

Chapter 5: Fixed Bed Reactor

Design, Construction and Performance

5.1 Introduction

The investigation of the decomposition of sulphur trioxide to sulphur dioxide and oxygen using a packed bed reactor laboratory apparatus is reported in the chapter. The system is discussed with specific mention to the design and layout of the experimental apparatus. The acid vaporizer, reactor and condensation/trap section are described in full detail. A long and a short catalyst bed were investigated to obtain a variety of process conditions. The operating procedure, as well as experimental planning, is provided and explained. The system was investigated by using a variety of analysis techniques which are discussed. A model was developed in Aspen Plus® to account for the solubility of sulphur dioxide in water and the model was validated against experimental results. The inert pre-heating packing was investigated to establish whether the packing, as well as other units, catalysed the reaction in the absence of catalyst as this was necessary to obtain inlet conditions to the catalyst bed. The packed bed system was investigated with regard to performance by changing the inlet temperature to the catalytic bed while the Weight Hour Space Velocity (WHSV) and total molar flow rate was kept constant. The second variable investigated was a change in WHSV where the following experiments were conducted:

- Constant inlet temperature, change in WHSV (acid flow rate)
 - Two inlet temperatures kept constant, change in WHSV (catalyst mass)
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The third variable that was investigated was a variation in residence time where four different inlet temperatures were investigated while the acid flow rate was kept constant and the nitrogen flow rate also varied.

5.2 Experimental

5.2.1 Design and Layout

The experimental layout for the decomposition of sulphur trioxide into sulphur dioxide and oxygen was designed and built after careful consideration of units reported in literature (Gelbard, 2005) (Thomey, 2012). The system had three major sections required investigation; the acid vaporizer and pre-heater, the reactor section where sulphur trioxide was decomposed and the cooling section where acid was condensed and scrubbed from the gas sample going to the analyzer. An illustration of the apparatus can be seen in Figure 5-1 and the process flow diagram can be seen in Figure 5-2.

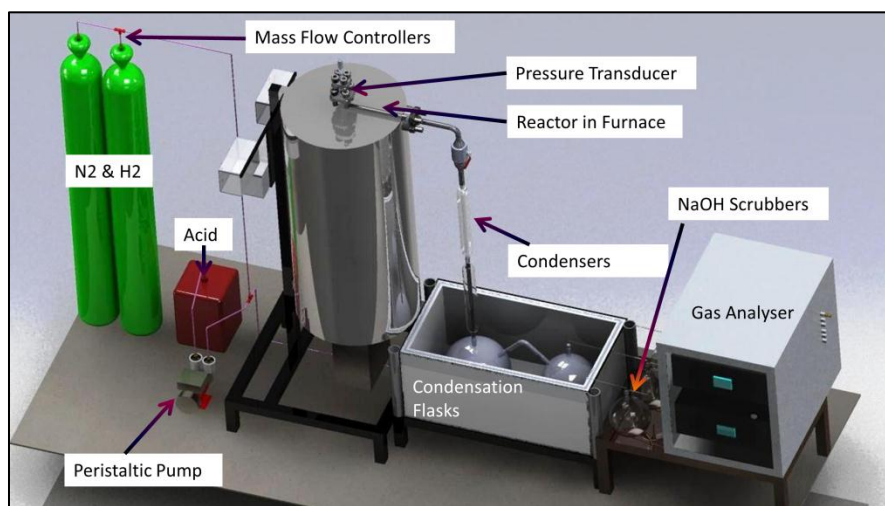


Figure 5-1: Physical layout of the packed bed reactor system

The entire reactor system can be visualized in a Computer Aided Design (CAD) drawing in Figure 5-1 to illustrate the different sections physically without too much detail, as will be shown later with an exact illustration. The main components as mentioned above can be seen in Figure 5-1. The packed bed reactor system was placed inside a laboratory which was under constant suction to extract fumes from the laboratory in case of leakage and to vent the analyser. The system will be described by elaborating individually on the three sections mentioned.

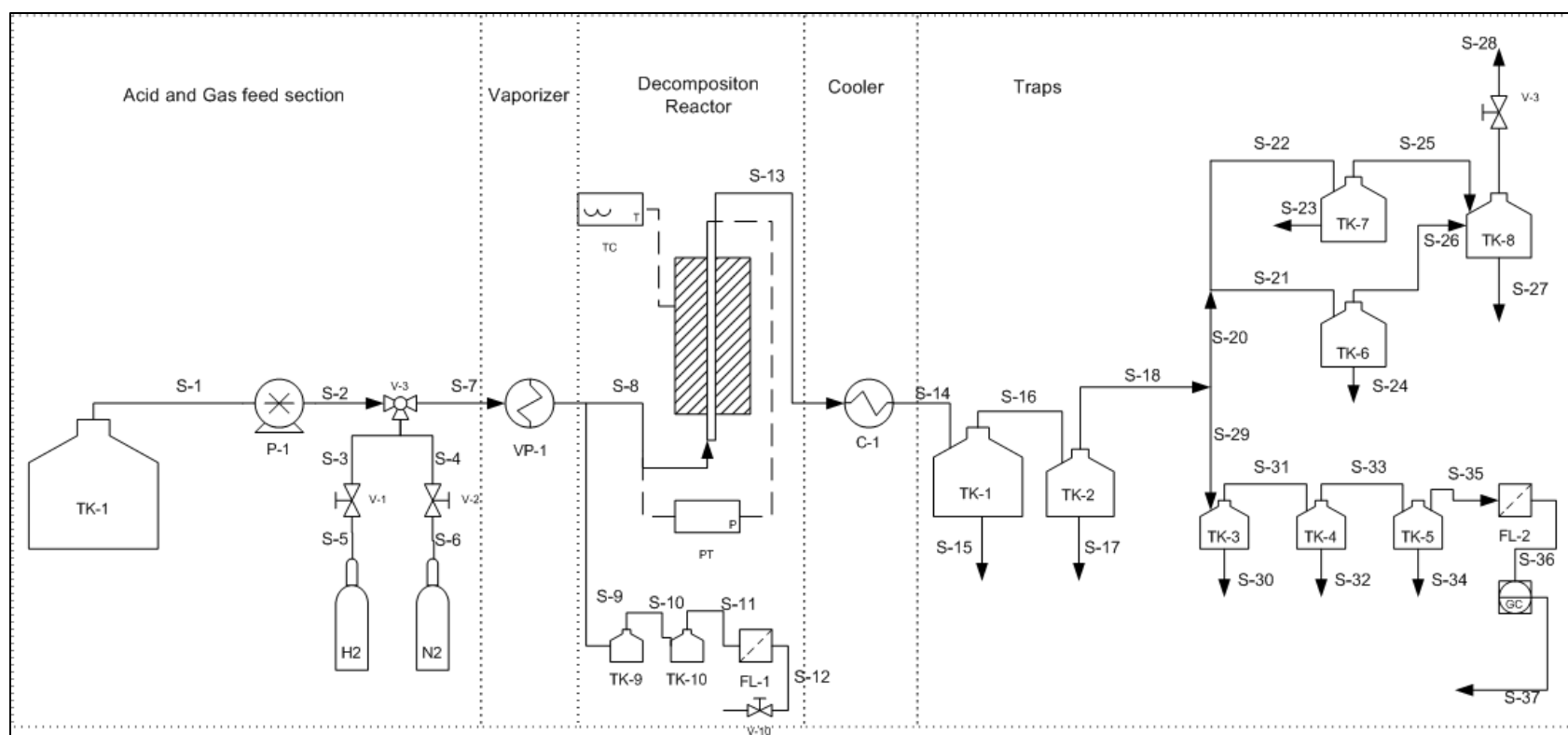


Figure 5-2: Process flow diagram of Packed Bed Reactor system

5.2.1.1 Acid Vaporizer

Although the main focus of the study was to investigate the decomposition of sulphur trioxide to sulphur dioxide and oxygen, sulphur trioxide as pure reactant was not available in vapour or liquid form due to its instability and low vapour pressure. The need to produce sulphur trioxide for a feed stream together with the effect of exploring real process conditions as in the HyS, required the decomposition of pure sulphuric acid. The main purpose of the vaporizer (VP-1) was to boil the H_2SO_4 and convert it to the vapour phase. During vaporization of the sulphuric acid it will start to decompose into sulphur trioxide and water. The vaporizer and condenser sections are most likely to be corroded at an accelerated rate. Gelbard et al. (2005) reported that sulphuric acid is most corrosive when undergoing a phase change. In the study of Gelbard et al. (2005) they used Hastelloy c-276 as construction material and the same material was utilized in this study as it provided moderate resistance against corrosion although SiC or quartz were recommended. SiC was discarded as construction material due to difficulty in sealing thermocouples to the ceramic, especially at high temperature. The vaporizer (VP-1) was constructed using a 10 mm O.D. Hastelloy c-276 tube with a length of 3 m bent into a coil to fit inside a box furnace with dimensions as indicated in Figure 5-3.

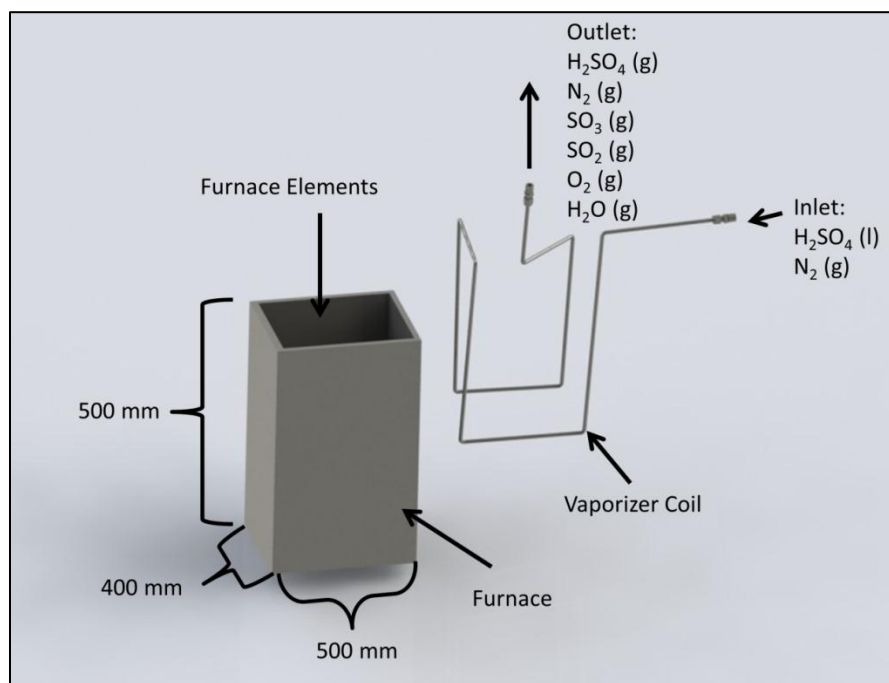


Figure 5-3: Configuration of vaporizer coil and box furnace

The box furnace (electrical, 220 V, 1.5 kW) was set to control the temperature at 1023 K, resulting in a reactor inlet temperature of approximately 753 K, depending on the flow rate. The lower temperature

was due to energy loss between the vaporizer and decomposer, which was exposed to the atmosphere. The vaporizer coil was constructed so that gravity feed of the acid (98 wt% Platinum Grade, ACE Chemicals) was possible. Sulphuric acid (TK-1) was fed to the system using a peristaltic pump (Gilson Minipuls Evolution, Max. flow 67 mL/min, Lasec). The inlet was located 300 mm outside the furnace to eliminate the problem that Gelbard et al. (2005) experienced with a higher corrosion rate when injecting sulphuric acid at high temperatures. The nitrogen (Baseline, Afrox) flow was controlled with a Siera Smart Trak-50 mass flow controller, which was also connected at the same point to increase total flow rate through the reactor without an acid flow rate too high for the system to handle.

The purpose of nitrogen was to serve as a carrier gas and get the species through the system more quickly. The gravity feeding made it convenient for the acid and inert nitrogen to mix. The gas feed pipe connected at the inlet of the vaporizer coil could switch between nitrogen and hydrogen when needed. The hydrogen (Baseline, Afrox) was used to reduce or activate the PGMs in the catalyst as described in Chapter 3. The process simulation software code Aspen Plus® was used with the NRTL equation of state model to evaluate the temperature at which sulphuric acid was completely decomposed into sulphur trioxide and water according equilibrium conditions. Some of the graphs which represent the conversion of H_2SO_4 at various temperatures and pressure can be seen in Appendix E. In Figure E-3 the fraction equilibrium conversion achieved with the presence with inert nitrogen can be seen and from the figure the conclusion can be made that complete dissociation of sulphuric acid is achieved at temperature of 700 K for the specific conditions. Thermodynamic data provide the only means to check whether the acid dissociated completely, as it is very difficult to verify this experimentally. The furnace temperature was thus high enough to ensure complete dissociation. Due to the temperature drop between vaporizer and reactor this temperature might have dropped below 700 K, but a temperature recovery was made in the inert region in the reactor tube resulting in complete dissociation of sulphuric acid.

