Investigation on using Supercritical Carbon Dioxide as Desorbing and Reaction Medium in the Surfactant Production Process

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2007

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

To date, an estimated 70% of energy consumed comes from fossil fuels, such as coal, oil and natural gas. The major source of sulfur dioxide (SO_2) emissions comes from combustion of these fossil fuels. Sulfur dioxide is a significant pollutant, because it and its higher oxidation product (SO_3) react with moisture in the atmosphere to produce sulfuric acid. This results in acid rain, which comes back to earth and affects people, animals, and vegetation. Therefore, the governments of Canada, US and European countries are issuing stricter and stricter regulation to control SO_2 emissions.

In conventional SO_2 removal processes, lime or limestone scrubbers are used, but they require large amounts of water and enough landfill sites to deal with the solid wastes. Previous attempts were made in our laboratory to recover SO_2 adsorbed on activated carbon to produce sulfuric acid using non-aqueous solvents. Unfortunately, in this adsorption/distillation process, the SO_2 recovery was low, as was the quality of sulfuric acid, that could not be marketable. The topic of this thesis was then conceived as an attempt to first recover SO_2 via SO_3 formation using supercritical carbon dioxide instead of water or non-aqueous flushing agents (desorption step) and then to use the recovered SO_3 to produce linear alkylbenzene sulfonates (LAS), the main component of detergent.

In the adsorption and oxidation experiments of this project, charcoal activated carbon (AC) was used to adsorb SO_2 and to catalyze SO_2 oxidation. The process started with a simulated flue gas, 3500 ppm SO_2, 5% O_2, balanced with N_2. When the simulated flue gas passed through the activated carbon bed reactor, more than 95% of SO_2 was oxidized to SO_3 (1).

In the desorption process, SO_3 contacted with the AC bed was removed using supercritical carbon dioxide ($SCCO_2$) and 95% sulfur removal was achieved at appropriate operating conditions, for example, for a carbon bed preheated at 250°C for 6 h, and flushed by recycled $SCCO_2$.

The LAS production experiments consisted in reacting liquid linear alkylbenzene (LAB) with the recovered SO_3 in an absorption column. Ceramic filters and glass beads were used in the absorption columns to break up the gas bubbles and increase the contact time between the gas and the liquid absorbent. When staged pressure columns were used and when LAB was heated to 40°C, nearly 95% of SO_3 reacted with LAB to produce LAS.

Acknowledgements

I wish to express my sincere appreciation to my thesis supervisors Dr. Peter Silveston, Robert Hudgins, Eric Croiset, and Ali Lohi for their valuable guidance, encouragement and support for this project. I also wish to express my great appreciation to Dr. William Epling for his valuable guidance and great support in helping me fulfill this project.

I would also like to acknowledge the work of all the students whose work is included in this project. In particular, Luke Coleman for his great help in experiments, as well as support from all members of the Chemical Reaction Engineering Research Group.

I wish to acknowledge the contribution of Petresa Canada Inc., Quebec, for donating LAB and LAS samples for use in this study.

Furthermore, I would like to thank everyone who has helped and encouraged me.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

For SO_2, the U.S. has set a national emission cap of 8.95 million tons for electric utilities and 5.6 million tons for industrial sources to be achieved by 2010. By comparison, in Ontario (2), through the Countdown Acid Rain Program between 1990 and 1999, industrial sources achieved a reduction of approximately 500 kilotonnes of SO_2. Despite this effort, in 1999, industry (excluding electricity) remains a significant contributor, at about 68 per cent of provincial SO_2 emissions. The electricity sector, which accounts for about 27 per cent of SO_2 emissions, has recently been required to reduce emissions under the Emissions Reduction Trading Regulation. However, most other industrial point sources remain without such annual emissions limits. Projections indicate that some industry sub-sectors will increase production levels and SO_2 emissions (2).

In October 2001, Ontario announced its intention to begin consultations to introduce nitrogen oxides (NOx) and sulfur dioxide (SO_2) emission limits for major industry sub-sectors in Ontario and expanding its emission trading system to include large industrial emitters (3). Over the past years, the Ministry of the Environment (MOE) developed a plan for reducing SO_2 emissions from the industry sector (2).

Methods for SO_2 removal include absorption and adsorption (4). Both of them have their own advantages and disadvantages. In the absorption process, SO_2 is absorbed into aqueous solutions and converted to stable compounds by reaction with the absorbers. Conventional processes for SO_2 removal are lime or limestone scrubbers. In these processes, SO_2 reacts with lime to produce stable calcium sulfate. Such process has proven high efficient and is relatively economical for SO_2 capture. However, it requires large amounts of water and enough landfill to deal with the produced solid wastes (5). In adsorption process, the lower removal efficiency and difficult separation are the problems.

Another technology of SO_2 capture is using activated carbon (AC) as a catalyst to recover SO_2 as sulfuric acid. In this process, SO_2 is catalytically oxidized to SO_3 by oxygen in the flue gas on AC surface, and SO_3 is separated from AC by water or low boiling point nonaqueous solvents to produce H_2SO_4.

The major problem of washing with water is that the concentration of H_2SO_4 solution obtained is dilute and thus not marketable since excess amount of water is used to completely recover SO_3. Therefore, previous researchers of the University of Waterloo focused on using nonaqueous solvents, such as acetone, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK), as the flushing agents to desorb the SO_3 absorbed on activated carbon (Panthaky et al., 1998(1), 2001(6)). The energy required for their recovery would be much less than that needed to concentrate dilute sulfuric acid, because these flushing agents have lower boiling points than water.

As flushing agent, an ideal organic solvent should behave differently from water by not reacting with either SO_2 or SO_3. The effluent from stripping SO_3 from activated carbon is a mixture of the organic flushing fluid and SO_3. If there is any water vapor in the solvent or gas streams, some H_2SO_4 will also form in the mixture. For an economical process, the ideal solvent must be recoverable, probably using distillation. The previous work dealt mainly with the evaluation of the acid-solvent separation and extended the work of Panthaky et al. to additional solvents (7).

In the research of Wattanakasemtham et al (8), the near-critical CO_2 was used as a flushing agent, and the effects of pressure (P), superficial velocity (v) and temperature (T) on sulfur recovery were examined. But the SO_3 recovery was only about 80% (Wattanakasemtham, 2003) (9) and the H_2SO_4 concentration was low.

In this project, SO_2 was catalytic oxidized to SO_3 on AC surface and supercritical carbon dioxide ($SCCO_2$) was used to flush the bed in order to recover SO_3. Then, the SO_3 removed from the AC bed was reacted with linear alkylbenzene (LAB) to produce linear alkylbenzene sulfonates (LAS).

The first objective of this project was to improve the recovery of SO_3 from the AC bed. When SO_3 is adsorbed in the AC bed, it is very difficult to recover it because of the highly porous structure of activated carbon. The previous study at the University of Waterloo (Wattanakasemtham, 2003) showed that the recovery of SO_3 was about 80%, when near- critical CO_2 was used as a flushing agent. In this project, the flushing agent was $SCCO_2$, and the SO_3 recovery was targeted to be more than 90%.

The second objective was to improve the SO_3 absorption and reaction with LAB. In the absorption process, the amount of SO_3 absorbed by LAB must be maximized in order to reduce the amount of SO_3 emission to environment and improve the LAS production. LAS are the main components of laundry detergents and other cleaning products.

In summary, the goal of this thesis was to develop a process capable of removing SO_2 from flue gas using activated carbon, recovering the sulfur species in the form of SO_3 using supercritical CO_2, and finally reacting the recovered SO_3 to produce LAS, one of the main components in detergents. Such process is designed as an economical mean of reducing SO_2 emissions while recovering it to produce useful products (LAS for the detergent industry in the present case).

Chapter 2

Literature Review

2.1 SO_2 emission and control overview

Since the middle of the last century, increasing energy demands has become a big problem for every country, especially the developed countries. In the 21st century, the energy crisis is always the focus of news. In 2000, more than 70% of the energy came from fossil fuels, such as coal, oil and natural gas. Sulfur contained in such fossil fuels are oxidized to sulfur oxides (SO_2, sulfur dioxide, and SO_3, sulfur trioxide) when these fuels combust (12). When the combustion temperature is more than 350°C, more than 98% of sulfur oxides is sulfur dioxide, which is then emitted to the environment (7). Of the several air pollutants that plague the world, sulfur oxides (SO_2, sulfur dioxide, and SO_3, sulfur trioxide) have received special attention. The severity of the problem – effects on people, animals, and vegetation – is a matter on which there are varying opinions that will not be debated here.

Overall, sulfur dioxide, SO_2, has become a significant pollutant, because it and its higher oxidation state (SO_3) react with water, or moisture in the atmosphere, to produce sulfuric acid. The effect of acid rain on earth, people, animals, and vegetation was well recognized by Nixon (Nixon, 1995) (10).

