013).

2.1.4 Pressure Process

In this process, the conversion of sulfur dioxide to sulfur trioxide increases due to the increased operating pressure since there is a reduction in gas volume during the reaction:

$$2SO_2 + O_2 \longrightarrow 2SO_3 \quad (2.1)$$

The increased operating pressure can be achieved by maintaining an optimum temperatures in the catalyst bed. Increasing the process gas pressure can lead to the reduction of equipment size, but higher power consumption of the blower offsets the advantage gained. Thus, the operating pressure of most sulfuric acid plants are meant for only a little above atmospheric pressure. Nowadays, cold process has become economically viable at high pressure. Reduction in gas volumes can reduce both the required size of the equipment and the amount of catalyst required. A capital saving is possible, however the power consumption of blower is higher. The salient disadvantage of pressure contact process is that it consumes more power compared to conventional double-absorption process (Ashar, 2013).

2.1.5 Unsteady State Oxidation Process

This new alternative of sulfur dioxide oxidation is based on a periodic reversal of the direction of the reaction mixture flow over the catalyst bed. The developer of this process is Dr. Matros at the Institute of Catalysis of the former Union of Soviet Socialist Republics (USSR)**.** Basically, a large bed of catalyst is used both as a reversing and regenerating heat exchanger as well as a catalytic reactor for sulfur dioxide oxidation reaction. Cold sulfur dioxide gas is fed into the catalyst bed and is heated by the heat stored in the bed until a catalyst ignition temperature is achieved. At this point, the conversion reaction proceeds while producing heat. The heat is absorbed by the catalyst in the bed which increasing its temperature. The gas flow through the reactor is reversed when the front gas comes close to the exit side of the bed. The main advantage of this process is the operating line for the first bed is almost vertical which leads the bed to 80–90% conversion at a low exit temperature. The process is auto-thermal at low sulfur

dioxide gas concentration (0.5–3%). Several plants in Russia and other Eastern European countries had use this process operation (Ashar, 2013).

2.1.6 Hydrogen Peroxide (H_2O_2) Process

Hydrogen peroxide oxidizes the sulfur dioxide to sulfur trioxide which is then used to produce sulfuric acid. However, this process is not economical due to the high cost of hydrogen peroxide. Hence, hydrogen peroxide is used to oxidize the remaining traces of (dissolved) sulfur dioxide in the circulating acid in the plant which minimizes the escape of sulfur dioxide from tail gases at the final absorption tower (Ashar, 2013).

2.2 Reaction Mechanism

Catalytic oxidation of sulfur dioxide to sulfur trioxide is a key step for sulfuric acid making. (King et al., 2013) stated that the ratio of oxygen (vol%) to sulfur dioxide (vol%) in industrial catalytic oxidation feed gas are in the range of 0.75 – 2 which is 1.5 – 4 times the stoichiometric $SO_2 + 0.5\ O_2 \longrightarrow SO_3$ requirement of 0.5 moles oxygen per mole of sulfur dioxide. The excess oxygen gas promotes rapid oxidation. The oxidation is always conducted by passing warm sulfur dioxide-bearing gas through horizontal beds of catalyst which also promotes rapid oxidation. Sulfur dioxide oxidation is thermodynamically efficient at temperature 400-600^oC. Industrially, a sequence of three to five catalyst beds with gas cooling between beds is used to carry out the oxidation reaction. Heat removal from the gas between catalyst beds allows it to leave the last bed at a low temperature (~450^oC) where the equilibrium oxidation efficiency is high (98+%).

Flow of ~400^{o}C sulfur dioxide bearing gas around the loaded catalyst causes it to form a molten vanadium oxide film on the surface of the catalyst's porous silica substrate. It is in this melt that catalytic sulfur dioxide oxidation occurs. The steady-state *in situ* composition of the catalyst melt is affected by the gas composition that is passing around the melt and it varies down the catalyst beds. The amount of sulfur dioxide oxidized at equilibrium is the maximum extent to which the sulfur dioxide feed can be oxidized. This maximum conversion depends on the equilibrium temperature and pressure as well as the feed gas composition.