5.2.1.2 Sulphur Trioxide Decomposer

The reactor tube used for the decomposition reaction was constructed of a 25 mm O.D. Hasteloy c-276 tube with wall thickness of 2 mm (tube wall based on availability from supplier). The material of construction was chosen as it was used by Gelbard et al (2005). The tube diameter was chosen so that thermocouple probes could be easily inserted and the same time not become limiting with regard to heat transfer. The length of the reactor tube was 1400 mm where the bottom 150 mm was thermally insulated, followed by 1000 mm in the heated zone and another insulated section of 150 mm. The

length were chosen as acid flow rates was limiting and a long catalyst bed would be close or at equilibrium for most of process conditions. The outlet was inserted in the side of the tube with a downward angle so that condensed acid could flow out of the reactor and not accumulate in the system. At the top of the reactor tube a flanged connection facilitated the insertion and extraction the catalyst pellets. A pressure transducer was also mounted on the flange to evaluate the pressure at the outlet of reactor. Another pressure transducer (PT) was inserted between the vaporizer and the reactor inlet. Tubes were used to place the pressure transducer (SA Gauge, WIKA) some distance away from the furnaces as the transducers required a limited operating temperature. Two different bed lengths were evaluated, namely a 400 mm active bed length (long bed) and a 100 mm active bed length (short bed). Thermocouples (Type K, Inconel 600 sheath, WIKA) were placed along the length of the reactor tube inside the 1 m heated zone of the furnace. The placement of the thermocouples (TC) (Figure 5-4) for the long bed were as follows: 10 thermocouples placed inside the reactor tube to obtain the centreline temperature; 9 thermocouples placed on the wall of the reactor to obtain the wall temperature profile as the heat supplied by the furnace (Electrical, 360 V, 9 kW, Hi-Tech Elements) did not provide a homogeneous heat distribution. Although electrical heating is not proposed for the HyS cycle it was utilized in the experimental apparatus since investigating the catalytic side is of greater importance. One of the centreline thermocouple probes was used to control the furnace by an on/of controller to control the energy to the resistance element wire to produce radiant heat. The placement of the thermocouples can be seen in Figure 5-4 for the long and short beds investigated.

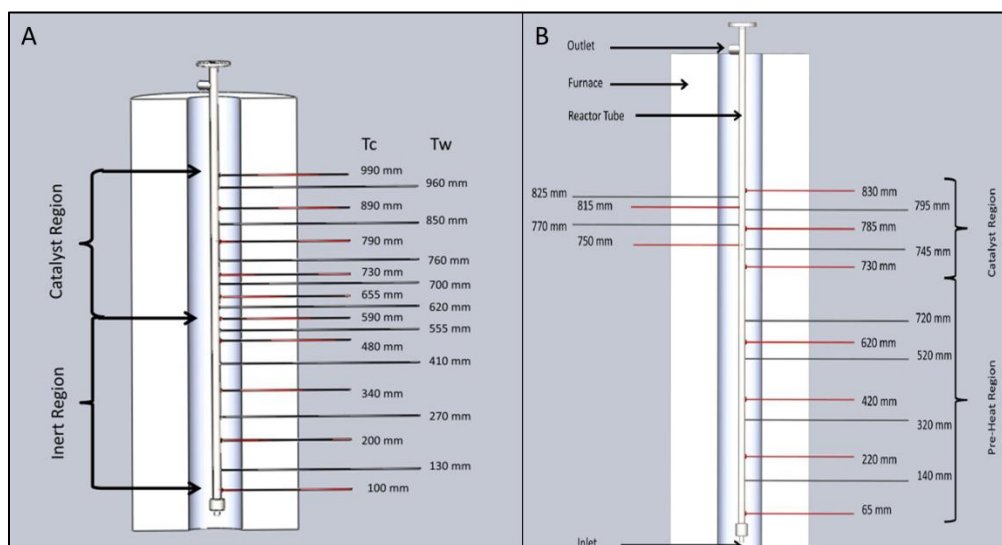


Figure 5-4: Thermocouple placement in reactor tube for long (A) and short bed (B)

The altered reactor comprised a shorter bed section of 100 mm with 5 centreline thermocouple probes and 5 wall thermocouple probes to monitor the temperature change in the short section of bed. Figure 5-4 depicts the 100 mm bed section (B) with the 5 centreline probes. In Figure 5-4 the longer thermocouples are shown on the wall (T_w) and the shorter thermocouples on the centreline (T_c). The thermocouple probes were sealed in type 316L stainless steel sleeves constructed of 6 mm OD tube and Swagelok SS316 compression fittings. Inert silicon carbide spheres (± 1.7 mm diameter) were used as a ceramic pre-packing in the catalyst bed to promote heat transfer, enhance flow distribution and to eliminate the possibility of a reactive support that could influence experimental results. For the long bed the reactor tube was filled with the SiC balls to a length of 600 mm and for the short bed a length of 700 mm. The catalyst cylinders were placed on the inert carbide spheres. The flange was sealed with a carbon seal which could resist moderate temperatures as it was some distance from the furnace. After every experiment a new seal was inserted.

5.2.1.3 *Condensers and Scrubbers*

The components used in the condenser and scrubber section can be seen in Figure 5-2 (process flow diagram). The outlet of the reactor tube was supplied with a custom-made fitting where a glass connection piece could be screwed in and sealed with PTFE thread sealing tape. From this connection piece three Liebig coolers (C-1) were connected in series and connected to a 20 l (TK-1) round bottom flask. Cold water (kept below 283 K with a chiller and ice) was pumped through the coolers. A glass connection piece was used to connect a 10 l round bottom flask (TK-2) to the 20 l flask, all submerged in an ice bath. At that point the stream was split; one stream passes through three 500 mL Erlenmeyer flasks (TK-3 to TK-5), also submerged in an ice bath followed by a filter to remove any remaining mist.

This stream was then sent through a 0.3 micron silica filter to remove any particles or water vapour before being sent to the gas analysers. The other streams were sent to two 5 l round bottom flasks (TK-6 & TK-7) filled with sodium hydroxide to scrub sulphur dioxide, sulphur trioxide and sulphuric acid from the stream. The outlets of these two scrubbers joined to form the feed to the third scrubber (TK-8) to ensure all harmful chemicals are removed from the gas stream. The stream from the third scrubber was vented to the atmosphere. In Figure 5-5 the complete experimental sulphur trioxide decomposition reactor setup can be seen.

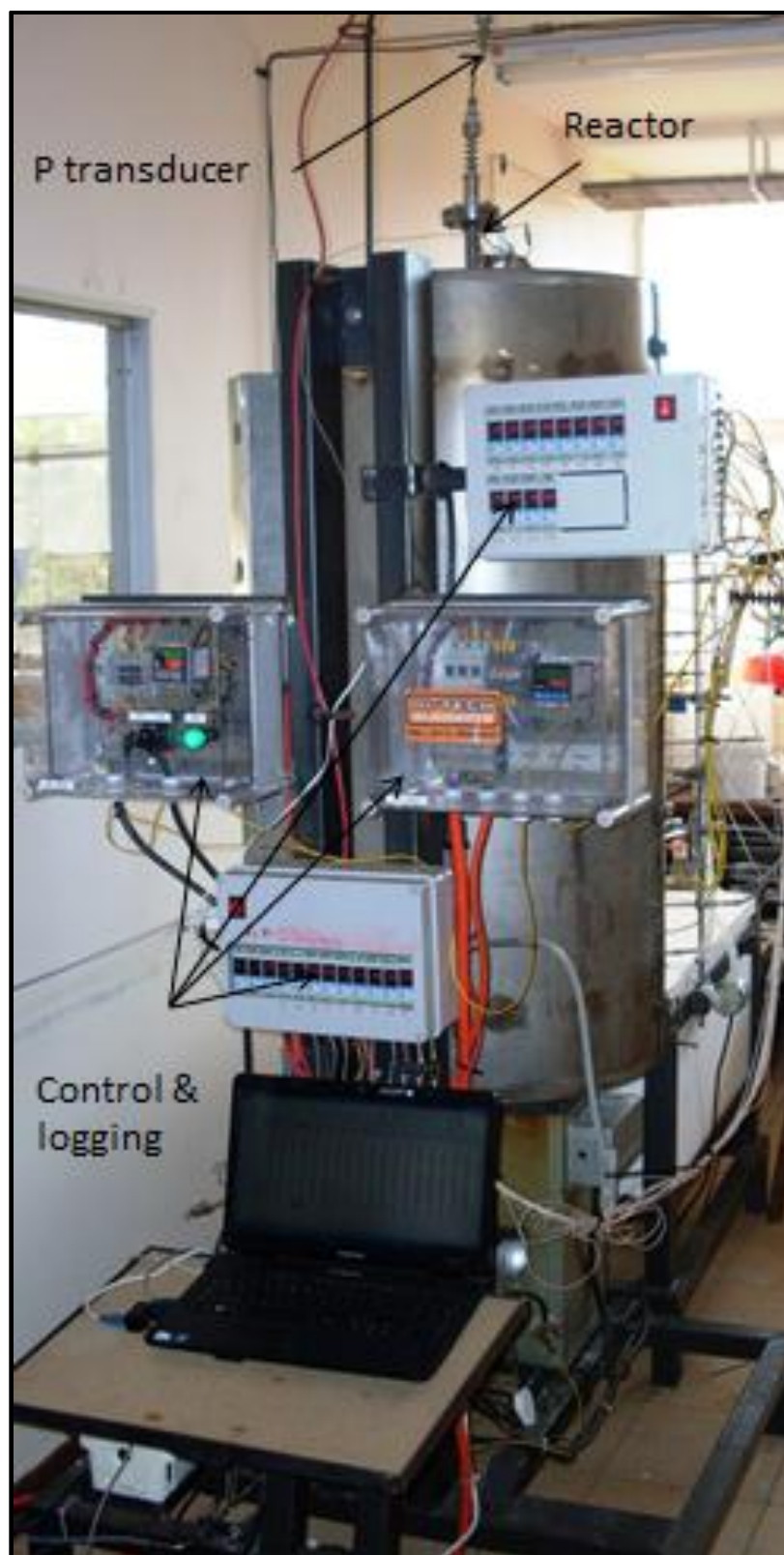


Figure 5-5: Sulphur trioxide decomposition reactor system

5.2.2 Procedure and Planning

The experimental procedure for an experiment entailed three separate investigations, namely establish the performance of the pipe used for the vaporizer and reactor, the inert pre-packing and the catalyst. Firstly, the Hastelloy c-276 pipe was evaluated under the process conditions for a certain time. Secondly, the inert SiC pre-packing was evaluated under process conditions to determine the extent to which it catalysed the reaction. These pre-investigations were necessary to determine the conversion achieved by the catalyst alone since the vaporizer, reactor tube and inert packing may catalyse the reaction especially at high temperatures.

The third procedure was to add the catalyst section and evaluate the conversion and temperature profiles for that section. The catalyst pellets were inserted so that the packing could be assumed a random packing. Catalyst and inert pellets were weighed and the length that the particles occupied was evaluated in a volumetric flask with the same internal diameter as the reactor tube and could be measured. This made it possible to accurately assign the correct amount of inert packing to the specific region, as well as observe the temperature profiles in the correct region when catalyst amounts varied. Catalyst pellets were sintered as discussed in Chapter 3. To fully evaluate the performance of the reactor system the PGM-based catalyst was investigated under different process conditions. Experimental planning was conducted and the different experiments completed can be found in Table 5-1. The experiments conducted are classified into three different process variables, namely inlet temperature variation, Weight Hour Space Velocity (WHSV) variation and residence time variation. In the table details of the inlet temperature, acid flow rate, nitrogen flow rate, WHSV and number of experiments conducted, are given.

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Table 5-1: Experimental planning

Variation	Temperature (K)	Acid Flow (mℓ /min)	Nitrogen Flow (Nℓ /min)	WHSV (h ⁻¹)	Number of Experiments
Inlet Temperature	953; 1003; 1053; 1103	2	3	1.2	3 x For all temperatures
WHSV	1103	3	2.1	1.8	2
		4	1.2	2.6	1
	1103	4	1.2	2.6	4
				9.2; 43; 86; 865	1 x For all WHSVs
	953	4	1.2	9.2; 43; 763	1 x For all WHSVs
Residence Time	953; 1003; 1053; 1103	4	2.80	15	1 x For all temperatures
	953; 1003; 1053; 1103	4	3.37	15	1 x For all temperatures
	953; 1003; 1053; 1103	4	3.78	15	1 x For all temperatures

All units and streams mentioned and described can be found in Figure 5-2. Sulphuric acid was stored in a 5 l round bottom flask (TK-1) and pumped into the vaporizer (VP-1) by a peristaltic pump (P-1). Nitrogen and hydrogen were inserted into the system as streams S-3 and S-4. The pressure before the reactor (RX-1) was continually measured and a sample could be taken via stream S-30. Thermocouples were used to measure the temperature distribution inside the tube and the pressure at the outlet of the tube was also continually measured. The pressure measuring equipment was not sensitive enough to establish pressure drop over the packed bed, rather only the inlet pressure to the bed. The process gas was cooled in three Liebig coolers (C-1) and the condensed acid was collected in Flasks TK-1 to 5 submerged in an ice bath. The streams were split into two - the first was sent through 5 l flasks (TK-6 to 8) filled with sodium hydroxide (ACE Chemicals) solution. The stream was open to vent to the atmosphere and the analysis was also completed on that stream. The other stream was sent through filters to remove acid mist (FL-2) and send to the GC for sulphur dioxide analysis.

5.2.2.1 Procedure for Start-up and Reduction

The box and tube furnace were turned on to obtain the specified operating temperature. The time needed to obtain steady temperatures was ± 3 hours depending on ambient conditions. During this time nitrogen was used to flush the system at 1 Nl/min (S-3). The logging software was started to log a data point for each of the thermocouple probes as well as the pressure transducers every minute. For the catalyst, hydrogen was used to reduce the PGM into the metal state at a flow rate of 1 Nm³/min (S-4). After both furnaces reached a steady state (no variation in temperature from data logging) the nitrogen flow was closed and hydrogen opened. Hydrogen was used to reduce the PGM on the TiO₂ support to the active metal state during exposure to hydrogen for 2 hours. The ice bath trap section (containing TK 1-5) was filled with ice prior to starting the experiment. The condenser pump (C-1) was started and the chiller cooling the water was turned on and set to a temperature of 278 K. Depending on the ambient temperature the condenser temperature was usually below 288 K (the ambient temperature varied greatly between summer and winter). After the reduction period the hydrogen was closed and nitrogen opened to flush the system for 15 min to ensure that all hydrogen that might react with sulphur species has been removed from the system.