For SO_2, the U.S. has set a national emission cap of 8.95 million tons for electric utilities and 5.6 million tons from industrial sources to be achieved by 2010 (3). As the industrial cap has already been achieved and since over 70 per cent of the country's emissions of SO_2 are from electric generation (4), the U.S. is now primarily targeting the electricity sector for SO_2 reductions. By comparison, in Ontario, the emissions from electricity generation only account for 27 per cent of emissions of SO_2 while other industrial sources account for 65 per cent of SO_2 emissions. In addition, in the U.S., SO_2 emissions from non-ferrous smelting process are insignificant whereas, in Ontario, non-ferrous smelting account for approximately 45 per cent of provincial SO_2 emissions. Therefore, the best mix of tools for reducing emissions in Ontario needs to reflect the different mix of emission sources.

Over the past years, the Ministry of the Environment (MOE) has been consulting with industrial and non-governmental associations (health and environmental) on the policy questions identified to develop a plan for reducing SO_2 emissions from the industry sector (2). The MOE has also examined requirements in the U.S. where SO_2 limits have been established for the electricity sector and some industry sub-sectors. This would ensure that the industry sector makes a reasonable contribution towards achieving Ontario's emission reduction targets of 50% SO_2. SO_2 Emission trends in Ontario are shown in table 2.1.

Table 2.1: SO_2 Emission Trends in Ontario (kilotonnes) (3)

	Source	Sulfur Dioxide (SO_2)			
		1990	1999	2010 (estimate)	2015 (estimate)
Industry Sources	Iron and Steel	27	23	20	19
	Cement	21	23	24	24
	Petroleum Refining	63	55	59	60
	Chemical	8	10	10	10
	Pulp and Paper	17	8	8	8
	Non-Ferrous Smelting	693	264	245	245
	Other Manufacturing	67	17	18	19
	Electricity	197	144	131	131
	Industry Total	1093	545	516	517
Non-industry Sources	Transportation	21	15	4	4
	Off-Road/Rail/Air/Marine	30	21	18-23	17-25
	Residential/ Commercial	13	7	6-8	6-8
	Other	0	0	0	0
	Ontario Total	1158	588	544-551	544-554
	Ontario Target	442			
	Gap	102-112			

The major sources of sulfur dioxide in the United States and Ontario are shown in Figure 2.1. In U.S.A., combustion of fossil fuels is clearly the primary contributor of sulfur dioxide emissions. Industrial processes, such as nonferrous metal smelting, also contribute to sulfur dioxide emissions.

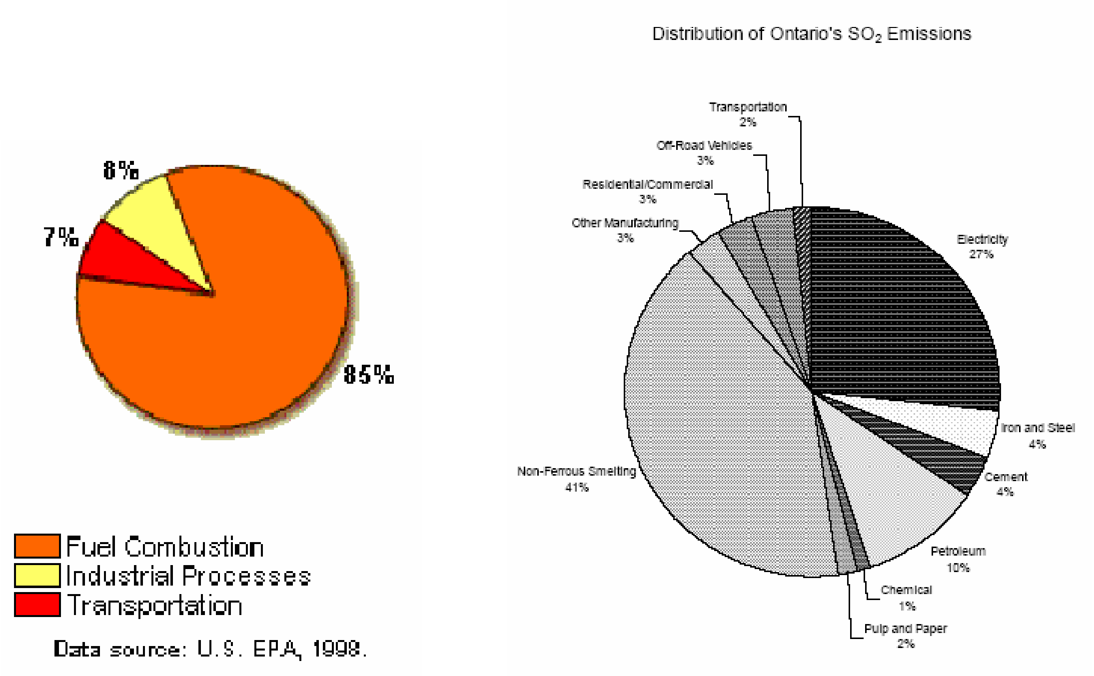


Figure 2.1: The major sources of sulfur dioxide in the United States and Ontario.(11) and (8)

Major considerations in SO_2 removal from flue gas

The technology of SO_2 removal from flue gas has been developed in different directions, each with its own advantages and disadvantages. Conventional SO_2 removal methods (from EPA) include absorption and adsorption (11).

1. Absorption

Absorption processes use the solubility of sulfur dioxide in aqueous solutions to remove it from the gas stream. Once sulfur dioxide has dissolved in solution to form sulfurous acid (H_2SO_3), it reacts with oxidizers to form inorganic sulfites (SO_3^{2-}) and sulfates (SO_4^{2-}). This process prevents the dissolved sulfur dioxide from diffusing out of solution and being re-emitted.

Using non-aqueous solutions to remove SO_2/ SO_3 from the gas stream was also studied (see previous studies of University of Waterloo, Panthaky, 1998 (5, 2001(6)).

Typical removal efficiencies for sulfur dioxide in wet scrubbers range from 80 to 95% (7). The waste products are also an important consideration in selecting the removal method; the absorber or absorbed materials need to be treated before drained to the environment.

The conventional processes for SO_2 removal from flue gas are lime or limestone scrubbers (De Nevers, 1995)(12). These methods proved to be highly efficient and relatively economical for SO_2 capture. However, they require large amounts of water, because of the low solubility of lime, and the used water needs to be retreated before being discharged back into the environment. In these treatment processes, SO_2 is converted to calcium sulfate, which is discarded as a solid waste to a landfill. Therefore, there is a major problem in finding enough landfill sites to deal with these solid wastes.

2. Adsorption

Sulfur dioxide can also be collected by adsorption systems. In this type of control system, a dry alkaline powder is injected into the gas stream. Sulfur dioxide adsorbs on the surface of the alkaline particles and reacts to form compounds that do not re-enter the gas stream. Hydrated lime (calcium hydroxide) is the most commonly used alkali.

However, the dry injection system is slightly less efficient, and requires more alkali per unit of sulfur dioxide (or other acid gas) collected. Accordingly, the waste disposal requirements and costs are higher for adsorption systems than absorption systems.

2.2 Activated carbon

Another adsorption technology uses activated carbon as the adsorption material and catalyst.

Activated carbon is produced from a solid carbonaceous based material (13). The precursor is transformed or activated by means of medium to high temperature treatments, which remove solid mass, and at the same time, create pores where the removed mass was previously located (14). The common properties of activated carbon are their well developed pore network. The production processes include pretreatment, carbonization and activation. Details of this have been presented by Teresa J. Bandosz (13). In the different adsorption processes, both in gas and liquid phase, the adsorbable molecules or atoms are fixed (adsorbed) on the carbon (adsorbent) surface by physical interactions and/or chemical bonds. Therefore, a relatively large specific surface area is one of the most important properties that characterize carbon adsorbents.

It is estimated that every year around 100 million tones of SO_2 and NO_2 are emitted to the atmosphere from anthropogenic sources mainly from plants (15), where fossil fuel is burned. The major sources of air pollution originate in the highly industrialized countries such as the United States and European nations.

Complaints about SO_2 pollution were known at least back to thirteenth century (16). The effects caused an increase in the acidity of natural waters, fast rate of abrasion of buildings and monuments, and associated health problems. To remedy these problems, the desulfurization of fossil fuels along with the removal of SO_2 from stock gases is the technologies which have been developing rapidly during the last thirty years. Although conventional methods for SO_2 abatement utilize basic scrubbers where acidity of sulfur dioxide is neutralized and salts are formed, for removal of low concentrations of SO_2, activated carbons were shown as feasible removal media. Numerous studies indicate good efficiency of SO_2 removal on these materials at either low or high temperatures (17, 18).

Activated carbon is a cheap material and has high adsorption capacity. For example, the Brunauer-Emmett-Teller (BET) surface area of activated carbon is from 1000 to 1500 m^2/g, and activated carbon has high pore volume. At the same time it is a common catalyst for SO_2 oxidation, and this oxidation can occur at a low temperature, such as room temperature (19).