2.3 Previous Research Works on Sulfur Dioxide Conversion

The literature study shows that during the last few decades, the research in the area of sulfuric acid production captures interesting topics requiring reliable (dynamic) modelling, as for example Hong et al. (1997) conducted one-dimensional two-phase unsteady-state model describing a fixed-bed catalytic reactor which was derived from the mass conservation of sulfur dioxide and the heat for each phase. The Crank-Nicolson predictor-corrector method on a non-uniform spatial grid was used in solving the derived partial differential equations. The prime feature of the numerical method was the second-order accuracy both in time and in space. The two-way linked list is selected to store the temperature and concentration in the node points for adapting the change of the node number. Thus, the computation accuracy and speed were improved remarkably. Numerical simulation of sulfur dioxide oxidation over vanadium catalysts in a small reactor was presented as an example. Numerical results showed that autothermal oxidation of low concentration sulfur dioxide is feasible. The parameter sensitivity using different influences (bed length, gas velocity of bed, initial bed

temperature, feed concentration and cycle time) on maximum gas temperature and average conversion, etc., was carried out carefully for the mathematical model.

Xiao et al. (1999a) presented a novel flow reversal of sulfur dioxide converter for relatively concentrated gases with the catalyst bed divided into three stages and inter-stage quenching. The typical operation mode, effects of the quenching ratio, the flow cycle duration, and the catalyst activity had been investigated based upon modelling and simulation. Comparison with the inter-stage heat removal converter and simulation for a commercialized converter had been done too. The calculated results showed the new converter was very effective for the tested cases

In the same year, Xiao et al. (1999b) developed a research work in commercialization of a sulfur dioxide converter with flow reversal and interstage heat removal. It started with modelling of the converter, and experimental verification of the model with a laboratory reactor and a pilot scale converter. An appropriate converter configuration was suggested to deal with the strongly fluctuating sulfur dioxide concentrations from 1 % to higher than 4% based on the simulation conducted. The converter consists of three catalyst packed stages, and two interstage heat exchangers, with two temperature buffers mounted at both ends. A dual position control strategy to open or shut the interstage heat exchanger was developed, which had been proven to be effective.

Xiao et al. (1999c) also worked on the modelling and simulation of the unsteady-state sulfur dioxide converters with one or two inter-stage heat exchangers. In this paper, the effects of the input sulfur dioxide concentration, the superficial velocity, the cycle duration of the flow reversal and the heat removal capacity of the inter-stage heat exchangers, and even the inert packing sections sandwiching the catalyst bed, had been discussed. The results obtained show considerable performance improvements by

using the inter-stage heat removal over the adiabatic unsteady-state converters for the relatively concentrated gases involving sulfur dioxide.

In a separate study done by Book and Challagulla (2000), they used the attainable region (AR) method to obtain the optimal design and operating conditions for the adiabatic oxidation of sulfur dioxide to sulfur trioxide. The optimum process layout for this exothermic, catalytic, reversible reaction was a complex interconnection of reactors that achieved a conversion in excess of the equilibrium value for a single adiabatic reactor. The complex design obtained from the AR method was technically and economically superior to a single adiabatic reactor but it was inferior from a safety perspective as a result of its complex interconnections and its high preheat temperature. The strategies of inherently safer design (minimize, substitute, moderate, and simplify) was applied to the complex design to compare it with the conventional adiabatic reactor designs.

A multi-bed adiabatic reactor for the catalytic oxidation of sulfur dioxide, using a heterogeneous plug flow model was simulated in a study by Nodehi and Mousavian (2007). It was shown that the effectiveness factor could be obtained by applying the orthogonal collocation (OC) method with only two collocation points. Different catalyst distributions were obtained by applying the intrinsic rate of reaction, and actual rate of reaction in the optimization criteria. The results show that the minimum amount of the catalyst could be reached at lower temperatures and at a wide range of the first bed inlet temperatures.

A systematic approach based on nonlinear experimental design as an efficient tool for the validation of kinetic models was proposed by Schöneberger et al. (2009) which hold the objective of computing experimental layouts, setups, and controls in

order to optimize the statistical reliability of parameter estimates from the resulting experimental data. This paper represented an interaction between proposed experiments (e.g., inlet temperature and concentration), their evaluation, parameter estimation, and new design information such as reactor layout, sampling points, and temperature measurement positions.

The current legislation imposed tighter restrictions in order to reduce the environmental impact of chemical process industry. In a context by Kiss et al. (2010), this study presented the dynamic model, simulation and optimization results for an industrial sulfuric acid plant. The dynamic model includes a catalytic reactor (five pass converter), heat exchangers such as economizers and feed-effluent heat exchangers, mixers, splitters and reactive absorption columns. The SO_x emissions could be significantly reduced to more than 40% by optimizing the operating parameters such as air feed flow rates or split fractions. However, only minor increases in energy production could be achieved as the plant already operating near full capacity. The simulations also showed that operational problems might be occur when the process was disturbed due to production rate changes or catalyst deactivation, the non-linear response of the plant leading to sustained oscillations.