5.2.2.2 *Procedure for Reaction*

The nitrogen was set to the specific flow rate (V-2, S-4) and the specific flow streams to the respective analysis systems were opened. The peristaltic pump (P-1) was set to the required pump rate and turned on. When the acid started decomposing in the vaporizer (VP-1) the flows of the nitrogen carrier gas and the acid, now in the vapour phase, combined. The acid flow rate increased the total flow rate since the density of liquid sulphuric acid is approximately 1840 kg/m^3 and that of acid vapour (actually SO_3 and H_2O) is 0.35 kg/m^3 (depending on pressure and operating temperature). Thus the large change in density increased the volumetric flow rate drastically. The system was monitored continually with regard to pressure at the inlet to the bed. This was the quickest way to establish if there was a leak, blockage or other problems in the system. The process gas leaving the decomposer (S-13) went through the 3 condensers where SO_3 and H_2O recombined to form H_2SO_4 . The stream was split into streams S-21 and S-22. One stream was sent to NaOH scrubbers to remove sulphur species from the stream prior to venting. The other stream was sent through three 500 mL Erlenmeyer flasks filled with ceramic balls and glass wool filter packing to remove any mist that might be present in the stream (S-19). The system was operated on stream, depending of the specific experiment, for no longer than 6 hours. The analysis methods used in the study will be described later.

5.2.2.3 *Procedure for Shut-Down*

After the time on stream for the experiment had been completed the acid pump was shut off and the flow of nitrogen reduced to 1 NL/min . Both furnaces were left on temperature for another half hour to ensure all acid had been decomposed and removed from the reactor and vaporizer sections. After the half hour the furnaces were shut down, with nitrogen left open. After two hours the nitrogen flow and logging software were stopped and the furnaces left to cool down to room temperature over night. The system was taken apart and cleaned before a following run could be conducted.

5.2.3 *Analysis of Products*

The analyses for both inlet temperature and WHSV variation was conducted on a GC and the amount of sulphur dioxide found was used to calculate the conversion. However, the results obtained from Gas Chromatograph analyses showed a discrepancy due to the low amounts of sulphur dioxide measured and the fact the system had been close to, or at equilibrium. This was shown by the results: the WHSV

was changed dramatically, but the conversion was unchanged. Analysis of products was important for completing a mass balance over the system, as well as establish the conversion achieved in the system. The solubility of sulphur dioxide can be quite significant under particular process conditions (low temperature and presence of water) and its effect on the system was clearly noticeable. The analyses done with a GC delivered values lower than expected, as explained in Section 5.2.3.1. The effect of the sulphur dioxide solubility in sulphuric acid and water has been investigated in literature (Chapter 2.6) and although the various authors found that the solubility is highly dependent on the partial pressure of SO_2 , temperature and acid concentration, the loss of sulphur dioxide could not be accounted for from the literature alone. An Aspen Plus® model with NRTL equation of state was developed to account for this effect by adding Henry constants for $\text{SO}_2/\text{H}_2\text{O}$, $\text{O}_2/\text{H}_2\text{O}$ and $\text{N}_2/\text{H}_2\text{O}$ in the system. The Henry constant's relation to temperature is given by the following equation (Wilhelm, 1977):

$$\ln H = a + \frac{b}{T} + c \ln T \quad [52]$$

With constants a , b and c given as 83.96, -5578.8 and -8.7615, respectively. Figure 5-6 visualizes the model as developed in Aspen Plus®.

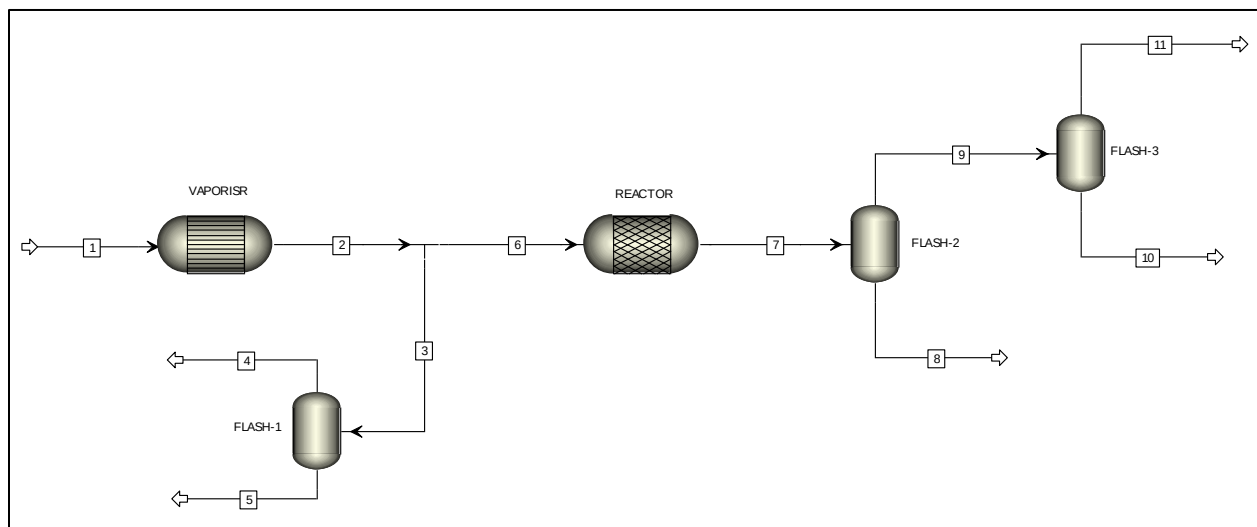


Figure 5-6: Aspen Plus® model to account for solubility of sulphur dioxide in system

The system consists of the following units as indicated in Figure 5-6:

- VAPORSR – the vaporiser in the system where all the acid is decomposed into sulphur trioxide and water and sulphur trioxide is fractionally converted into sulphur dioxide and oxygen as evaluated experimentally
- FLASH-1 – represents the ice bath section where analysis was done on an external GC
- REACTOR – the fractional conversion of sulphur trioxide was varied in this unit to evaluate the fraction sulphur dioxide in stream 11 and compare oxygen in that stream
- FLASH-2 – represents the condensers to cool the process gas leaving the reactor
- FLASH-3 – represents the ice bath to remove all other condensable species

A block variable was used to vary the conversion in REACTOR to obtain the experimental fraction of sulphur dioxide measured on the GC and compare that against analysis done on a paramagnetic oxygen analyser. The feed to the experimental setup was inserted in stream 1. Stream two was split into two sections, the first for extraction of a sample from the vaporizer and the main stream was the inlet to the reactor. For most of the simulations the splitting fraction was zero, i.e. no samples were taken during the benchmark experimental runs. The model was verified with two experiments with the following process conditions:

Table 5-2: Experimental conditions used in Aspen Plus[®] model

	Calculation 1	Calculation 2
Acid Molar Flow Rate (mol/min)	0.078	0.037
Nitrogen Molar Flow Rate (mol/min)	0.035	0.088
Water Molar Flow Rate (mol/min)	0.009	0.004
Inlet Pressure (kPa)	103	101
Vaporizer Conversion (%)	26	6
Condenser Temperature (K)	278	278
Temperature Ice Bath (K)	273	273

The electrolyte option with NRTL thermodynamic model was chosen for the calculations. The model was validated by a variety of analytical methods, which included analysis on a GC, oxygen analyser, titrations and physical measurements of condensed products. Conversion provided was always based on the amount of sulphur trioxide converted into sulphur dioxide and oxygen. The analytical method used to quantify products from the system will be described in the following section.

5.2.4 Analytical Methods

To complete a total mass balance over the system and justify the results obtained, or disregard them due the solubility of sulphur dioxide in water and sulphuric acid, titrimetric analyses had to be conducted of the condensed products and vapour product and evaluation of product species with an oxygen analyser. The first titrimetric analysis was a simple acid/base titration to determine the weight percentage of the sulphuric acid. The second analysis was iodine titration wherein the amount of sulphur dioxide in a solution could be analysed.

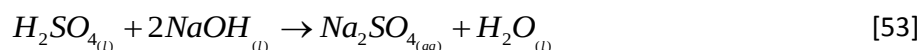
5.2.4.1 GC/Paramagnetic Cell

The amount of conversion achieved by the vaporizer was evaluated by taking a sample at S-12 (Figure 5-2) in a 500 mL Restek sample bag at regular intervals. The samples were analysed on a SRI 8610C injection GC with Haysep D column. The amount of sulphur dioxide was measured at S-36 (Figure 5-2) on a HP 6980 GC for experimental variables, inlet temperature as well as WHSV. After the two variables had been investigated thoroughly it was found that sulphur dioxide was absorbed in the stream and subsequently another method of analysis had to be implemented to account for this loss. A paramagnetic cell (the same as used in Chapter 4) was connected to S-28, which only comprised oxygen and nitrogen in the stream. Since oxygen is barely soluble in water the analysis was more reliable and it offered the opportunity to establish the amount of sulphur dioxide absorbed in the system.

5.2.4.2 Acid/Base Titration

The acid/base titration is a standard method that is well known in literature (Jeffery, 1989). The sulphuric acid condensed in the flasks has an unknown concentration and titrating with a sodium

hydroxide solution with a known concentration, the amount of H_2SO_4 produced could be evaluated. The following reaction takes place during titration:

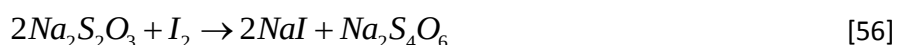


The amount of acid collected in the five flasks (TK-1 to 5, Figure 5-2) was measured in terms of volume and mass prior to titrimetric analysis. A sodium hydroxide solution was mixed on a regular basis and prior to each of the titrations the solution had to be standardized due to the characteristic of NaOH to absorb CO_2 from the air, thereby influencing the concentration of the mixture. This mixture was standardized with potassium hydrogen phthalate ($C_8H_5KO_4$), which has a high purity and could be used to get an accurate molar concentration of the NaOH solution. The procedure was as follows:

- A sample from collection flasks was weighed (2 ml)
- A few drops of methyl red indicator was added
- The solution was titrated with the standardized NaOH solution until colour change
 - Methyl red: Red/pink turns to yellow

5.2.4.3 Iodine Titration

The second set of titrimetric analysis was conducted to evaluate the amount of SO_2 in the vapour stream by bubbling the product stream through NaOH with specific molar concentration. The Iodine titration method involves the following reactions:



In the reactions above the SO_2 gas reacts with sodium hydroxide to form sodium sulphite. The sodium sulphite will react with iodine to form a sulphate. A specific amount of iodine solution is added to the sodium sulphite solution. Since sodium thiosulphate also reacts with iodine, the rest of the iodine present will react with sodium thiosulphate and thus the amount of iodine reacted with sodium sulphite can be calculated. This can be used on a molar basis to calculate the amount of SO_2 that reacted with

sodium hydroxide. The iodine was standardized with the method of As_2O_3 to validate the concentration used for titrations.

5.3 Results and Discussion

5.3.1 Process Mass Balance

5.3.1.1 Product Analysis Section

The model developed in Aspen Plus® was used to account for the solubility of sulphur dioxide in water. A simplified mass balance was conducted and verified by using the various analysis techniques described. Two experiments were conducted at different temperatures and concentrations to validate the model under various conditions. The error for both experiments was less than 5% based on oxygen molar flow predicted versus measured. The following table gives the results of the two experimental results and model:

Table 5-3: Experimental results comparison against Aspen Plus® model

	Calculation 1			Calculation 2		
	Model	Experiment	Error (%)	Model	Experiment	Error (%)
Molar Fraction SO_2	0.42	0.4215	0.35	0.124	0.121	2.47
Oxygen Molar Flow (mol/min)	0.027	0.0282	4.25	0.01	0.01038	3.6

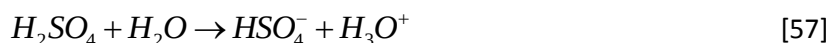
With a relatively small error and the fact that the oxygen was calculated by the ideal gas law, in which the exact pressure could bring the results even closer, the model was successfully verified by experimental results from two different experiments with completely different process conditions. The model was used to rectify other experimental results that were only measured by means of GC analysis. The comparison between the model and experimental results was further compared with the amount of acid formed in the condenser stream, as well as the amount of SO_2 absorbed in that stream. The mass balance for experimental run 1 can be seen in Table 5-4 in which some of the important streams were included, as can be found in Figure 5-6.

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Table 5-4: Mass balance for Calculation 1

	Stream 1	Stream 2	Stream 6	Stream 7	Stream 8	Stream 9
Temperature (K)	298	1023	1023	1143	283	283
Pressure (kPa)	103	103	103	100	87	87
Vapour Fraction	0.288	1	1	1	0	1
Mole Flow (mol/min)	0.122	0.21	0.21	0.227	0.095	0.11
Mass Flow (gm/min)	8.792	8.793	8.793	8.793	3.919	4.874
Volume Flow (ℓ/min)	0.849	17.353	17.353	21.618	0.003	2.943
Mole Flow (gm/min)						
H ₂ O	0.162	1.567	1.567	1.567	0.817	0
N ₂	0.98	0.98	0.98	0.98	0	0.98
O ₂	0	0.324	0.324	0.915	0	0.915
SO ₂	0	1.299	1.299	3.666	0.624	3.042
SO ₃	0	4.621	4.621	1.664	0	0
H ₂ SO ₄	7.65	0	0	0	0	0
H ₃ O ⁺	0	0	0	0	6.395	0
OH ⁻	0	0	0	0	0	0
HSO ₄ ⁻	0	0	0	0	2.017	0
HSO ₃ ⁻	0	0	0	0	0	0
SO ₃ ⁻²	0	0	0	0	0	0
SO ₄ ⁻²	0	0	0	0	0	0

The amount of acid formed in the condensate collection stream can be seen in stream 8, which consists mainly of two ionic species. The following reaction is representative of the acid dissociation when combined with water:



From the Aspen Plus® results the first dissociation step is the main contributor, resulting in an equivalent molar amount of bisulphate and hydronium ions. The theoretical amount of acid condensed in the flask was 86 wt% acid while the concentration of acid evaluated by means of the acid/base titration method discussed earlier delivered 78 wt% acid. This gives an error of 12%, which is reasonable if taken into consideration that some of the acid reacted with the Hasteloy c-276 construction material and stainless steel type 316L fittings used in the system. Some analysis conducted on the acid can be seen in Appendix G where it was found that for a stainless steel 316L reactor with fittings metal sulphates were found in the acid condensate.