SO_2 adsorption has been studied extensively and such parameters as porosity, surface chemistry, and constituents of ash have been taken into consideration (Davini, 2001).

2.3 Supercritical Carbon Dioxide Technology

Different technologies are used to remove SO_2/SO_3 from AC surface. Acetone, Methyl Ethyl Ketone, and Methyl Isobutyl Ketone (Panthaky et al., 2001) and near-critical CO_2, supercritical CO_2 ($SCCO_2$) technologies (Wattanakasemtham et al., 2005) were studied at the University of Waterloo. It was found that $SCCO_2$ was a good desorption agent of SO_3 removal.

Supercritical carbon dioxide, with its moderate critical properties, non flammable nature and low cost, provides an attractive alternative for replacing organic solvents traditionally used in chemical manufacturing processes. Minimizing liquid waste generation, easy separation of solutes and fast reaction rates are some of the advantages of the supercritical fluid extraction technology over conventional solvent extraction methods (20).

When a gas is compressed to a sufficiently high pressure, it becomes liquid. If, on the other hand, the gas is heated beyond a specific temperature, no amount of compression of the hot gas will cause it to become a liquid. This temperature is called the critical temperature (T_c) and the corresponding vapor pressure is called the critical pressure (P_c). The state of the substance is called supercritical fluid (SCF) when both the temperature and pressure exceed the critical point values as schematically described in a pressure-temperature phase diagram shown in Figure 2.2.

This “fluid” now takes on many of the properties of both gas and liquid. It is the region where the maximum solvent capacity and the largest variations in solvent properties can be achieved with small changes in temperature and pressure. It offers very attractive

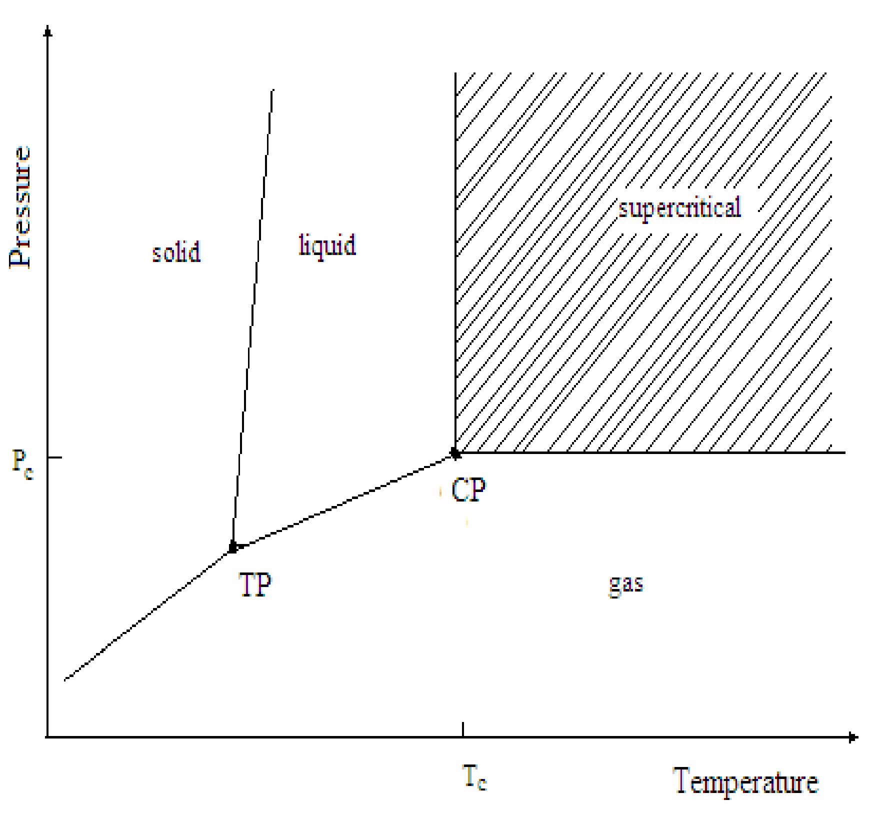


Figure 2.2: Pressure-temperature diagram for a pure component.

extraction characteristics, owing to its favorable diffusivity, low viscosity, moderate to low surface tension and other physical properties. Its diffusivity is one to two orders of magnitude higher than those of other liquids, which facilitates rapid mass transfer and faster completion of extraction than conventional liquid solvents. The gas-like characteristics of SCF provide ideal conditions for extraction of solutes giving a high degree of recovery in a short period of time. However, it also has the superior dissolving properties of a liquid solvent.

Carbon dioxide is the most desirable SCF solvent for extraction of natural products for foods and medicines today. It is an inert, inexpensive, easily available, odorless, tasteless, and environmental-friendly solvent (18). Further, in SCF process with CO_2, there is no solvent residue in the extract, since it is a gas in the ambient condition. Also its near-ambient critical temperature (31.1°C) makes the energy requirement for attaining supercritical state of CO_2 to be less than that of conventional organic solvents.

Thermodynamically, supercritical fluid is a state where the pressure and temperature are beyond the critical point values. In practice, an SCF solvent is mostly used as an extractant in the approximate range of temperatures up to 1.2 times the critical temperature, T_c, and pressures up to 3.5 times the critical pressure, P_c. This range of operating condition provides liquid-like densities as can be seen from Figure 2.3.

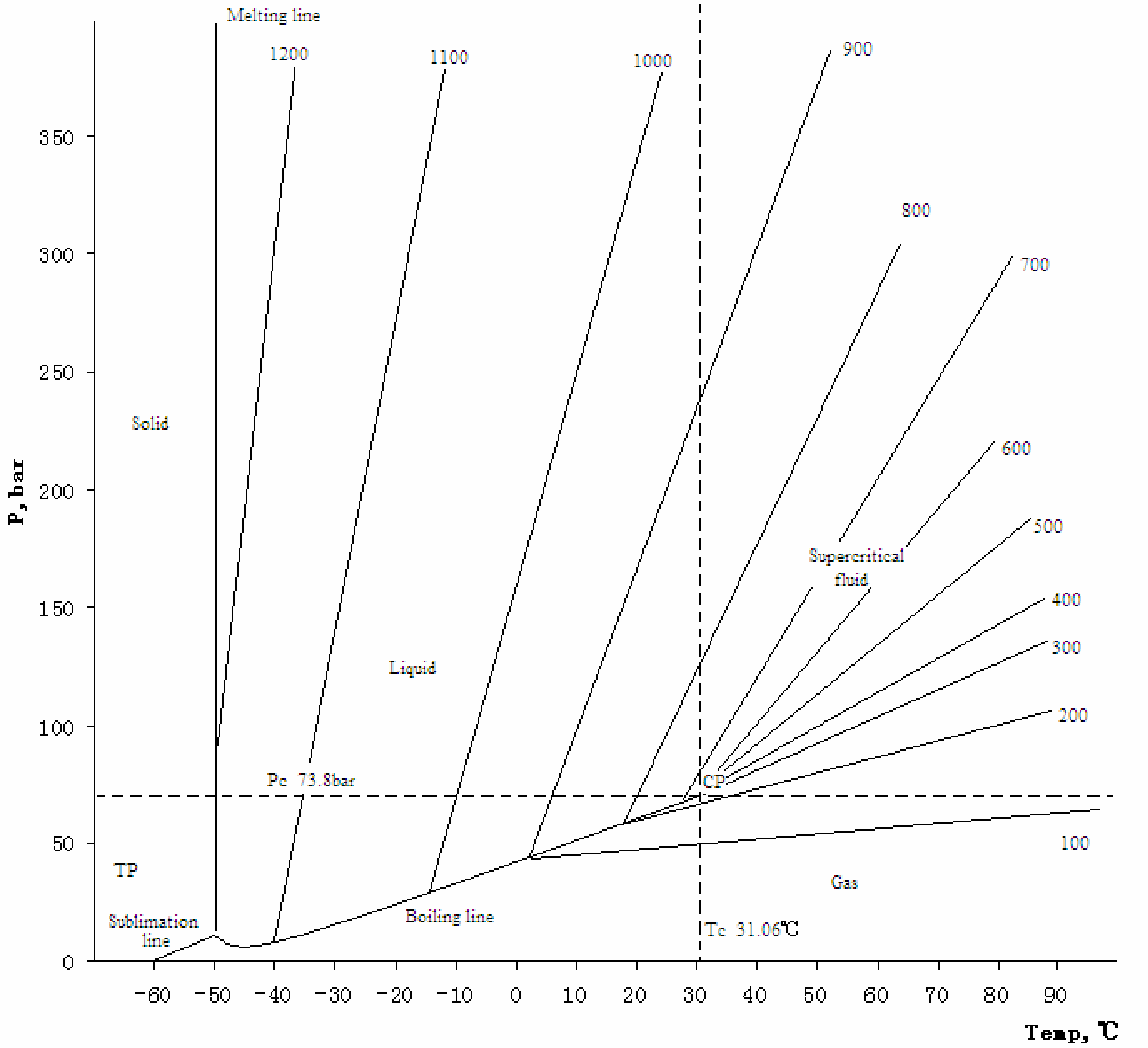


Figure 2.3: P-T diagram of CO_2 at densities from 100 to 1200 g/L $^{\text{from (18)}}$.