In a study by Benzinger et al. (2011), sulfur trioxide was produced via contact process in the gas phase catalytic oxidation reaction. The contact process consists of multiple catalyst beds of a microstructured reactor with inter-stage cooling and an absorption step in the case of sulfuric acid production. The unique heat and mass transport properties of this reactor made it possible to develop a small scale one pass synthesis well suited for on-site sulfur trioxide production, e.g., for surfactant making. A detailed model of the flow, the heat distribution and the surface chemistry was used to perform numerical simulations for a single channel configuration. A reaction

mechanism based on elementary reactions was proposed with sulfur dioxide di-coordinated, which was energetically favoured. A sensitivity analysis showed that the adsorption/desorption of sulfur dioxide and the heterogeneous reaction were close together in their sensitivity coefficients as the relative importance of the system reactions. It might be concluded that a change of the experimental conditions could cause a shift of the rate determining step from adsorption of sulfur dioxide to the heterogeneous oxidation reaction.

Bendjaouahdou (2013) addressed the simulation problem by controlling the magnitude of maximal catalyst temperature, or hot spot in a four catalyst beds sulfur dioxide converter by manipulating the volumetric flow rate of reaction mixture. The control of the maximal catalyst temperature was carried out in order to avoid the occurrence of a hot spot inside the catalyst mass and to keep high catalyst efficiency. The performance and robustness of the controller were evaluated for the case of a kinetic complex and reversible exothermic reaction. The results obtained by numerical simulation showed the possibility of the regulation of the hot spot temperature below a pre-specified value despite the occurrence of strong perturbations.

Sulfur trioxide is produced industrially by the contact process which consists of several catalytic beds and inter-cooling stages between them (Wegerhoff and Engell, 2013). This process is highly energy intense and inexible due to long periods of start-up and shut-down caused by the thermal inertia. A new approach for producing sulfur trioxide is currently being investigated to improve the exibility of the production process. A micro-structured reactor has been constructed by the Karlsruhe Institute for Technology (KIT) which consists of only one cooling passage. In their work, a three dimensional dynamic reactor model was developed that described the dynamic behaviour of the micro-structured reactor. This model was used to simulate the

efficiency and the distribution of temperature and reactants in the system and particularly in the start-up investigation of the reactor.

New dynamic models by Sørensen et al. (2015) for special process equipment like absorbing/desorbing catalytic reactors and condensing heat exchanger had been set up and successfully used for simulating transient pilot scale and industrial data. The closed-loop simulation of a complete wet sulfuric acid (WSA) plant was exemplified by simulating the plant behaviour receiving a typical fluctuating off-gas produced by the non-ferrous metallurgical industry which employs Peirce–Smith converters and Electric Furnaces.

Another study of a rigorous heterogeneous model by Gómez-García et al. (2015) was developed and implemented for steady state simulations of an industrial adiabatic multi-bed catalytic reactor for sulfur dioxide oxidation. This paper evaluated the behaviour of each catalytic bed (e.g. conversion, temperature and pressure profiles) and the effectiveness factor variation along the reactor. The Maxwell-Stefan model was appropriately justified for the diffusion intraparticle model. The precision in plant data estimation made the model a very useful tool and led to a better understanding of the effect of diffusional resistances on reactor performance.

From the above studies, it can be noticed that the research works have been conducted using the dynamic numerical models to be compared with industrial plant data to validate the approach efficiency by achieving the highest possible conversion of sulfur dixode. Table 2.2 shows the summary of the literature works discussed above and their respective process models.

Table 2.1: Previous study of sulfur dioxide oxidation

No.	Process	Reactor and catalyst	Model	Simulation	References
1.	Auto thermal oxidation of low concentration sulfur dioxide Periodic flow-reversal operation	Fixed - bed catalytic reactor Vanadium catalysts	One - dimensional two - phase unsteady - state model Predictor - corrector finite difference method based on the Crank-Nicolson scheme	Numerical simulation Computer program coded in language C *Simulation software name was not stated	(Hong, 1997)
2.	SO_2 oxidation	The flow reversed fixed - bed reactors Vanadium catalyst	Mathematical model for quenching unsteady state (QUS) converter	*name of simulation software was not stated	(Xiao, 1999a)
3.	SO_2 conversions Control variable: the quantity of the cooling capacity	A pilot-scale reverse-flow reactor V_2O_5 catalysts	A vigorous dynamic heterogene-ous model	USSC (Unsteady State SO_2 Converter)	(Xiao, 1999b)