The acid measured in terms of mass and volume was within an error of 10 and 16%, respectively which is reasonable when the reaction with metal is taken into consideration, which will cause a change in the density of the solution and thus also mass and volume changes. The iodine titration method described earlier was used to test the acid condensate for the presence of SO₂, and although it is not the best method to determine exact quantities, SO₂ was found in acid condensate. It should also be noted that when SO₂ and H₂O mix H₂SO₃ does not form as mentioned in Chapter 2.7, but rather different complex combinations of ionic species. The iodine titration on the NaOH scrubber solutions delivered satisfactory results, with the amount of SO₂ titrated in the solution within 10% of that theoretically formed. Thus to conclude, various methods were used to verify the mass balance over the system, as well as validate the Aspen Plus® model to correct the under-predicted results obtained. The method includes GC analysis, O₂ paramagnetic cell analysis, acid/base titrations, SO₂ titrations and physical measurement & analysis of condensate. The Aspen Plus® model was validated within a small error margin and the mass balance was validated within 10 to 15% error for various analyses. A sensitivity analysis was conducted on the Aspen Plus® model where the condenser temperature was varied at different reactor fractional conversions specified and the fraction of the SO₂ measured on the GC as a result of SO₂ solubility. Figure 5-7 can be used to predict the conversion achieved in the reactor system.

When the fraction of SO_2 measured on the GC is known, as well as the condenser temperature, the amount of SO_3 that was converted could be obtained for the specific experimental conditions.

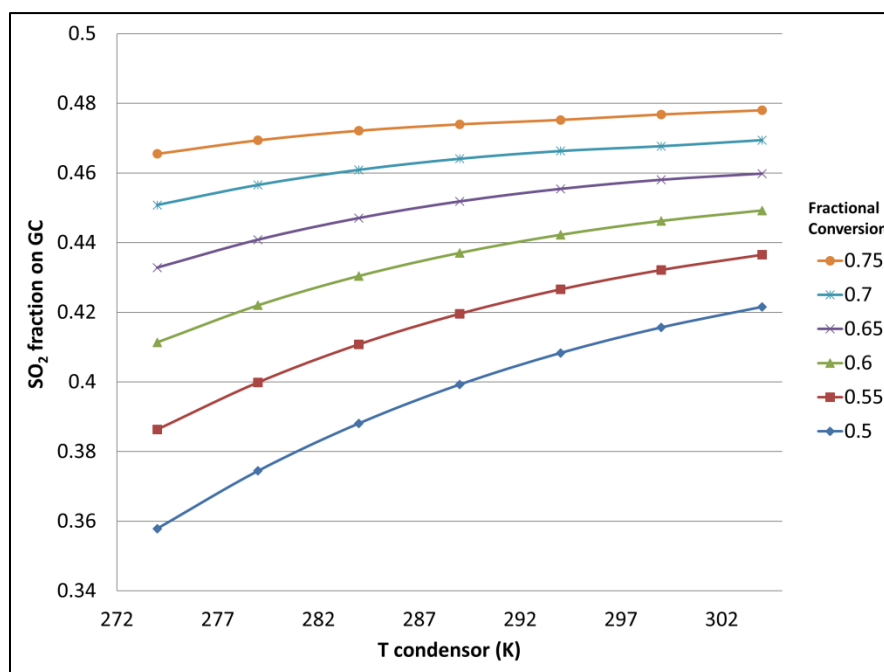


Figure 5-7: Variation in sulphur dioxide fraction readable as a function of condenser temperature at various reactor conversions

5.3.1.2 Overall Process Mass Balance

An overall mass balance was conducted over experimental condition from the residence time variation experiment in Section 5.3.2.3 for a temperature of 953 K and velocity of 1 m/s. The conversion achieved was based on the amount of oxygen measured at the outlet of the system. The mass and mole balance was conducted and the streams provided can be found from Figure 5-2, which is the process flow diagram. The complete mole and mass balance can be seen in Table 5-5 and Table 5-6, which were divided into two tables for ease of viewing. . The amount of oxygen measured were within 5% error of theoretical amount; the amount of sulphur dioxide titrated in sodium hydroxide (I_2 titration) were within 12% error compared to calculated value; the amount of acid collected were within 12% error with regard to mass and 15% with regard to volume collected and the concentration of acid titrated (Acid/Base) were 13% error. Due to the quantity of data for all experimental results only one mass balance is provided, but mass balances were conducted for all experimental conditions and were all within a satisfactory error margin.

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Table 5-5: Mass and mole balance over whole system part 1 (values $\times 10^{-3}$)

Mol flow (mol/min)	1	2	4	6	7	8	13	14	15	16	17	18	19	20
SO ₃	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.38E-02	4.97E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SO ₂	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.90E-03	2.80E-02	2.80E-02	0.00E+00	2.80E-02	0.00E+00	2.80E-02	1.40E-03	2.66E-02
O ₂	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.90E-03	1.40E-02	1.40E-02	0.00E+00	1.40E-02	0.00E+00	1.40E-02	7.00E-04	1.33E-02
H ₂ O	9.00E-03	9.00E-03	0.00E+00	0.00E+00	9.00E-03	8.63E-02	8.63E-02	3.66E-02	3.66E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
N ₂	0.00E+00	0.00E+00	1.18E-01	1.18E-01	1.18E-01	1.18E-01	1.18E-01	1.18E-01	0.00E+00	1.18E-01	0.00E+00	1.18E-01	5.88E-03	1.12E-01
H ₂ SO ₄	7.80E-02	7.80E-02	0.00E+00	0.00E+00	7.80E-02	0.00E+00	0.00E+00	4.97E-02	4.97E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total	8.70E-02	8.70E-02	1.18E-01	1.18E-01	2.05E-01	2.83E-01	2.96E-01	2.46E-01	8.63E-02	1.60E-01	0.00E+00	1.60E-01	7.98E-03	1.52E-01

Mass (g/min)	1	2	4	6	7	8	13	14	15	16	17	18	19	20
SO ₃	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.90E-03	3.98E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SO ₂	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.50E-04	1.79E-03	1.79E-03	0.00E+00	1.79E-03	0.00E+00	1.79E-03	8.96E-05	1.70E-03
O ₂	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.08E-05	4.48E-04	4.48E-04	0.00E+00	4.48E-04	0.00E+00	4.48E-04	2.24E-05	4.26E-04
H ₂ O	1.62E-04	1.62E-04	0.00E+00	0.00E+00	1.62E-04	1.55E-03	1.55E-03	6.59E-04	6.59E-04	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
N ₂	0.00E+00	0.00E+00	3.30E-03	3.30E-03	3.30E-03	3.29E-03	3.29E-03	3.29E-03	0.00E+00	3.29E-03	0.00E+00	3.29E-03	1.65E-04	3.13E-03
H ₂ SO ₄	7.64E-03	7.64E-03	0.00E+00	0.00E+00	7.64E-03	0.00E+00	0.00E+00	4.87E-03	4.87E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total	7.81E-03	7.81E-03	3.30E-03	3.30E-03	1.11E-02	1.11E-02	1.11E-02	1.11E-02	5.53E-03	5.53E-03	0.00E+00	5.53E-03	2.77E-04	5.25E-03

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Table 5-6: Mass and mole balance over whole system part 2 (values $\times 10^{-3}$)

Mol flow (mol/min)	21	22	23	24	25	26	27	28	29	31	33	35	36
SO ₃	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SO ₂	1.33E-02	1.33E-02	1.06E-02	1.06E-02	2.66E-03	2.66E-03	5.32E-03	0.00E+00	1.40E-03	1.40E-03	1.40E-03	1.40E-03	1.40E-03
O ₂	6.65E-03	6.65E-03	0.00E+00	0.00E+00	6.65E-03	6.65E-03	0.00E+00	1.33E-02	7.00E-04	7.00E-04	7.00E-04	7.00E-04	7.00E-04
H ₂ O	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
N ₂	5.58E-02	5.58E-02	0.00E+00	0.00E+00	5.58E-02	5.58E-02	0.00E+00	1.12E-01	5.88E-03	5.88E-03	5.88E-03	5.88E-03	5.88E-03
H ₂ SO ₄	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total	7.58E-02	7.58E-02	1.06E-02	1.06E-02	6.51E-02	6.51E-02	5.32E-03	1.25E-01	7.98E-03	7.98E-03	7.98E-03	7.98E-03	7.98E-03

mass (g/min)	21	22	23	24	25	26	27	28	29	31	33	35	36
SO ₃	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SO ₂	8.51E-04	8.51E-04	6.81E-04	6.81E-04	1.70E-04	1.70E-04	3.40E-04	0.00E+00	8.96E-05	8.96E-05	8.96E-05	8.96E-05	8.96E-05
O ₂	2.13E-04	2.13E-04	0.00E+00	0.00E+00	2.13E-04	2.13E-04	0.00E+00	4.26E-04	2.24E-05	2.24E-05	2.24E-05	2.24E-05	2.24E-05
H ₂ O	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
N ₂	1.56E-03	1.56E-03	0.00E+00	0.00E+00	1.56E-03	1.56E-03	0.00E+00	3.13E-03	1.65E-04	1.65E-04	1.65E-04	1.65E-04	1.65E-04
H ₂ SO ₄	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total	2.63E-03	2.63E-03	6.81E-04	6.81E-04	1.95E-03	1.95E-03	3.40E-04	3.55E-03	2.77E-04	2.77E-04	2.77E-04	2.77E-04	2.77E-04

5.3.2 Analysis of Pre-Heat Section

The experimental system was firstly commissioned with nitrogen flow experiments as well as some experiments with nitrogen and acid under process conditions. The pre-heat region was investigated to establish the correct inlet conditions to the catalyst bed with specific attention to the inlet concentration. The results given in this section are for a certain set of process conditions since many experimental results were available and all will not be reported. The inlet concentrations to the catalytic bed were evaluated for all process conditions and the pre-heat region (inert) for variation in residence time will only be discussed and results provided since the results were used for modelling purposes. Three different flows were evaluated to get an outlet temperature of 953 K, which was the inlet temperature to the catalytic bed. The three different flow rates with regard to acid flow rate as well as nitrogen flow rate can be seen in Table 5-7.

Table 5-7: Process conditions for pre-heat packing investigation

Parameter	Flow = 1 m/s	Flow =1.23 m/s	Flow = 1.32 m/s
Acid Flow Rate (mℓ/min)	4	4	4
Nitrogen Flow Rate (ℓ/min)	2.80	3.37	3.78
Residence Time (s)	0.1	0.081	0.07

The pre-heating section was investigated with regard to centreline temperature distribution and conversion achieved without the presence of catalyst. The conversion achieved by the vaporizer alone, the vaporizer- blank tube and combined vaporizer-blank tube-inert packing was investigated for a set of process conditions. The conversion achieved for the inlet temperature of 953 K and three flow variation were also investigated.

(I) Temperature

The results obtained for the centreline and wall temperature profiles for the process conditions provided in Table 5-7 can be seen in Figure 5-8.

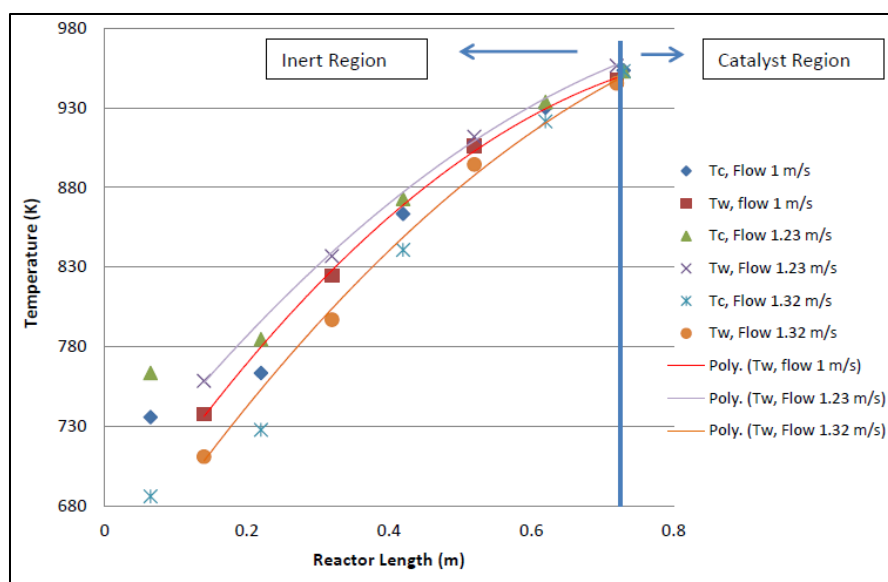


Figure 5-8: Centreline and wall temperature profiles for inert-heating region in fixed bed reactor

From Figure 5-8 it can be seen that for the flow rate variations the inlet temperatures of the centreline vary considerably. This could be due to the variation in atmospheric temperature that influences the heat transported and lost to the atmosphere. Although the inlet temperature varies quite much it is not worrying since the furnace is set to control the unit so that the outlet temperature, temperature at length 0.7 m, in Figure 5-8 should be at a specified value, as was found.