The solvent capacity at the supercritical fluid state is density dependent and it is the sharp variability of density with pressure and temperature in this state that provides uniqueness to a SCF solvent.

Among the unique features characteristic of the solubility behavior of a solute in an SCF solvent are the exponential solubility enhancement. The solubility behavior of solute in a SCF solvent is analyzed in terms of pressure and temperature. At higher densities, the molecular interactions between the solvent and the solute are enhanced and as a result, more solute is dissolved. From the Figure 2.3, for SCF, at the lower pressure and lower temperature, the density of $SCCO_2$ is higher, and the $SCCO_2$ has higher solubility (18).

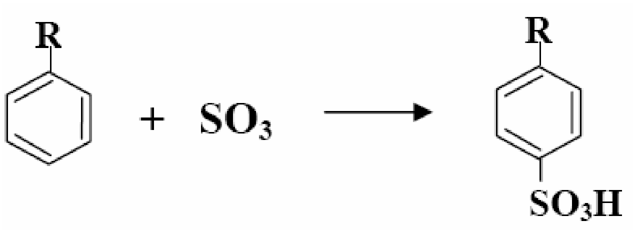
2.4 Properties and Production of Linear Alkylbenzene Sulfonates (LAS)

SO_3 removed by $SCCO_2$ from AC bed is absorbed by water to produce sulfuric acid (Wattanakasemtham N., 2003). It also can be absorbed by linear alkylbenzene to produce linear alkylbenzene sulfonates.

Linear alkylbenzene sulfonates are components of laundry detergents and other cleaning products that were created in the early 1960s to help put an end to foaming in rivers and streams caused by the poorly degradable product used, called BABS (Branched Alkylbenzene Sulfonates), which were the traditional surfactant of choice for detergents until that time (21). The focus on alternatives became biodegradability, and LAS were selected because of its high rate of biodegradability.

Such replacement was the result of a vast research effort followed by investments to provide the world surfactant & detergent industry with one of the most cost-effective and environmentally safe surfactants. These investment activities have continued during the last 40 years and have yielded continuous improvements in quality and safety as well as new developments in both LAB production (Linear Alkylbenzene, the raw material for LAS) and sulphonation processes.

LAS are a mixture of homologues and phenyl positional isomers, each containing an aromatic ring sulfonated at the para position and attached to a linear alkyl chain of C_{10}-C_{14} at any position except the terminal one $^{(22)}$. LAS are anionic surfactants which were introduced in the 1960s as more biodegradable replacements for highly branched alkylbenzene sulfonates. LAS are produced by sulfonation of linear alkylbenzene with sulfur trioxide (SO_3), as shown below, usually on a falling film reactor or with oleum in batch reactors. The hydrocarbon intermediate, LAB, is currently produced mainly by alkylation of benzene with n-olefins or n-chloroparaffins using hydrogen fluoride (HF) or aluminium chloride ($AlCl_3$) as a catalyst.



The industry production process is shown in Figure 2.4.

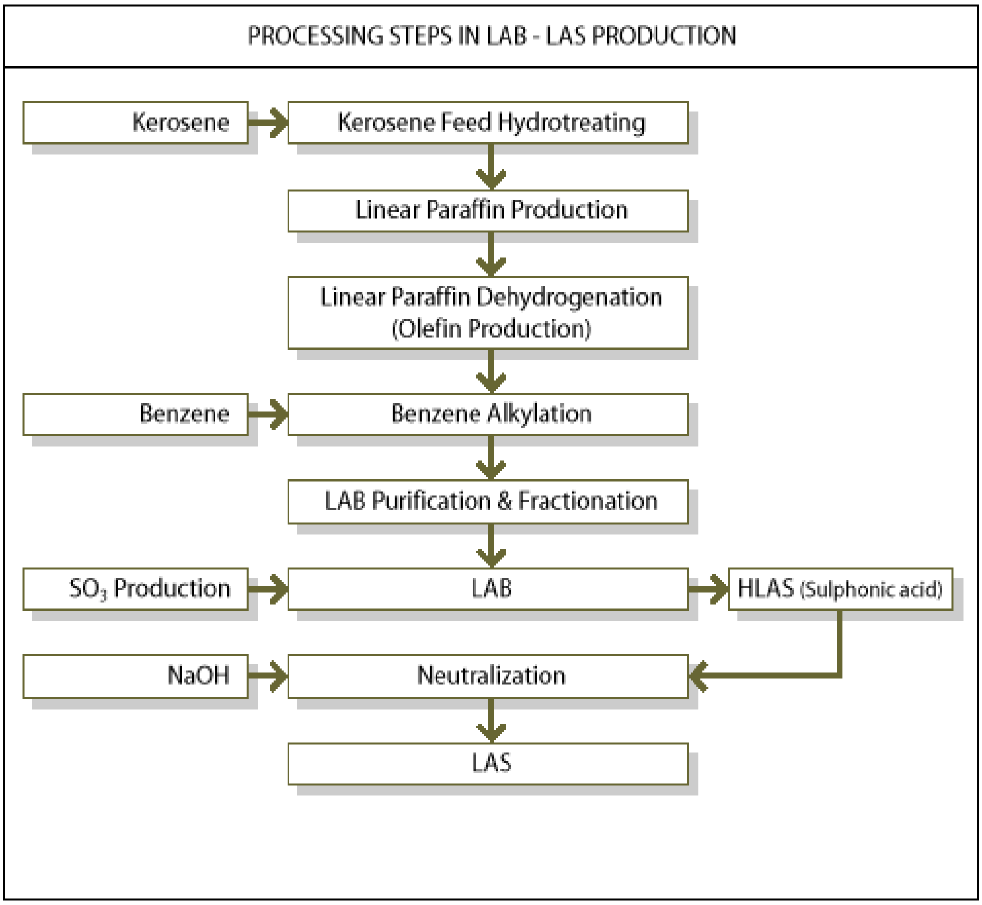


Figure 2.4: The industry process of LAS production (22).

In the past, oleum (fuming sulfuric acid) as well as sulfuric acid was the predominant agents used either in batch reactors or in the so-called "cascade" systems. The sulfonation technology, however, has been considerably improved since the middle 60s and nowadays, although oleum is still used, modern falling film reactors (FFR) (mono-tube or multi-tube) and SO_3 gas are the state-of-the-art technology in most of the sulfonation facilities in Europe. These modern plants generally sulfonate LAB and fatty alcohols directly on site.

Linear alkylbenzene (LAB), the material used to produce LAS, is derived exclusively from petroleum derivatives: benzene and linear paraffins. Total LAB world production capacity in the year 2002 was estimated at 2.5 million tons (23). LAS currently represent one-third of the active ingredients in detergents worldwide. Virtually all LAB is transformed into LAS.

The result of sulfonating LAB is the formation of alkylbenzene sulfonic acid, which has the consistency of a liquid with a high active content (>97%), containing about 2% of unsulfonated matter and 0.5% of H_2SO_4 (24). The acid is then neutralized with a base to give the final LAS surfactant salt. Sodium neutralized LAS are by far the predominant grade. As salt, it can also be supplied in various forms, for example as paste (50-75%) and powder (80-90%).

Although LAS are also employed in industrial processes, mostly as an emulsifier or a wetting agent, its main use is as a surfactant or "surface active agent" in detergents. As a surfactant, LAS are used in most detergents, dishwashing liquids and all-purpose cleaners because its chemical composition is vital to the removal of dirt, oil and grease from clothes, surfaces and dishes. They lower the surface tension of water so that it can wet and penetrate fabrics more easily to loosen and remove soils and stains. If a soil stain is on a cloth, water alone cannot remove the stain, primarily because the oil in the soil does not react with the water molecules. The role of LAS as a surfactant is to eliminate this problem by suspending the oil in water, so that with some mechanical energy in the form of the movement in a washing machine or rubbing by hand, the soil can be pulled free from the shirt. This is possible because the surfactant as a molecule has one end that will attach itself to the oil in the soil and another end that will attach itself to the water molecules. Without surfactants, we would use more water, potentially more cleaning agents, and certainly more energy.

Because of LAS's environmental safety, cleaning effectiveness and cost competitiveness, LAS has experienced more than 30 years of ever-increasing use around the world. LAS may be considered as the first "green" cleaning agent, because it was the first surfactant introduced to solve an environmental problem (25).

The world surfactant consumption is shown in Figure 2.5.