Table 2.1: Previous study of sulfur dioxide oxidation (Continued)

No.	Process	Reactor and catalyst	Model	Simulation	Author
4.	SO_2 oxidation Design variables: 1. inlet SO_2 concentration 2. superficial velocity Control variables: 1. cycle duration 2. heat removal capacity	The heat removal unsteady-state SO_2 converters with one heat exchanger (HRUS-1) and two heat exchangers (HRUS-2)	Mathematical model for an unsteady-state SO_2 converter with the flow direction reversed	*name of simulation software was not stated	(Xiao et al., 1999c)
5.	Adiabatic oxidation of sulfur dioxide to sulfur trioxide	Single adiabatic reactor	Attainable region (AR) method	Aspen HYSYS	(Book and Challagulla, 2000)
6.	Catalytic oxidation of SO_2	A multi-bed adiabatic reactor Vanadium catalyst	Heterogeneous plug flow model	*name of simulation software was not stated	(Nodehi and Mousavian, 2007)
7.	Catalytic SO_2 oxidation	Fixed-bed reactor Vanadium pentoxide-containing catalyst	Steady-state model of nonlinear optimal experimental design	MatLab	(Schöneberger et al., 2009)

Table 2.1: Previous study of sulfur dioxide oxidation (Continued)

No.	Process	Reactor and catalyst	Model	Simulation	Author
8.	Converting SO_2 to sulfur trioxide (SO_3) using oxygen (O_2) from air	Multi - pass catalytic converter (five pass converter)	Axial dispersion model	gPROMS	(Kiss et al., 2010)
9.	Multistep mechanism involves coordination of SO_2 on two surface sites Elementary reaction mechanism with SO_2 di - coordinated	Microstructured reactor Pt catalyst	Detailed kinetic model based on elementary steps occurring on the catalyst surface Surface chemistry; multistep heterogeneous reaction mechanism	ANSYS FLUENT 12.0 Special Properties of the microchannel Single channel configuration	(Benzinger et al., 2011)
10.	Manipulative variable: inlet gas volumetric flowrate Adiabatically with no flow reversal	Four catalytic fixed beds SO_2 converter	Generalised predictive control (GPC) with off line process identification Crank-Nicolson scheme Pseudo – random binary sequence (PABS) Recursive least - squares identification method	*Simulation software name was not stated Controlling the magnitude of the maximal catalyst temperature, or hot spot	(Bendjaouahdou, 2013)

Table 2.1: Previous study of sulfur dioxide oxidation (Continued)

No.	Process	Reactor and catalyst	Model	Simulation	Author
11.	Oxidation of SO_2 to SO_3 Controlled variable: Temperature of process fluid at the end of reactor	Microstructured reactor	Three dimensional dynamic distributed parameter model	gPROMS; 3D simulation model MATLAB; controller tuning	(Wegerhoff and Engell, 2013)
12.	SO_2 oxidation Manipulated variables: 1. feed flow rate 2. feed temperature 3. feed composition	Absorbing / desorbing catalytic reactors	Dynamic tanks–in series model: 1. dynamic reactor model 2. dynamic sulfuric acid condenser model	Commercial dynamic simulator Closed - loop simulation of WSA plants *name of simulation software was not stated	(Sørensen et al., 2015)
13.	Sulfur dioxide oxidation	Adiabatic multibed catalytic reactor Vanadium (V) oxide supported on silica	Maxwell – Stefan diffusional model	MatLab Steady state simulations	(Gómez-García et al., 2015)

Technology is fundamental to the profitable design and operation of environmentally friendly sulfuric acid processes. Aspen Plus software is an integral part of aspenONE Engineering and the electrolytes feature in Aspen Plus can improves the conversion of sulfur dioxide to sulfur trioxide (Bhat and Pinjala, 2010). Rate-based modelling approach in this work use a custom user kinetic model to simulate and calculate the conversion of sulfur dioxide along the reactor. Aspen Plus Sensitivity Tool enables a quick sensitivity study of the simulated process can be done which in this case is sulfur dioxide conversion, through changes in a wide range of key operating variables at a time.

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 oxydation of sulfur doxide to sulfur trioxide is developed using the Aspen Plus V8.8 simulator. The process model created is then used to study the relationship of reactor temperature, pressure drop and the conversion of sulfur dioxide.