(II) Concentration

The conversion achieved by individual units in the packed bed system was investigated to accurately assign the conversion achieved in the catalytic bed alone. It was found necessary due to the presence of the Hastelloy c-276 (vaporizer) at the specific temperature to determine whether the vaporizer converted sulphur trioxide into sulphur dioxide, and if so, by how much. During three experiments samples were taken between the vaporizer coil and the inlet to the reactor and injected into a GC to evaluate the amount of sulphur dioxide produced. For the specific flow rate and molar concentration the amount of sulphur trioxide converted into sulphur dioxide can be seen in Figure 5-9.

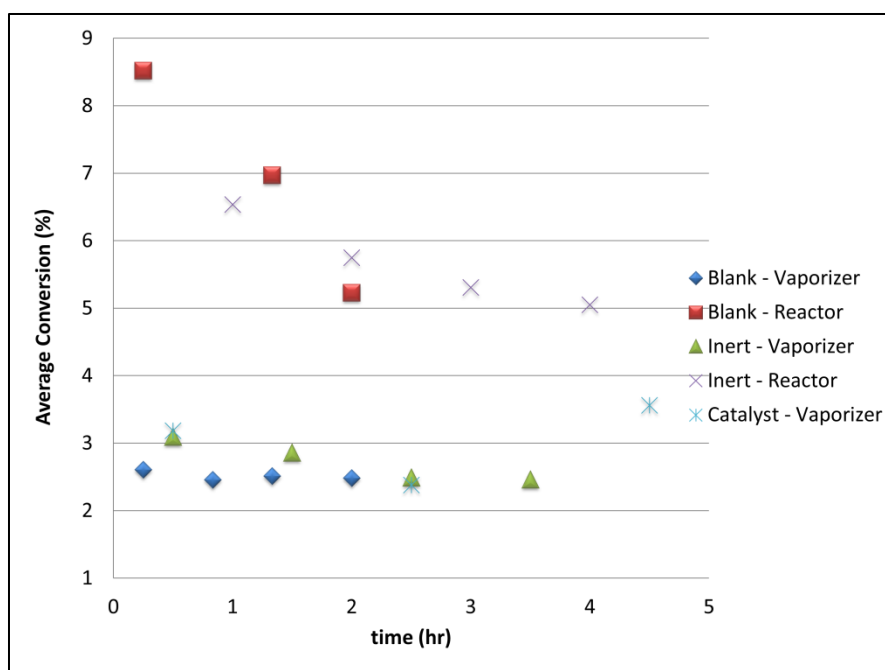


Figure 5-9: Conversion of sulphur trioxide in absence of catalyst

Taking the average of all the data points of the three runs as shown in Figure 5-9 the average conversion achieved by the vaporizer was 2.76%. To ensure that the reactor tube constructed of Hastelloy c-276 and the inert packing before the catalytic bed do not catalyse the reaction to a great extent, runs were completed with the blank tube under process conditions as well as the tube with only inert packing present. The samples taken to evaluate the amount of sulphur dioxide produced were not taken at exactly the same time for each experiment. The average conversion achieved for the blank tube was 6.90 % while for the tube plus the inert ceramic packing it was 5.66 %. This can be expected due to the thermodynamics of the reaction where lower pressure results in higher conversion.

The packing inside the tube caused an increase in the pressure drop and in turn an increase at the inlet of the bed; therefore, lower conversion was expected. After establishing that all units in the packed bed system catalysed the reaction to some extent, the overall conversion achieved by all units combined was measured prior to all variations in process conditions to obtain inlet conditions for the catalytic bed. The total combined pre-catalyst conversion achieved was evaluated for all the process conditions variations. The total conversion achieved without catalyst for the process conditions provided in Table 5-7 can be seen in Figure 5-10.

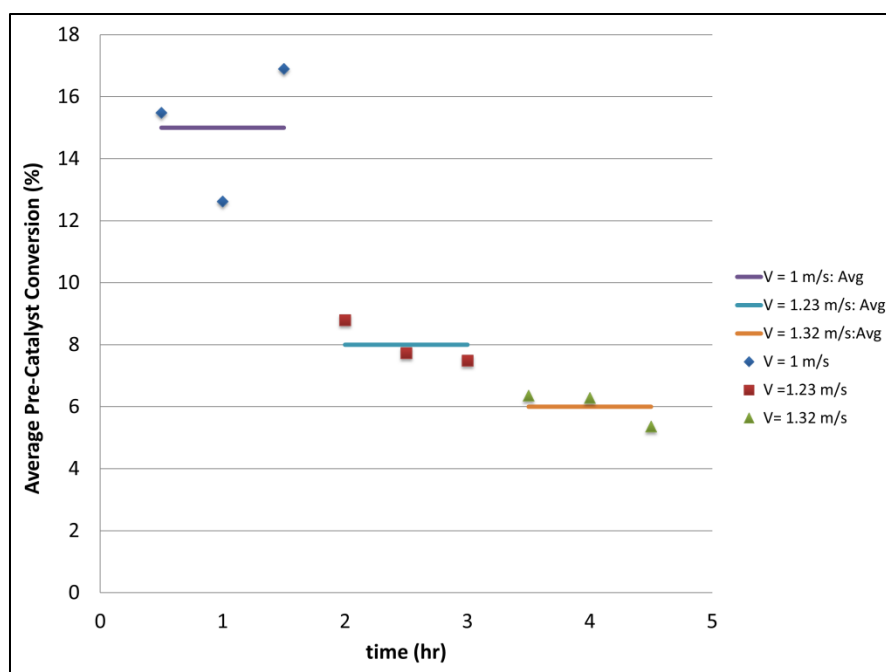


Figure 5-10: Average pre-catalyst conversion achieved for three flow variations at inlet temperature of 953 K

The averaged conversion achieved for the 1, 1.23 and 1.32 m/s flow conditions was evaluated as 15, 8 and 6%, respectively. From the results obtained in Figure 5-9 and Figure 5-10 it is evident that the vaporizer, inert SiC packing as well as reactor tube catalysed the reaction to some extent and the severity of catalysing changed with process conditions. A table summarizing some of the inlet conditions used for modelling purposes for the catalytic bed region in Chapter 6, can be seen in Table 5-8.

Table 5-8: Inlet conditions for catalytic bed obtained from pre-heating bed section

Velocity	Inlet Concentration SO ₃ (mol/m ³)	Inlet Concentration SO ₃ to Cat. Bed (mol/m ³)	Inlet Temperature to Cat. Bed (K)	Inlet Pressure Bed (kPa)
1	3.04	2.53	953	104.3
1.23	3.04	2.74	953	109.8
1.32	3.04	2.80	953	113.8

5.3.3 Packed Bed with Reaction

The packed bed experimental system was investigated by changing the catalyst bed length, operating temperature, acid flow rate and nitrogen flow rate. The different experimental conditions investigated included variations in inlet temperature to the catalyst bed (long bed), variation in WHSV (long bed) and variation in residence time (short bed). The analysis section was investigated by completing a mass balance over the system with analyses conducted, included sulphur dioxide on a GC, O₂ on an oxygen analyser, sulphur dioxide titrations, acid titrations and physical measurements on collected acid. For a summary of all the experiments conducted in this section Table 5-1 can be revisited.

5.3.3.1 Effect of Inlet Temperature

The temperature at which the sulphur trioxide decomposition reaction occurs is of outmost importance due to the highly endothermic nature and thermodynamics of the reaction. To evaluate the influence of temperature on the packed bed system the process conditions were kept constant and the inlet temperature to the catalytic bed was varied to get four different temperatures with a constant difference in temperature of 50 K. The catalyst bed was filled so that ± 400 mm length (long bed) of catalytic bed was available for reaction. The process conditions kept constant for duration of temperature variations can be seen in Table 5-9.

Table 5-9: Process conditions for variable inlet temperature experiments

Parameter	Value
Inlet Temperature (K)	953, 1003, 1053, 1103
Acid Inlet Flow Rate (mL/min)	2
Nitrogen Inlet Flow Rate (L/min)	3

For the inlet temperature variation three experiments at four temperatures were conducted. The approach was to get the same length in catalyst bed rather than precisely the same amount of catalyst. The vaporizer temperature was set at 1023 K for the duration of all experimental work. The parameters measured and presented for the catalyst packing in the reactor included the following:

- Centreline temperature along the length of reactor tube

- Wall temperature along the length of the reactor tube
- Inlet pressure for reactor tube
- Conversion achieved at outlet of tube

The first results obtained from the experiments were the conversion as a function of time for all four different inlet temperatures and can be seen in Figure 5-11.

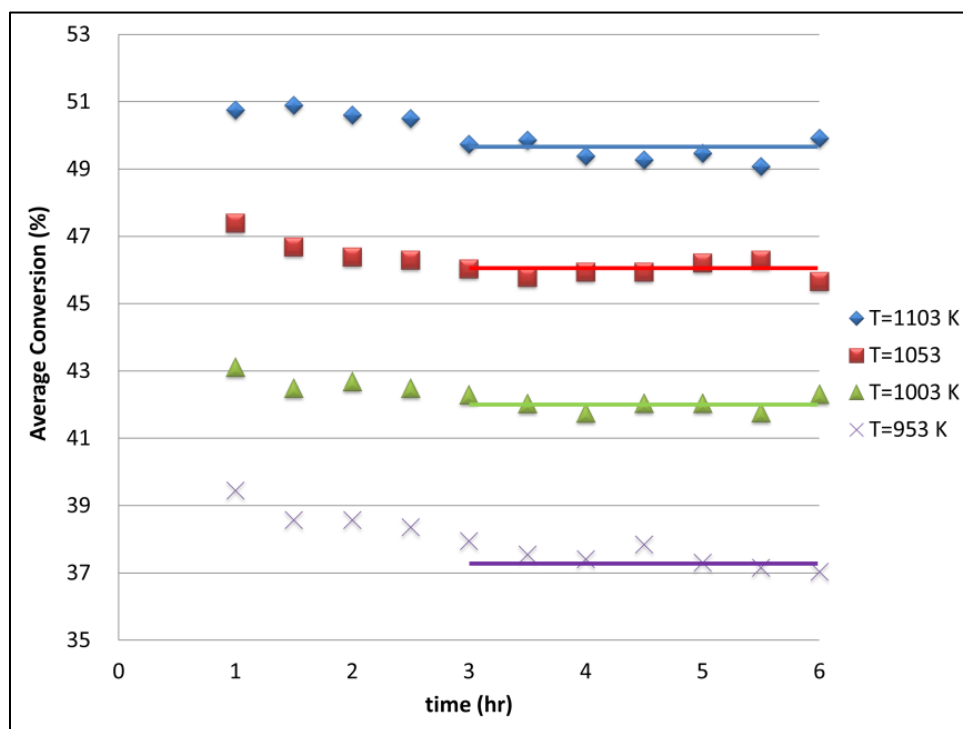


Figure 5-11: Average conversion achieved as a function of time (WHSV = 1.2 h^{-1})

The steady state operating conditions obtained from the catalyst and time on stream was very satisfying. The stability in the catalyst could be attributed to the sintering the catalyst was subjected to, to ensure that the phase transition did not influence the stability of the catalyst. The stability observed is comparable to results obtained in Chapter 4 for the kinetic analysis where it was found that stability was reached earlier than 6 hours on stream. For both experimental apparatuses the catalytic evaluation indicated achievement of steady state conditions. Conversion achieved was difficult to compare since the flow conditions as well as catalyst amount were very different. The conversion achieved and shown in Figure 5-12 was calculated as the average conversion over 6 hours on stream and then the average for the three experimental runs per temperature. The steady state average conversion achieved can be seen in Figure 5-12 for the catalyst, together with equilibrium conversion.

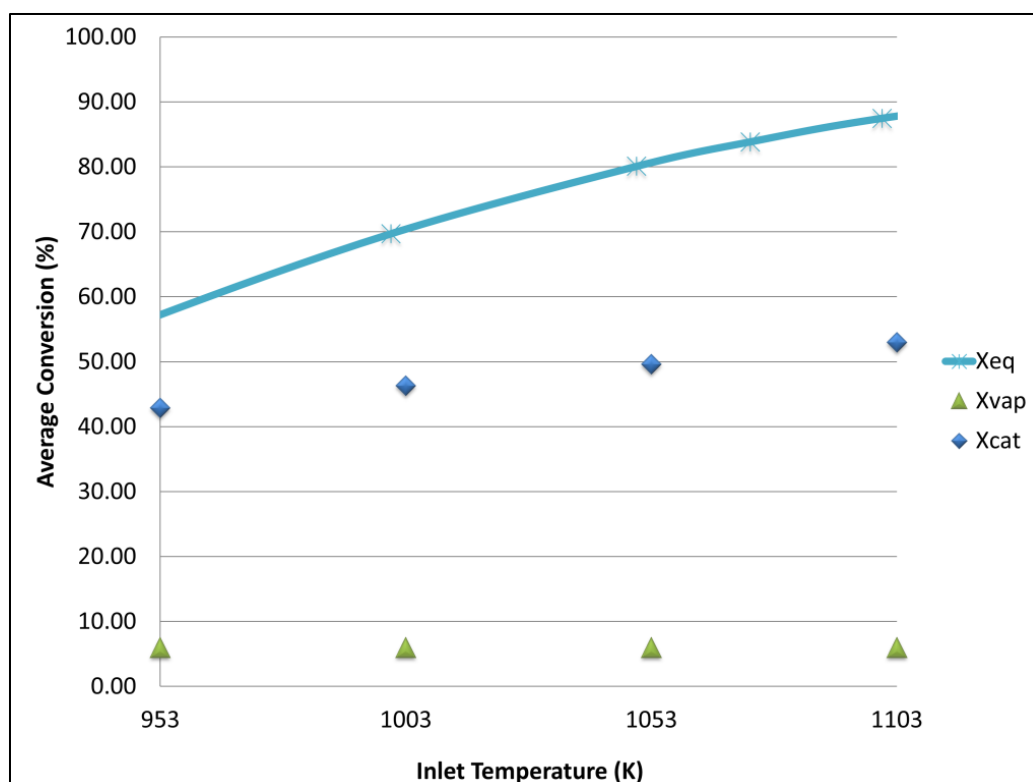


Figure 5-12: Average conversion at steady state for different catalyst bed inlet temperatures (WHSV = 1.2 h^{-1})

The average conversion that was a result of non-catalytic reaction (X_{vap}) is quite low at 5.66%. The conversion for both catalyst batches is not too far away from equilibrium at 953 K inlet temperature but as the temperature increases the conversion does not follow the same upward trend. The difference in conversion for an increase in 150 K amounts to approximately 10%, which is a small amount. Similar trends were observed by Gelbard et al. (2005) who investigated a fixed bed type configuration with Pt/Zr₂O₃ catalyst for inlet temperature variations between 1023 and 1148 K (acid flow 4.2 ml/min) where an increase in conversion fraction was observed from 0.4 to 0.45. The main difference, however, was the operating pressure of 600 kPa. It is again difficult to compare completely, but it is worth noting that the behaviour of the catalyst and system is surprising. The trend suggests that the reaction is limited by diffusion (Levenspiel, 1999). The dynamic centreline temperature distribution in the catalytic bed can be seen in Figure 5-13 where oscillation in the experimental data is observed.