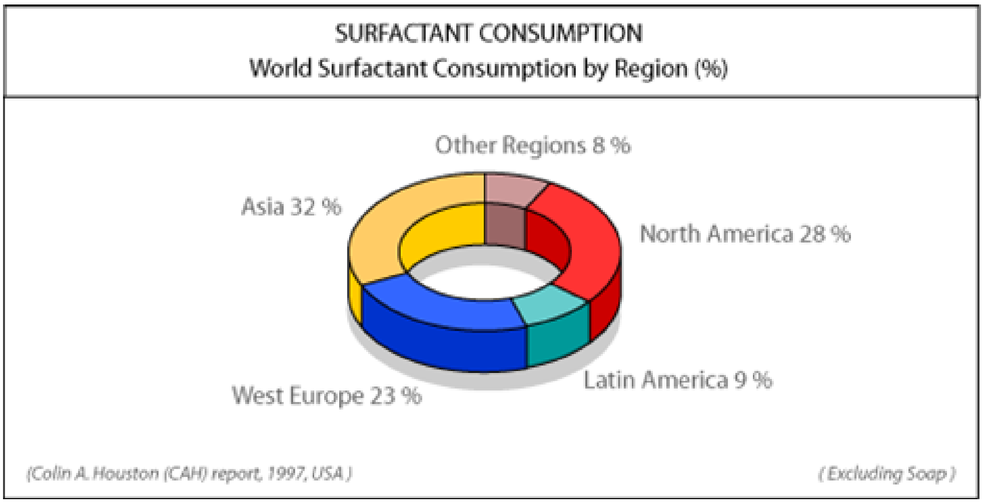


Figure 2.5: World surfactant consumption (22)

Supporting this history of safe usage is a large archive of environmental research that has been conducted on LAS. This environmental research, performed by top environmental scientists and research agencies, has investigated virtually every part of the environment that could have been exposed to LAS. The studies have repeatedly proven LAS's environmental acceptability and safety.

In summary, using $SCCO_2$ as the SO_3, catalytically oxidized from SO_2, desorption agent looks promising, and the removed SO_3 can be used as the reactant of LAS production. The advantages of the method are follows:

- SO_2 in flue gas can be efficiently removed and oxidized to SO_3 by activated carbon.

- Compared with other liquid flushing agents, CO_2 has lower viscosity. Low viscosity implies high diffusivity and better penetration in pores, which result higher mass transfer efficiency. Therefore, the removal efficiency is better.

- The energy requirement for attaining SCCO2 is less than conventional organic solvent because of the low T_c and P_c.

- The CO_2 can be easily separated in absorption system and there is no solvent residue in the absorber since CO_2 is a gas in the ambient condition. In an organic solvent flushing system, the unwanted products from side-reactions are usually well mixed and are very hard to separate.

Chapter 3.

Experimental Methods

In this research project, SO_2 is oxidized to SO_3 and adsorbed on activated carbon (AC). Then the adsorbed SO_3 on AC is desorbed by supercritical carbon dioxide ($SCCO_2$) and reacts with Linear Alkylbenzene (LAB) to produce Linear Alkylbenzene Sulfonates (LAS), which is one of the main components of the detergent.

Therefore, the experimental set-up includes two systems. The first one is the adsorption/catalyst system. SO_2 is adsorbed on the activated carbon and oxidized to SO_3 by the oxygen in simulated flue gas. The second is the desorption system. The absorbed SO_3 on the activated carbon is desorbed by $SCCO_2$ and is carried into the absorber columns, and reacts with the absorber (LAB) to produce LAS.

3.1. Sulfur dioxide absorption and oxidation experiment

3.1.1 Experimental Apparatus

In the SO_2 adsorption and oxidation experiment, the apparatus included a reactor and a SO_2 analyzer.

3.1.1.1 Reactors

There are two different sizes of reactors used in the experiments. Both of them are stainless steel tubes and the pressure ratings were safe for operation up to 41 MPa at room temperature.

The outer diameter of the smaller size reactor is 12.7 mm and the wall thickness is 1.5 mm. The reactor was packed with about 8 g of activated carbon to give a 24 cm packed bed depth. The weight of fully loaded activated carbon is different because of the different packing density of the activated carbon. For example, there was 8.13g AC packed in the reactor at first; after several adsorption and desorption experiments, 8.62g fresh AC was packed in the reactor instead of the one before.

The outer diameter of the larger reactor is 25.4 mm and the wall thickness of the tube is 3.0 mm. The fully load bed depth was 56 cm. The weight of fully loaded activated carbon was 65.2g. The property of the activated carbon is described in section of 3.1.1.3.

Three heating tapes (silicone rubber extruded heating tape, Fisher Scientific, Canada) were used. One of them was used to heat the reactor; the other two were used to heat the absorber columns, as explained later.

3.1.1.2 SO_2 Analyzer

The SO_2 concentration in the gas flow down stream from the adsorption and oxidation system was monitored by a sulfur dioxide analyzer (model 721 AT; Western research, Calgary, Alberta, Canada). The maximum SO_2 concentration that this analyzer can measure is 5000 ppm. A rotameter was used to control the flow rate of the gas that went to the analyzer. In order to get the correct result, the flow rate of gas passing through the SO_2 analyzer during the calibration process should be the same with that in the SO_2 absorption and oxidation process.

The analyzer was calibrated at each start-up with zero gas (nitrogen) and a span gas (2536 ppm of SO_2 in N_2).

3.1.1.3 Activated Carbon

Activated carbon was the adsorption material and catalyst in SO_2 adsorption and oxidation, therefore, the properties of AC are important.

The model of activated carbon used in this study was BPL 6×16, supplied by Calgon Carbon Corp. BPL 6 x 16 is a bituminous coal-based virgin granular activated carbon designed for use in vapor phase applications. The physical properties and particle size distribution of BPL 6 x 16 offer maximum adsorption capacity for applications that require minimum carbon bed depth due to space limitations. Because of its surface area, density, and strength characteristics, BPL 6 x 16 can be reactivated for reuse (26).

The characteristics of BPL carbon are shown in Table 3.1.

Table3.1: The characteristics of activated carbon (BPL6×16) (26)

Properties	Value
Brunauer-Emmett-Teller surface area, m^2/g	1200
Average pore radius, nm	1.184
Pore volume, mL/g	0.710
Apparent density, g/mL	0.43
Average diameter, mm	2.18

3.1.2. Experimental details

The system was located in a fume hood for safety reasons. The schematic flow diagram of SO_2 oxidation and adsorption is shown in Figure 3.1.

The reactor was packed with activated carbon to a depth of 240 mm (for the smaller size of reactor). It was fed by simulated flue gas mixtures with volumetric compositions of 0.35% SO_2 (3500 ppm) and 5% O_2, with the balance being N_2. This is typical of the flue gas composition from coal-fired power plants (Kolker et al, 2003) (27). Mass flow controllers (Units Instruments Inc., Orange, CA) connected to the data acquisition system (Scienmetric Instruments, Kanata, Ontario, Canada) were used to regulate the mass flow rate of each gas. Compressed air supplied by Praxair, Inc. (Kitchener, Ontario, Canada), was used as the source of oxygen. The blended flue gas mixture passed through a moisture trap to remove the remaining moisture from the compressed air. Then it was fed to the reactor in an upward flow. The exiting gas passed through a filter and a SO_2 analyzer (model 721 AT; Western research, Calgary, Alberta, Canada). A Rotameter was used to control the flow rate of the gas, which went into the analyzer. The breakthrough behavior was determined for SO_2 oxidation on activated carbon by measuring the SO_2