Firstly, a suitable reactor block in Aspen Plus is chosen to simulate the industrial data obtained from the literature by Gómez-García et al. (2015). This literature is chosen to be used because it stated sufficient information for this simulation work to be conducted. Thus, the industrial reactor specifications and feed conditions are used to validate the model in order to determine whether the model is comparable with the literature results. If the validation succeeded, operating variables such as inlet temperature and pressure are manipulated using the Sensitivity Analysis Tool in Aspen Plus. A general flow of the methodology is shown in Figure 3.1.

3.2 Steps of Research Methodology

The overview of research methodology involved in this project is shown in Figure 3.1 below:

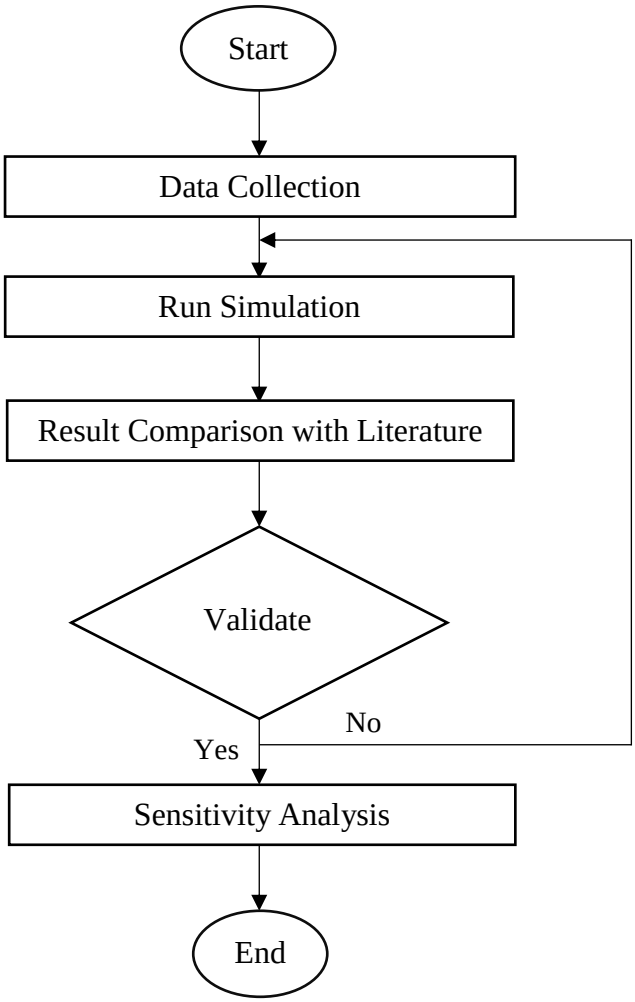

Figure 3.1: Methodology flow chart

3.2.1 Data Collection

The system considered in this simulation work is the sulfur dioxide converter in an established sulfuric acid production plant. It is the main reaction where sulfur dioxide is oxidated into sulfur trioxide which is an intermediate product to produce the

desired sulfuric acid. The oxidation of dry sulfur dioxide takes place by contact in gas phase in the presence of excess oxygen and the presence of vanadium pentoxide (V_2O_5) catalyst pellet supported on silica (SiO_2).

$$SO_2 + 2V^{5+} + O^{2-} \longrightarrow 2V^{4+} + SO_3 \quad (3.1)$$

$$^1/_2O_2 + 2V^{4+} \longrightarrow 2V^{5+} + O^{2-} \quad (3.2)$$

Overall reaction:

$$SO_2\,(g) + {}^1/_2O_2\,(g) \longrightarrow SO_3\,(g) \quad (3.3)$$

In this research study, there will be just a single process will take place which is oxidation of sulfur dioxide to produce sulfur trioxide and no side reaction is estimated to occur. Since the reaction is exothermic, the gas is heated adiabatically and its temperature rises until the SO_2-SO_3 equilibrium is approached (Amiri and Alihosseinpour, 2015).

Ranade (2002) stated that the commercially important process like oxidation of sulfur dioxide is in the fixed bed of reactor type. Fixed bed reactor is generally modelled as plug flow or axial dispersed plug flow type model. The reactor used in the literature is an adiabatic multi-bed catalytic reactor which consists of four beds of catalyst pellets in a cylindrical vessel as shown in Figure 3.2. For each catalytic bed stream outlet, the stream need to be cooled using external exchanger to prevent catalyst deactivation at high temperature since this process is an exothermic reaction. Due to unavailability of this type of reactor in Aspen Plus Version 8.8 database, four adiabatic plug flow reactors (RPLUG) and three exchangers as the coolers were chosen to model and simulate the sulfur dioxide oxidation as shown in Figure 3.3.