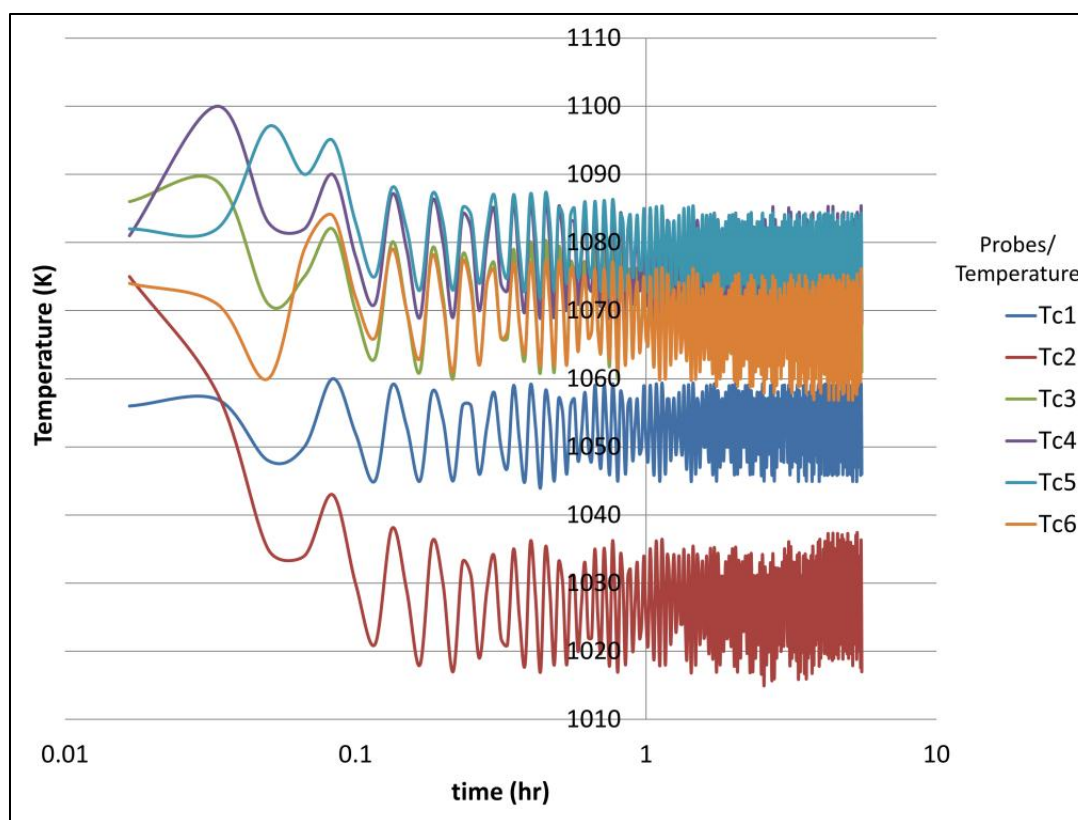


Figure 5-13: Centreline temperature profiles over time

This was due to the furnace that supplied heat to the system that was controlling on/off and the controller was not that sensitive. The temperature profiles indicate that after the acid started to decompose the second thermocouple probe decreased much more than the other probes due to the endothermic nature of the reaction. The standard deviation for the temperature profiles given in Figure 5-13 was 1.2% of the average values compared. Due to the fact that the experimental data as a function of time on stream was quite stable and since all the experimental results were similar with regard to stability, the experimental data as a function of time will not be given for other experiments. From Figure 5-14 it can be seen that, for the different steady state inlet temperatures, the basic profile for the average temperature distribution along the length of the reactor bed follows the same tendency.

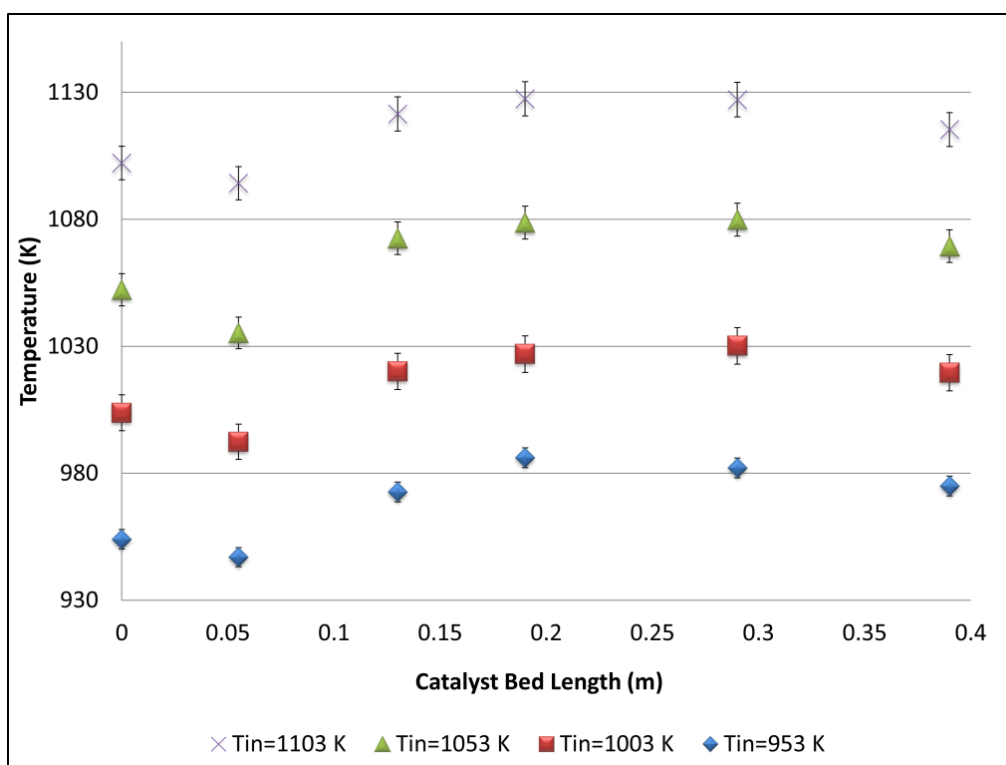


Figure 5-14: Centreline temperature profiles along the length of reactor tube for various catalyst bed inlet temperatures at constant WHSV (1.2h^{-1})

A decrease in temperature is visible, after which the temperature increases. This is to be expected due to the highly endothermic nature of the reaction. Heat is consumed at a higher rate than it is supplied through the radial direction of the tube in the initial stage of the reactor. As soon as the reaction rate, which usually decreases exponentially, stabilizes, the heat transfer rate is sufficient to drive the catalytic reaction as well as increase the gas mixture temperature. The centreline temperature is highly dependent on the heat flux supplied to the wall of the reactor tube. The temperature profile, and in turn flux supplied to the system, can be seen in Figure 5-15.

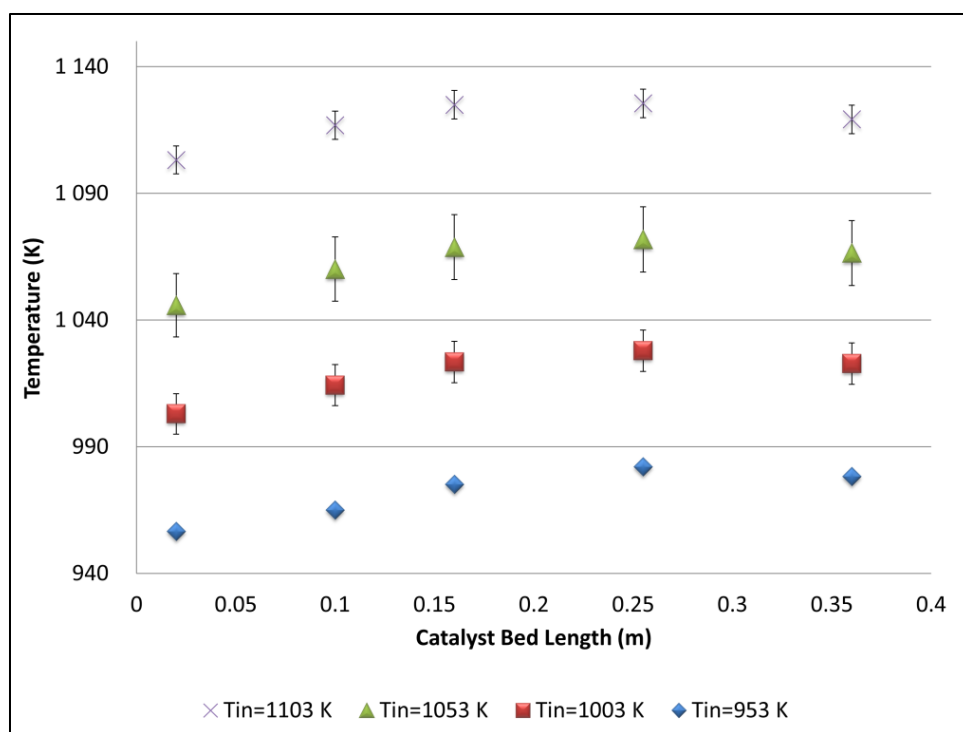


Figure 5-15: Wall temperature profiles along the length of reactor tube for various catalyst bed inlet temperatures at constant WHSV (1.2h^{-1})

The temperature at which the process gas entered the reactor was lower than the temperature of the vaporizer, which was kept constant at 1023 K for the duration of experimental work. This was due to the gap between the vaporizer outlet and reactor inlet which was open to ambient temperature. This was necessary to ensure that the reactor tube could be removed easily from the vaporizer. This became a difficult task when working with compression fittings at high temperature. The difference between the centre and wall temperature measurements can be seen in Figure 5-16 where the wall temperature profile has a parabolic shape, increasing and decreasing, while the centreline temperature decreases and then increases and a definite difference in temperature is observed.

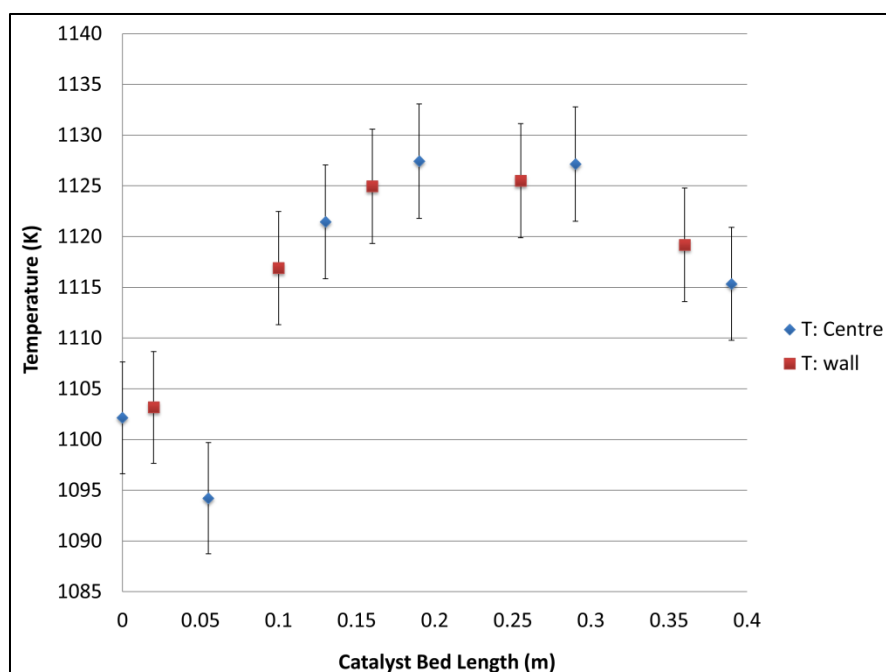


Figure 5-16: Centreline and wall temperature for inlet conditions of 1103 K and constant WHSV (1.2 h^{-1})

The endothermic effect of the reaction on heat distribution is observed in the first 100 mm of the bed after which the heat transfer seems to be sufficient to drive the reaction, which has slowed down as a result of the Arrhenius exponential trend (Fogler, 2006).

5.3.3.2 Effect of Weight Hour Space Velocity

The second variable that was varied in the system was the Weight Hour Space Velocity. The first set of variables was to change the inlet concentration and thus the WHSV of the sulphur trioxide by keeping the same number of catalyst particles in the bed (bed length constant) and by keeping the total molar flow rate constant by increasing the acid flow rate and decreasing the nitrogen flow rate at the inlet of the vaporizer. To reduce the number of variables the inlet temperature to the bed was also kept constant at 1103 K. The process conditions of the system can be seen in Table 5-10, which include the acid flow rate, nitrogen flow rate and the different inlet concentrations.