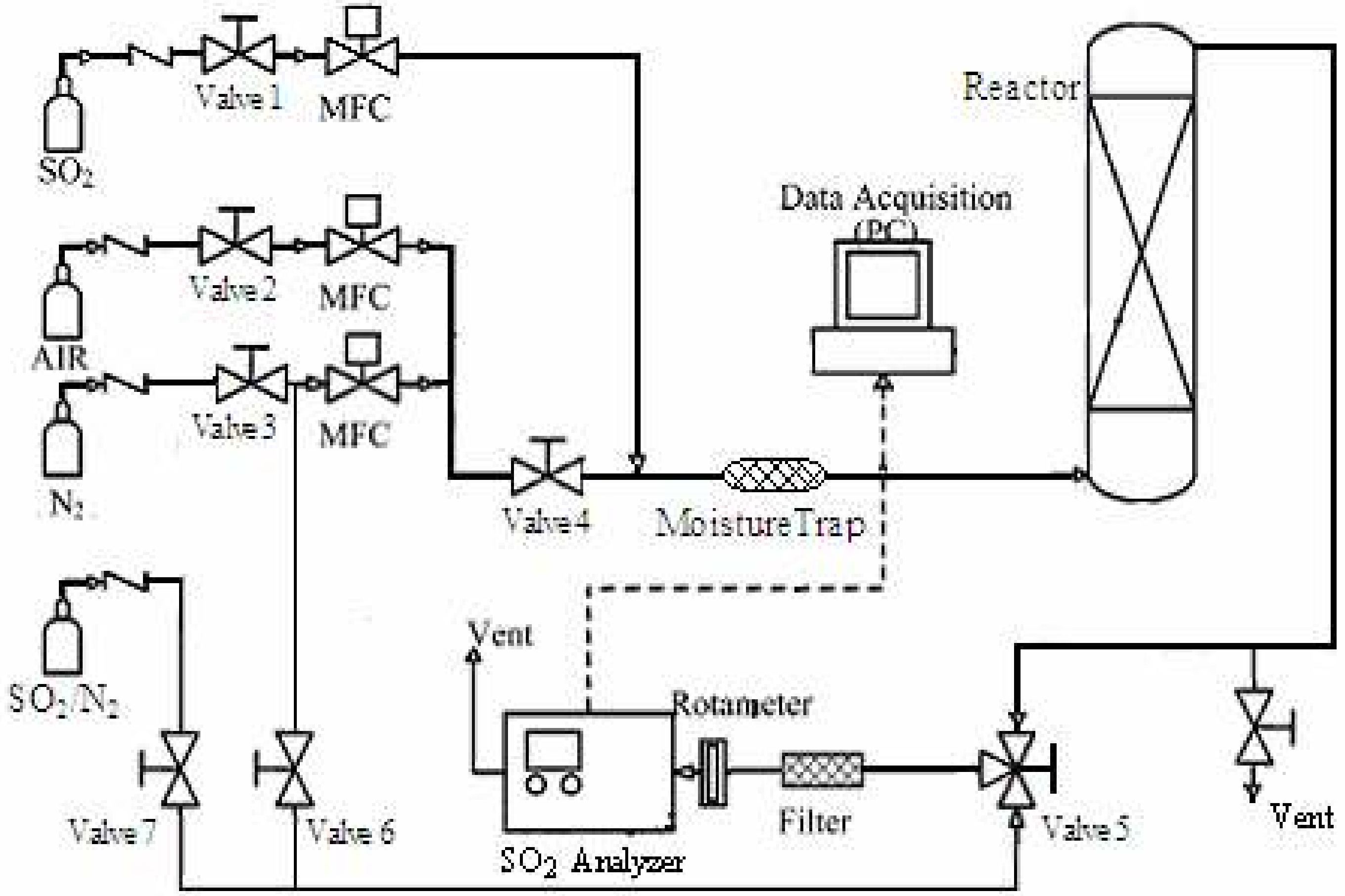


Figure 3.1: The schematic flow diagram of SO_2 oxidation and adsorption.

concentration at the exit by the online SO_2 gas analyzer until the absorption experiment finished.

We used N_2 and a calibrated standard SO_2 (concentration of SO_2 is 2560 ppm with the balance being N_2) as the zero and span gas to calibrate the SO_2 analyzer before each experiment.

The operation process is presented in Appendix A. All of the mass flow meters were calibrated before they were used and the data are presented in Appendix B. The experimental data and detailed calculations are described in Appendix C.

3.2. Sulfur trioxide desorption experiment

3.2.1 Experimental Apparatus

In the SO_3 desorption experiments, the apparatus included a syringe pump, a back pressure regulator and absorber columns. The schematic flow diagram of the SO_3 desorption and reaction with LAB system is shown in Figure 3.2.

3.2.1.1 Syringe Pump

The gaseous CO_2 was pressurized to supercritical conditions by a syringe pump (Model 260D, Teledyne Isco company, Lincoln, Nebraska, USA). The refill or depressurization rate ranged from 1.0 µl/min to 107 ml/min at any pressure from 0 to 517.1 bar, and the maximum pressure was 517.1 bar. There are constant pressure and constant flow operating modes. The gaseous CO_2 was pressurized to $SCCO_2$ and $SCCO_2$ was pumped into the reactor to flush the packing bed continually in order to remove SO_3 absorbed on activated carbon.

The detailed operation process is explained in Appendix A

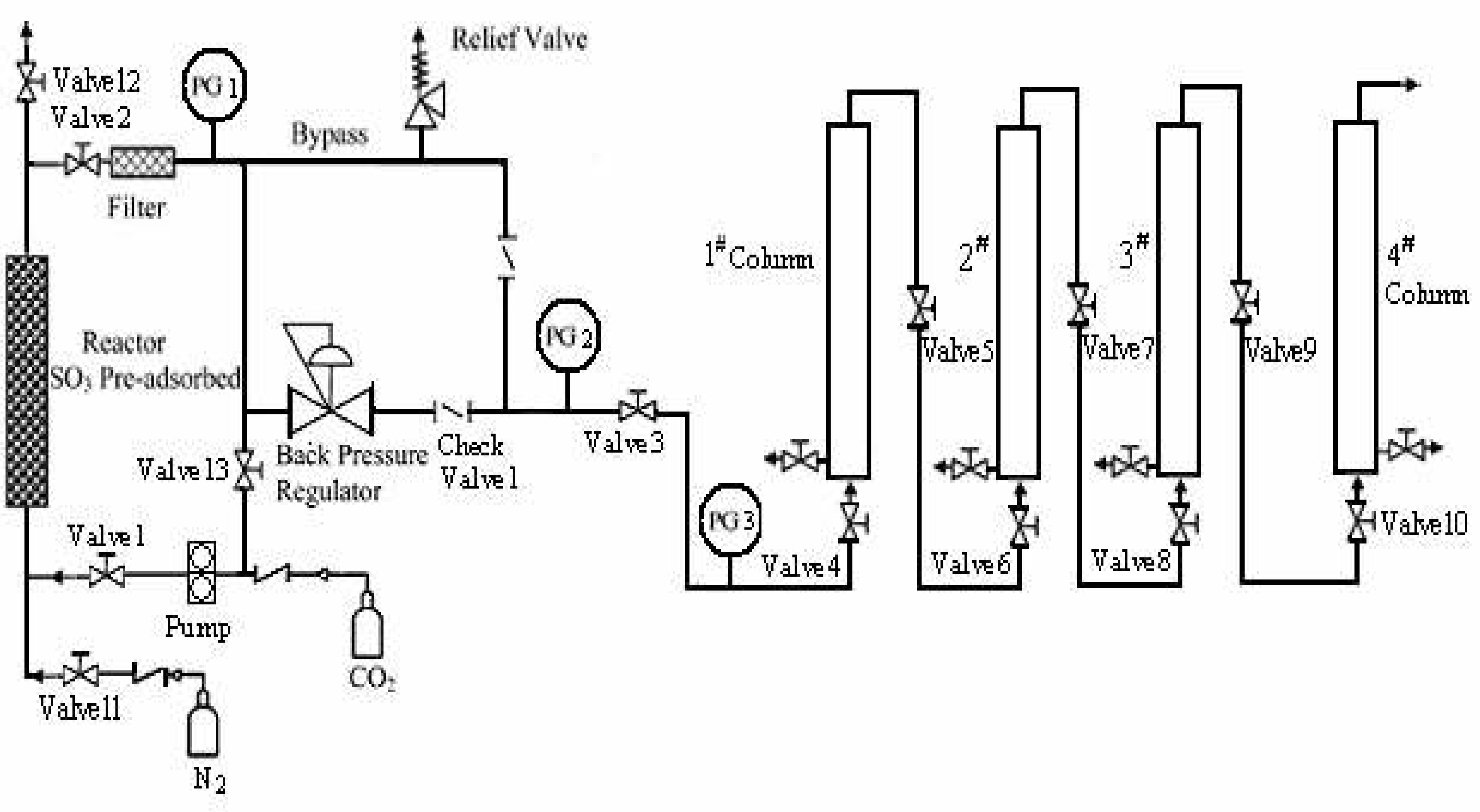


Figure 3.2: The schematic flow diagram of SO_3 desorption and reaction with LAB.