Table 5-10: Process conditions for variable WHSV (low)

Parameter	Acid Flow =2 mℓ/min	Acid Flow = 3 mℓ/min	Acid flow = 4 mℓ/min

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Inlet Temperature (K)	1 103	1 103	1 103
Acid Inlet Flow Rate (ml/min)	2	3	4
Nitrogen Inlet Flow Rate (l/min)	3.00	2.13	1.26
Weight Hour Space Velocity (h^{-1})	1.2	1.8	2.6

The conversion values presented were adapted by the Aspen Plus® model as was discussed in Section 5.2.3.4. The results obtained for experimental conversion achieved as well as equilibrium conversion can be seen in Table 5-11.

Table 5-11: Results obtained from acid flow rate (WHSV) variation

	Acid Flow Rate (mℓ/min)	WHSV (h^{-1})	Experimental Conversion (%)	Equilibrium Conversion (%)
Acid Flow 1	2	1.2	53	86
Acid Flow 2	3	1.8	75.3	80
Acid Flow 3	4	2.6	64	81

The values obtained for the conversion vary appreciably between the three different WHSV but no definite trend can be observed. The conversion for acid at 3 ml/min is very close to the equilibrium value with the 4 ml/min moving somewhat away from the equilibrium, but remains relatively close. Similar observations were made by Thomey et al. (2012) who investigated a solar type reactor and found that for low WHSVs a variation in WHSV (acid flow) did not display a clear trend. Similar temperature profiles were obtained for the 3 and 4 ml/min acid flow rates as with the 2 mℓ/min in Section 5.3.2.1. The centreline temperature profiles visible in Figure 5-17 show similar trends, i.e. in the first 100 mm of the reactor the temperature decreases quite sharply due to the endothermic nature of the reaction and because the heat consumed is more than the heat supplied. The temperature starts to increase again as a result of reaction rate slowing down exponentially and heat transfer becoming effective enough to increase the temperature. In comparison with the wall temperature profile this effect can also be seen as the wall temperature increases constantly and changes with the change in heat flux, with the large variation between centre and wall temperature compared initially and at the end.

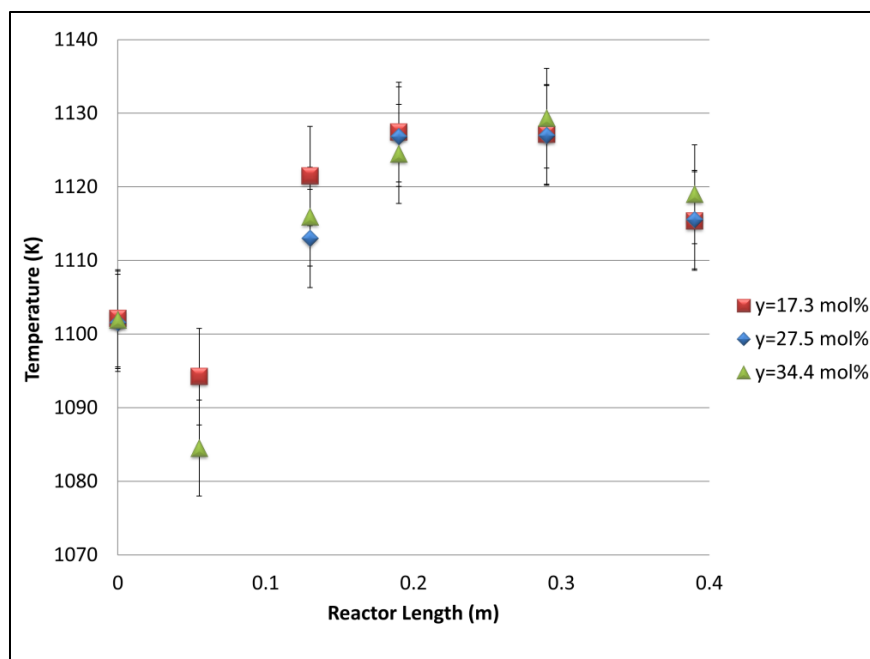


Figure 5-17: Centreline temperature profiles for the three different acid flow rates at temperature 1103 K

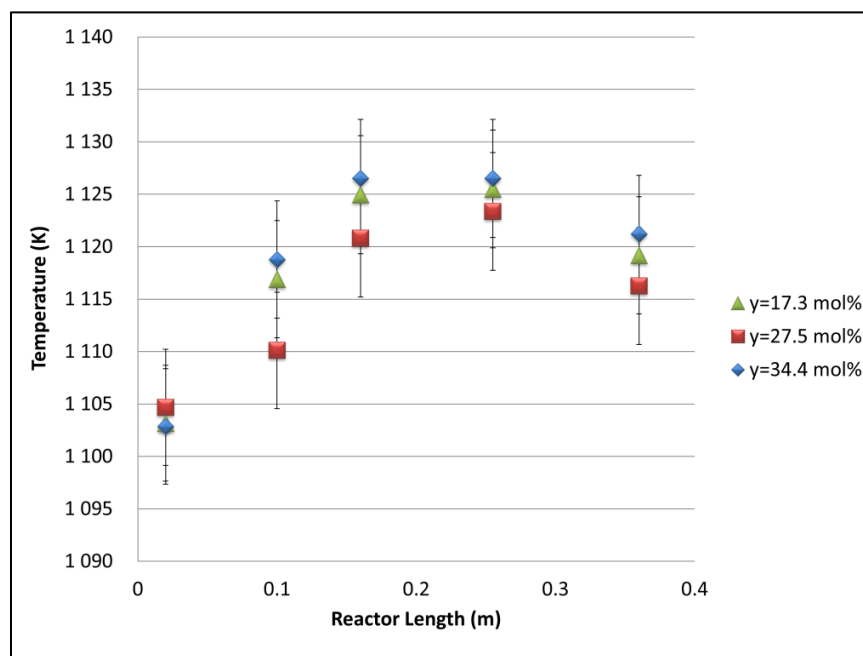


Figure 5-18: Wall temperature profiles for three different acid flow rates at inlet temperature of 1103 K

The second variation of WHSV was to keep the inlet temperature constant at 1103 K, the acid flow rate at 4 ml/min and changing the catalyst amount (bed length). Thomey et al. (2012) suggested that the process conditions they operated under were not sufficient to get distinguishable results with regard to

change in conversion with WHSV variation. The catalyst mass and corresponding WHSV for the two temperature variations are given in Table 5-12 where the flow condition was kept constant as flow condition three in Table 5-10.

Table 5-12: Process conditions for WHSV variation (catalyst mass)

Temperature	WHSV (h^{-1})	Catalyst W (g)
1 103 K	9.2	47
	43	10
	86	5
	865	0.5
953 K	9.2	47
	43	10
	763	0.45

Thomey et al. (2012) suggested that the WHSV should be increased to some extent to see a difference. The process conditions of Thomey et al. (2012) were similar to the process conditions in this study with regard to acid flow and temperatures. The WHSV was varied for 5 different catalyst packings as can be seen in Figure 5-19.

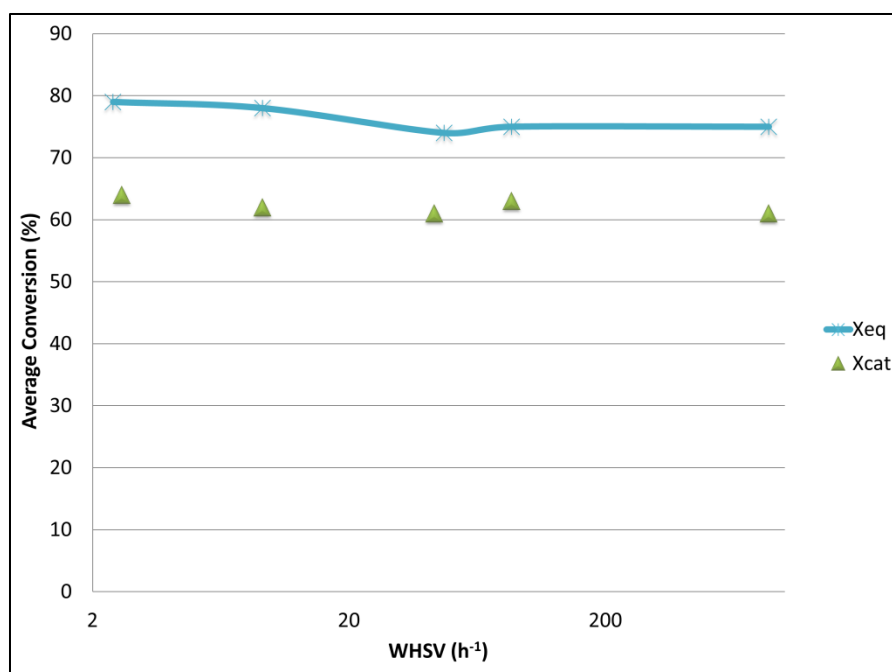


Figure 5-19: Conversion at various WHSVs for inlet temperature of 1103 K

The conversion achieved as a result of non-catalytic effects was evaluated as 26% of the sulphur trioxide fed into the system. From the fractional conversion of the sulphur trioxide reactor it can be seen that there is not a large difference between the data obtained for the various WHSVs. Together with the slight decrease in conversion the graph suggests that the results are close to equilibrium conversion from a thermodynamic point of view. Although the WHSV is quite higher than that of previous results presented and of that presented by Thomey et al. (2012) it is still not high enough to ensure that the system is far enough from equilibrium for modelling purposes.

The same scenario was used with an inlet temperature of 953 K and acid flow rate of 4 mL/min. The WHSV was varied for three different catalyst packings (Table 5-10). The variation of WHSV (catalyst mass) delivered results that were expected, which was that an increase in WHSV will decrease the conversion achieved over the catalytic bed. Although only three variations were done as seen in Figure 5-20 the trend is quite clear at the low inlet temperature of 953 K.

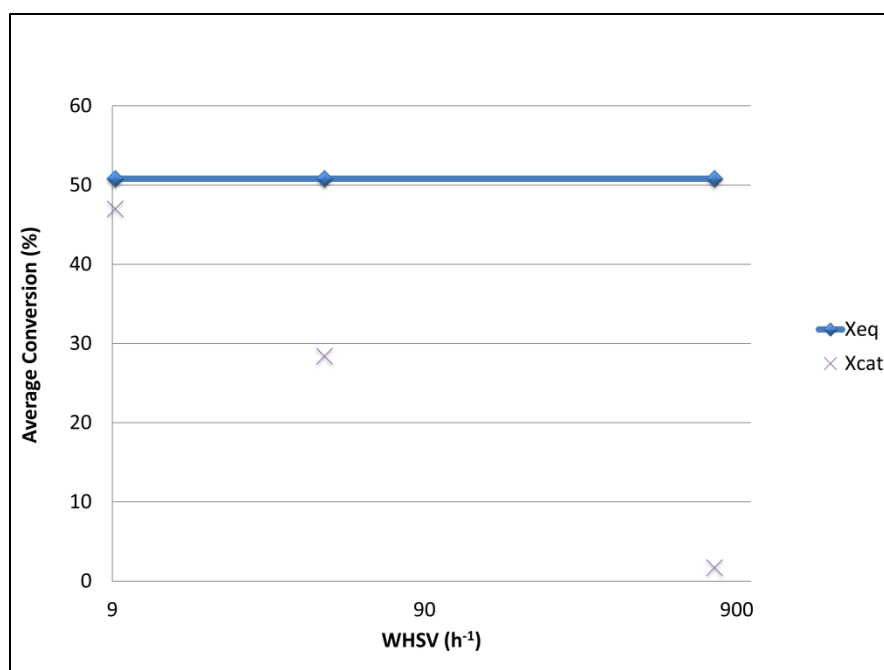


Figure 5-20: Conversion at three WHSVs for inlet temperature of 953 K

This clear decreasing trend, is however, not visible from the 1103 K inlet temperature variations. The increase in WHSV at the lower inlet temperature did deliver results that were distinguishable, but the drawback was the low temperature. The decomposition reaction requires thermodynamically that the temperature be as high as possible and as was seen from the 1103 K WHSV variations there was no distinguishable effect on conversion. Similar results were obtained by Thomey et al (2012) where the variation in WHSV, although lower than obtained in this study, did not deliver results at high temperature that could identify a trend. Higher WHSVs should be used at higher temperature but pumping the acid to the system proves to be a major obstacle. A rather large system should then be constructed that will be able to accommodate a high acid flow rate and should be constructed of a corrosion resistant ceramic as an increase in acid flow rate will mean an increase in corrosion rate.

The highest conversion achieved was at inlet temperature of 1103 K and acid flow of 4 mL/min with an average conversion of 75% obtained just below equilibrium conversion. As discussed earlier with results obtained and suggestions from Thomey et al. (2012) the WHSV had to be as high as possible. However, a big restriction was the amount of acid that could be fed to the system. Higher acid flow rates increase corrosion and require larger condensers and traps to effectively remove all acid mist prior to ventilation.

The only two variable investigated further was the inlet temperature to the bed and a change in the total residence time by manipulation with nitrogen feed.

5.3.3.3 Effect of Residence Time

The third process variable that was used to investigate the system was the residence time of the process gas in the catalyst bed. To ensure that the WHSV was as high as possible within the restrictions of the system, the reactor tube was altered so that a bed length of 100 mm could be filled with catalyst. This bed section was fitted with five centreline thermocouple probes and 5 wall thermocouple probes. The total residence time of the process gas was varied by keeping the WHSV constant and by changing the nitrogen feed to the system. The residence time variations were evaluated at different bed inlet temperatures, bringing the variables available for modelling to three. The residence time was defined as the open volume in the catalytic bed divided by the total volumetric flow rate:

$$\tau_{res} = \frac{V_{open}}{\dot{V}_{gas}} \quad [58]$$

Table 5-13 provides information about the process conditions for the experiments conducted:

Table 5-13: Process conditions for variation in residence time

Parameter	1	2	3
Inlet Temperature (K)	903, 953, 1003, 1103	903, 953, 1003, 1103	903, 953, 1003, 1103
Acid Flow Rate (mℓ/min)	4	4	4
Nitrogen Flow Rate (mℓ/min)	2.80	3.37	3.78
Residence Time (s)	0.1	0.081	0.07

Due to physical restrictions in the packed bed system the flow rate could not be increased more since pressure build-up in the system caused malfunctioning of units, in particular the peristaltic pump. The results obtained were evaluated by sulphur dioxide and oxygen analysis on a GC and an oxygen

paramagnetic cell. The conversion achieved can be seen in Figure 5-21 and from the graph the conversion for the various flow rates at different temperatures are observed.

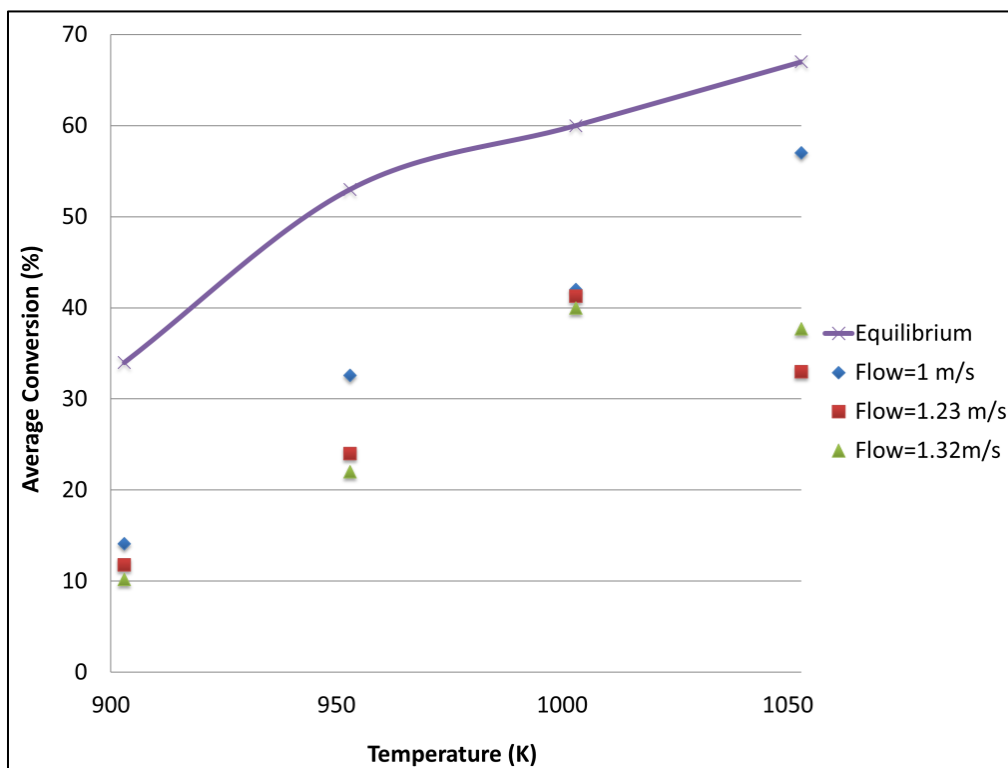


Figure 5-21: Conversion achieved at various operating temperatures and flow

For temperature 903, 953 and 1003 K the conversion of flow 1 is the highest since the residence time is the highest, as well as the inlet concentration to the catalytic bed. Since the total molar flow rate was not kept constant during the experiments the results will be discussed and referred to as four different temperatures at a specific flow rate and not different flow rates at a specific temperature. The amount of SO_2 produced per gram of catalyst for inlet temperature of 903 K (1 m/s flow) results in 7×10^{-7} mol/g.min which is much lower than similar conditions in Chapter 4. The temperature profiles for these experimental runs can be seen in Figure 5-22 and in the figure the wall and centreline temperature data points are shown for flow 1.

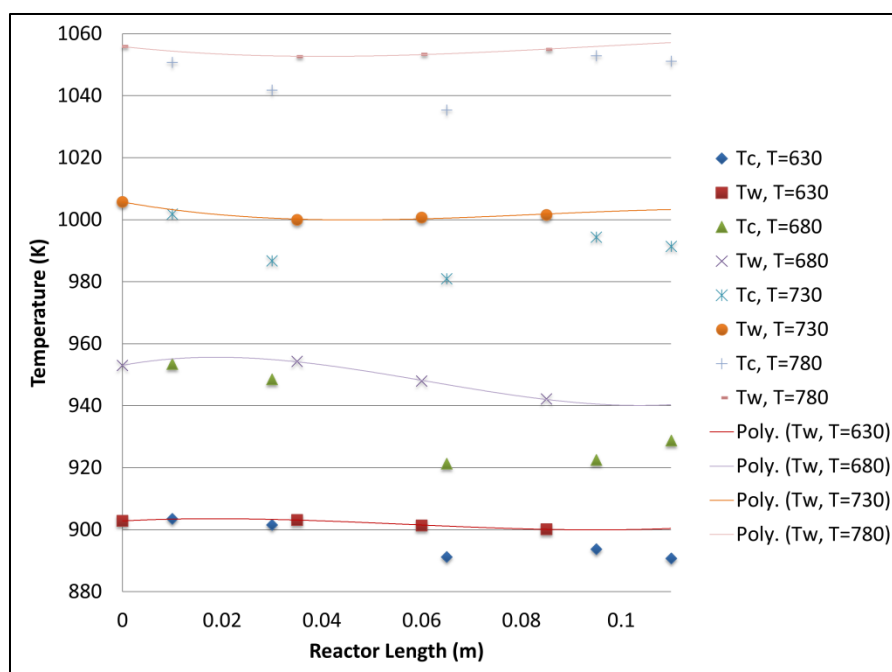


Figure 5-22: Centre and wall temperature profiles of flow 1

These profiles for flow 2 and 3 can be found in Appendix G. A polynomial was fitted through the wall temperature data points to make them more identifiable. As the temperature increase the results start to deviate from what is to be expected, as well as move closer to equilibrium. At the lower temperatures the conversion is almost halve of the equilibrium conversion. At a temperature of 1053 K the experimental value is close to equilibrium and the two higher flow rates deviate from the linear trend as seen for flow 1. The equilibrium conversion was calculated for the specific inlet conditions to the catalytic section and since conversion was already achieved by the vaporizer, sulphur dioxide and oxygen were in the inlet stream favouring the backward rate. The centreline temperature profiles show a tendency to decrease as soon as it enters the bed, after which at a certain point, the temperature starts to increase. The difference between the wall and centreline temperatures is not severe, with the largest, as can be seen in the figure, being approximately 20 K.

5.3.3.4 Inlet Pressure

The pressure of the process gas is a very important variable thermodynamically because a decrease in pressure results in an increase in equilibrium conversion. The results given and discussed were obtained from the variation in inlet temperature (Section 5.3.2.1). The ideal conditions for the highest equilibrium conversion for the sulphur trioxide decomposition reaction is low pressure and high

temperature. The pressure drop across the reactor system could not be measured accurately due to a lack of sensitivity and low pressure drop over small bed, and as a result, only inlet pressure to the bed is reported for calculation purposes. The inlet pressure profiles for one set of process conditions as a function of time can be seen in Figure 5-23.

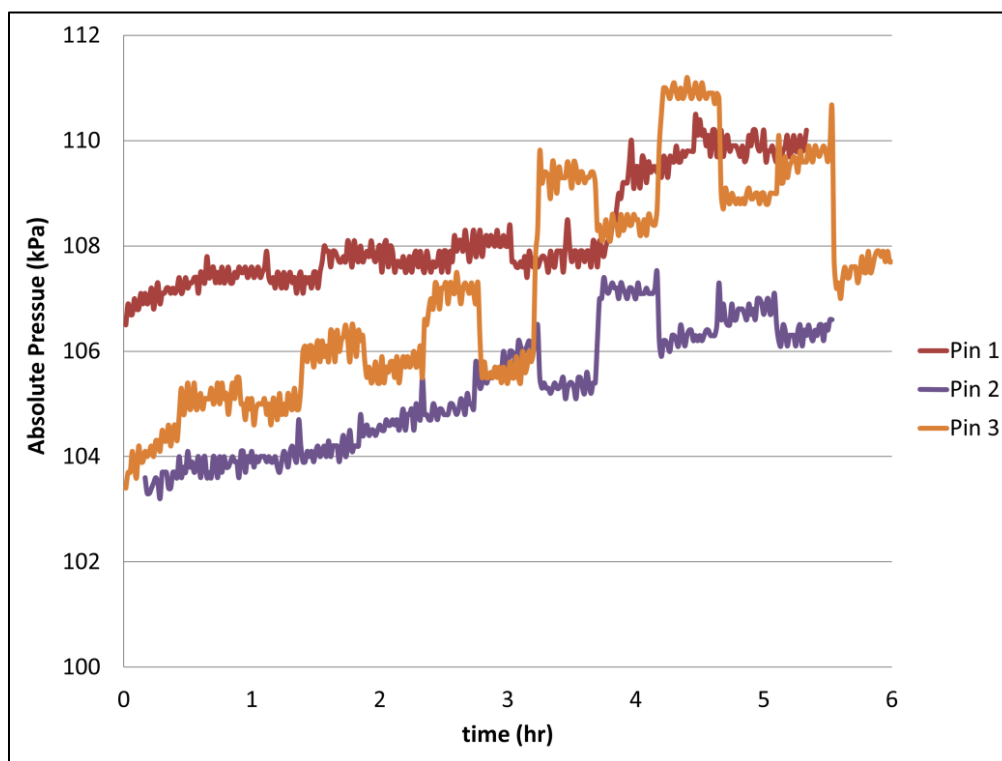


Figure 5-23: Absolute pressure before and after total reactor bed

In the absolute pressure as a function of time it can be seen that the pressure tends to increase as the experimental time progresses. This was due to corrosion in the vaporizer that caused some metal dust forming during corrosion to slowly block the inert packing at the fitting where the 10 mm vaporizer tube and 25 mm tube were joined. The small fluctuations in the pressure value can be attributed to the peristaltic pump. The pressure of three repeatability experimental runs can be seen in Figure 5-23. Some of the results and conditions obtained for the system which include inlet absolute pressure, WHSV and catalyst mass used can be seen in Table 5-14.

Table 5-14: Results for variable inlet temperature

	Inlet Temperature (K)			
	953	1003	1053	1103
P_{in} (kPa)	106.6	106.9	105.6	108.6
$WHSV$ (h^{-1})	1.16	1.14	1.19	1.11
W (g)	185.6	188.6	180.8	193.8

5.4 Summary

A fixed bed reactor system was constructed with three main sections which included the acid vaporizer, the sulphur trioxide decomposer and condensation/analysis section. The catalyst, consisting of 0.5 wt% platinum 0.5 wt% palladium loading on titania (anatase/rutile) support, was used to evaluate the conversion achieved over a specific bed length or catalyst mass. The system was commissioned with nitrogen/acid experiments prior to conducting catalytic experiments. During experiments it was found that during condensation of the acid leaving the reactor, sulphur dioxide was partially absorbed in the liquid phase altering results obtained on a GC (sulphur dioxide measured). Experiments were conducted and the mass balance was completed within an acceptable error range by measuring sulphur dioxide on a GC, oxygen on a paramagnetic cell, acid condensed weight, acid concentration (titrations) and the amount of sulphur dioxide (titrations). A model was developed in Aspen Plus® which incorporated Henry constants for sulphur dioxide solubility in water and the model was validated as being accurate to within 5% error against experimental data. The Aspen Plus® model was used to rectify results obtained only on the GC. The variation in condenser temperature was critical for the amount of sulphur dioxide lost; a lower temperature resulted in higher loss of sulphur dioxide.

Experiments showed that the inert silicon carbide pre-catalyst packing, the vaporizer and the reactor tube did catalyse the reaction in the absence of catalyst. The inlet conditions to the catalytic bed were obtained. The inlet temperature variable (long bed) was evaluated and the increase in conversion was approximately 10% for a temperature increase of 150 K. The conversion, pressure and temperature as a

function of time were given for some of the experimental conditions and it was found that steady state conditions were obtained, which compared quite well with results obtained in Chapter 4 from kinetic analysis. The results obtained from WHSV variations (long bed) indicated that at higher operating temperature (1103 K) the system was close to equilibrium (more than 80% of equilibrium conversion). At low WHSVs the variation in acid flow rate did not deliver results where a trend could be observed as was observed by the study of Thomey et al. (2012). The variation in WHSV (catalyst mass) at high temperature delivered results which indicated that the system was close to equilibrium and that an increase in WHSV caused a decrease in conversion. A trend could be observed were the conversion drastically decreased as the WHSV increased for a low inlet temperature (953 K) with variation in WHSV (catalyst mass).

For residence time variation the acid flow rate and catalyst mass were kept constant while the nitrogen flow was varied, as well as the inlet temperature. The results obtained from lower temperatures delivered satisfactory results with regard to equilibrium restrictions as they were away from equilibrium conditions (40-60% of equilibrium conversion). An increase in 150 K caused the conversion to increase by approximately 40%, unlike the inlet temperature variation conditions. A variety of results were obtained and the best result for the short bed was identified at a temperature of 1053 K for the residence time variation (1 m/s). The conversion achieved was 56 %. The best result from the long bed was for acid flow rate of 3 mL/min at temperature of 1103 K and WHSV of 1.8 h^{-1} , which delivered an average conversion of 75%. All experiments were carried out on fresh catalyst and as a result the re-usability or lifetime of the catalyst was not established.