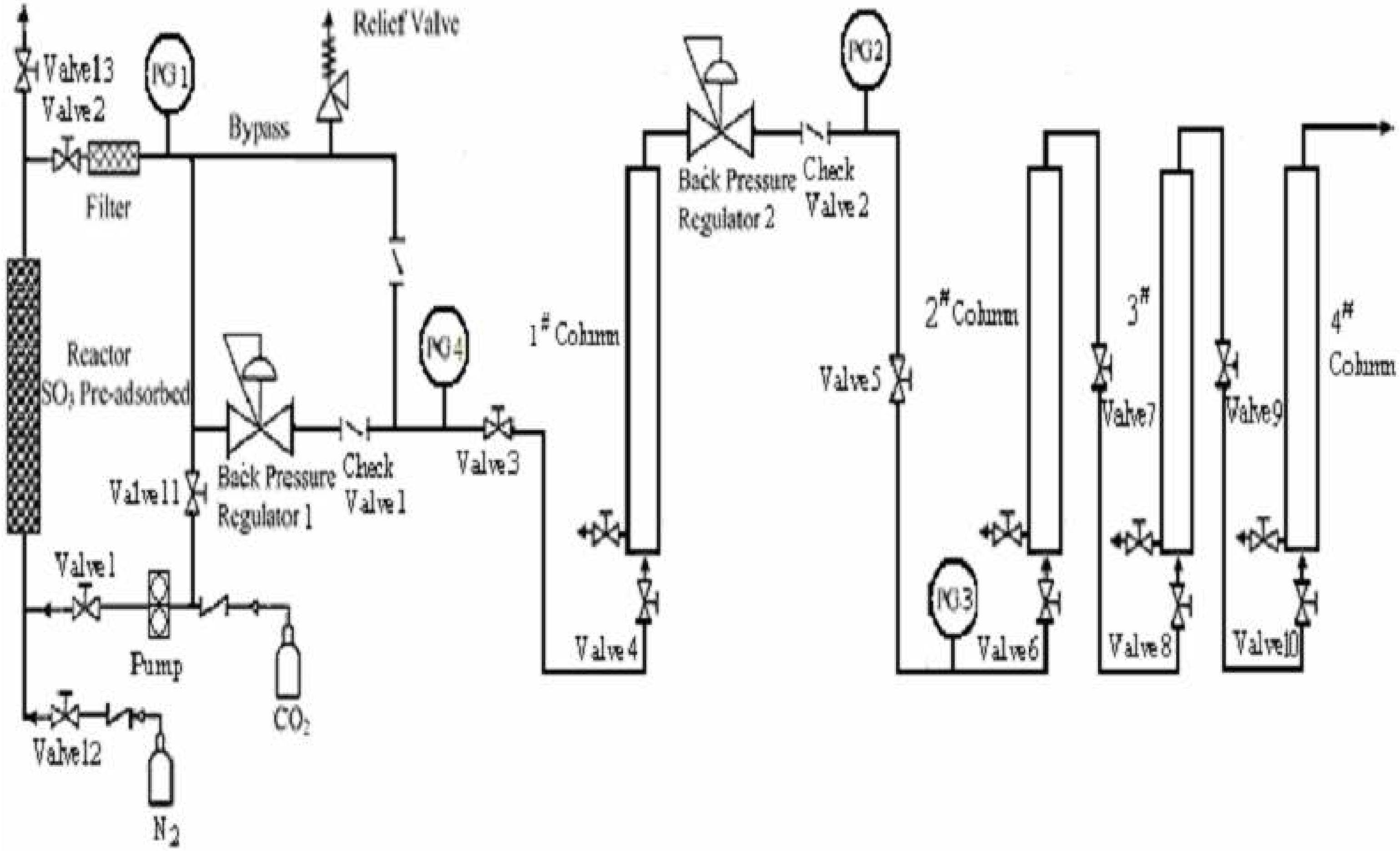


Figure 3.3: The schematic flow diagram of SO_3 desorption running at 2 BPR control and reaction with LAB.

3.2.1.2 Back Pressure Regulator

A back pressure regulator (BPR) controls the pressure of flushing $SCCO_2$ in the reactor. The model number is BP66-1A11CEQ151 (Go regulator, Mississauga, Ontario) and its maximum control pressure is 69 MPa. We can increase or decrease the hold pressure in the reactor by adjusting the handle of the BPR. If the handle was turned clockcounter, the hold pressure of the system before the BPR was increased; otherwise, the hold pressure of the system before the BPR was reduced.

In order to improve the SO_3 recovery in absorption experiments, stage pressure reducing experiments were done. In the stage pressure reducing experiments, we used the above BPR to control the pressure in the reactor, and used another back pressure regulator to control the pressure of the 1st column as shown in Figure 3.3. The model number of this BPR is BP60-1A11CEL121 and its maximum control pressure is 14 MPa.

Simply turning the handle sets the control pressure. The regulators have piston sensing to provide relief at high pressures. When the pressure before the BPR is larger than the set point, the fluid will pass through the BPR. If the pressure is smaller than the set point, the BPR will close and no fluid passes through it.

3.2.1.3 Absorber Columns

The $1^{\#}$, $2^{\#}$, $3^{\#}$, and $4^{\#}$ columns in Figure 3.2 were glass columns. In order to break big bubbles to smaller sizes and increase the contact time, ceramic filters were fixed on the bottom of each stage of columns. According to the experiment requirement, glass beads were used in the columns or not. The diameter of the glass beads was 1 mm.

The structure of the glass columns was shown in Figure 3.4. There was a ceramic filter fixed on the bottom of each stage of the column. An O-ring was used between two stages and a cycle with screw was used to connect the two stages. If we connect these stages one by one, the column can be built with 2, 3 or 4 stages.

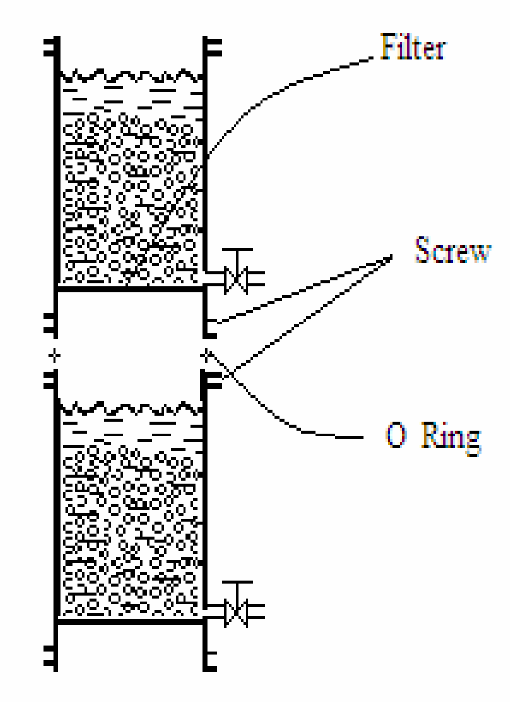


Figure 3.4: The structure of absorb columns

As shown in Figure 3.3, a 92 mm length stainless steel tube instead of the 1$^{\#}$ glass tube column in Figure 3.2 and was filled with glass beads. The outer diameter of it is 25.4mm and the wall thickness of the tubing is 3mm. The pressure rating for safe operation is 41 MPa at room temperature.

3.2.2 Experimental Details

The reactor, containing the activated carbon with absorbed SO_3, was heated by a heating tape, and a thermocouple was put into the middle of the packing AC bed. The temperature of the carbon bed in the reactor was controlled by a heating system controller. CO_2, compressed to supercritical conditions by a syringe pump, was fed to the reactor from the bottom. The $SCCO_2$, carrying SO_3, passed through the reactor and a filter to a back pressure regulator (model BP66-11). The BPR controlled the pressure of $SCCO_2$ in the reactor. The pressure of CO_2, downstream of the back pressure regulator, was decreased to about atmospheric pressure. Then the CO_2 passed through the columns, filled with different absorbers, and the SO_3 reacted with these absorbers. In some experiments, in order to compare the effects of different absorbers, two different absorbers, linear alkyl benzene and water, were used. The amounts of the absorbers are shown in the next chapter. If water was used as absorber, when SO_3 desorption process stopped, N_2 was used to purge the CO_2 remained in absorbers, because CO_2 can react with water and form H_2CO_3, and the presence of H_2CO_3 would affect the analysis of H_2SO_4.

When the pressure of CO_2 was decreased from high pressure to atmospheric pressure, the CO_2 volume had a huge expansion, so we used a needle valve, Valve 3rd in Figure 3.2, to control the flow rate of gaseous CO_2.

In the operation, the reactor was heated to the set point, and then CO_2 was fed into the syringe pump and was pressurized to supercritical conditions. The $SCCO_2$ flushed the packed activated carbon bed.

There were two flushing methods used in the series of experiments. In the first method $SCCO_2$ went through the AC bed continually in a single pass. We called it single pass-flushing method. The operation is:
The 13th valve was closed and the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th, 9th, and 10th valve were opened; $SCCO_2$ was pumped to single pass through and flush the packed activated carbon bed.

In the second method recycled $SCCO_2$ went through the AC bed. We called it recycle flushing method. The operation is:
When the fresh CO_2 was put into the syringe pump and was pressurized to supercritical conditions, we closed the 3rd valve and opened the 13th valve to let $SCCO_2$ recycle flushed the packed activated carbon bed for a while. Then, we closed valve 13th and opened the valve 3rd to release the flushing $SCCO_2$ and let SO_3, dissolved in CO_2, reacted with the absorbers. Then fresh CO_2 was fed into the syringe pump, and we repeated the above operation. There are two advantages about recycle flushing method.

First, the flow rate of the flushing agent ($SCCO_2$) was set to 20 ml/min, which was much larger than that of the non-recycled flush, which was about 0.15 ml/min (Wattanakasemtham, 2003). For example, if the carbon bed had been flushed for 1 hour using both flushing methods, 1200 ml $SCCO_2$ passed the carbon bed in recycle flushing method, whereas it was only 90 ml $SCCO_2$ in single pass-flushing method. In order to achieve the same SO_3 recovery, the flushing time was shortened and the total operation time was also shortened in recycle flushing experiments.

Second, the concentration of SO_3 in the flushing agent in recycle flushing experiment was greater than that in the single pass-flushing experiments. Even through, the flow rate of $SCCO_2$ was small enough; the concentration of SO_3 dissolved in single passed $SCCO_2$ was difficult to reached its maximum. However, when continually flushing recycled $SCCO_2$ through the carbon bed for enough time, we can maximize the concentration of SO_3. A high SO_3 concentration is important because it promotes the reaction in LAS production.

After the SO_3 desorption experiment, for avoiding SO_3 remaining on AC, water was used to slowly flush the packed activated carbon bed, since the remaining SO_3 will affect the next adsorption and oxidation experiment. Then N_2 as purge agent was used to allow the absorbed CO_2 to escape from the flushing solution. The volume of flushing water was 500 ml, and flushing time was about 30 min. If using NaOH solution to titrate the above 500 ml flushing water, we can determine how much SO_3 remained in the reactor.

The reactor was then heated to more than 200°C using N_2 to purge the remaining water in the reactor in order to prepare for the next adsorption. It was necessary to remove the water becasue water or water moisture remaining in the bed react with SO_2 or SO_3 in the next adsorption and oxidation experiment, producing sulfuric acid. The formation of sulfuric acid must be avoided because it would destroy the activated carbon structure.

In above operation process, we found that the pressure change was very large at the BPR. The pressure in the upstream system of the BPR was about 9 MPa, for 1 atmospheric pressure in the downstream system of the BPR. Even though, we controlled the flow rate of CO_2 at very small level, the gas bubbles in absorber columns were still large. The SO_3 carried by the CO_2 gas would therefore have poor contact with the LAB. Some of SO_3 would pass the absorbers and escape to the atmosphere. Another back pressure regulator was, therefore, used to improve the SO_3 recovery in absorption experiment. The schematic flow diagram is shown in Figure 3.3.

In the flow diagram of Figure 3.3, the first back pressure regulator controlled the pressure of the upstream system at high pressure (9 MPa). The second back pressure regulator controlled the pressure in column $1^{\#}$ at medium pressure (4 MPa).

The operation process is presented in Appendix A. The experimental data and detailed calculations are presented in Appendix C.

Chapter 4.

Analytical Methods

This chapter describes the major analytical methods employed in the research project, which include the methods for analyzing the amount of SO_2 and the concentrations of LAS and sulfuric acid

4.1 Analytical method for determining the amount of SO_2 adsorbed

In SO_2 adsorption and oxidation experiment, when the simulated flue gas, with a constant concentration of SO_2, came into the AC bed, some of SO_2 was adsorbed on AC, and other SO_2 passed out from AC bed. An online UV gas analyzer was used to analyze the volumetric concentration of SO_2 in the exit gas stream. The analyzer provided a continuous SO_2 concentration reading and was connected to a data acquisition system (DAQ) interface to monitor and record the change of SO_2 concentration as a function of time. The breakthrough behavior was determined for SO_2 oxidation on activated carbon by measuring the SO_2 concentration. The amount of SO_2 absorbed and oxidized was determined by integrating the breakthrough curve.

The detail of the SO_2 analyzer operation was inscribed in Appendix A.1

4.2 Analytical methods for determining LAS concentration

The LAS was produced by linear alkylbenzene sulfonation. Sulfur trioxide substitution occurs almost exclusively in the para position, since the large hydrophobic chain effectively hinders approach to the ortho positions. Conversion efficiency varies between 92 and 98%(24).

The analytical method was based on using of a mixed indicator as originally proposed by Holness and Stone (28) and by Herring (29).

The analytic methods available for determining LAS include specific methods involving techniques such as high-performance liquid chromatography (HPLC), gas chromatography (GC) and GC-mass spectrometry (MS), and nonspecific methods, involving colorimetric, fluorimetric, and atomic adsorption techniques (24).

1) Specific methods
Good progress has been made towards developing methods for the specific determination of the many homologues and phenyl- positional isomers of LAS in almost all laboratory and environmental matrices at concentrations down to micrograms per liter.

2) Nonspecific methods
The simplest procedure for the determination of LAS in aqueous solution is by a two-phase titration method. LAS are titrated in a mixed aqueous chloroform with a standard solution of a cationic reagent, such as benzethonium chloride (Hyamine 1622), and a small amount of indicator, such as a mixture of dimidium bromide and acid blue. The end-point is determined by a change in the color of the organic solvent (25).

Colorimetric techniques are routinely used to determine low concentrations of anionic surfactants, including LAS, in aqueous samples and have been used extensively in testing and environmental monitoring of these materials. The colorimetric methods have the same common analytical basis, that is, formation of solvent extractable compounds between the anionic surfactant and an intensely colored cationic species. The most commonly used cationic reagent for this purpose is methylene blue.

In nonspecific methods, the simplest procedure for determination of LAS is a two-phase titration method. LAS are titrated in a mixed aqueous chloroform medium with a standard solution of a cationic reagent, such as benzethonium chloride (Hyamine 1622), and a small amount of indicator, such as a mixture of dimidium bromide and acid blue. The end point is determined by a change in the color of the organic solvent.

Two different indicators (Mixed Indicator and Dimethyl Yellow) were used in the LAS analysis.

1. Mixed Indicator

The conventional method consists in using Mixed Indicator (Dimidium Bromide & Disulphine Blue) as indicator. The two indicators involved are the anionic diulfine blue VN (represented by HB in the following discussion) and the cationic dimidium bromide (DBr). When the mixture is added to an anionic surfactant, a pink complex is formed with the D+ ion, which is preferentially soluble in the chloroform phase [Eq. (1)] in a manner analogous to the interaction with methylene blue in the previous method.

$$D^{+}_{(aq)} + RSO_3{}^{-}_{(aq)} \rightarrow DRSO_{3(org)} \qquad (1)$$

The HB remains in the aqueous layer and imparts to it a green-blue color. As the quaternary cationic surfactants (Quat) titration is added, the main reaction is:

$$Quat^{+}_{(aq)} + RSO_3{}^{-}_{(aq)} \rightarrow QuatRSO_{3(org)} \qquad (2)$$

The two antagonistic surfactants occur in the titration solution. But as the supply of free anionic surfactant ions becomes exhausted, the pink complex yields its surfactant ion to the titration and the free dimidium ion returns to the aqueous layer:

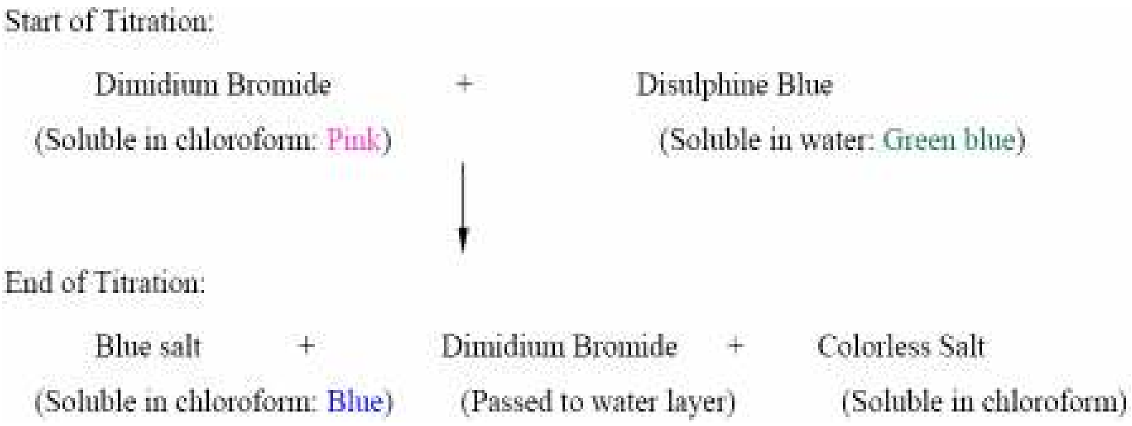
$$Quat^{+}_{(aq)} + DRSO_{3(org)} \rightarrow QuatRSO_{3(org)} + D^{+}_{(aq)} \qquad (3)$$

At the same time, a slight excess of cationic titrant reacts with the disulfine blue anion to produce a blue chloroform-soluble complex:

$$Quat^{+}_{(aq)} + B^{-}_{(org)} \rightarrow QuatB_{(org)} \qquad (4)$$

The color in the chloroform layer at the endpoint, therefore, changes from pink to blue.

The color change scheme is shown as follows:



As the end of titration is approached, the emulsion formed by shaking tends to break easily. The titration is then continued drop wise until the end point is reached, i.e., when the pink color is completely discharged from the chloroform layer which is then a faint gray-blue (30, 31).

2. Dimethyl Yellow indicator

The cationic dye Dimethyl Yellow gave a sharper end point than the mixed indicator during our tests. Since the dye has low water solubility, the aqueous phase remains nearly colorless, and the organic phase changes sharply from red to yellow at the end point, as the dye responds to the change in its environment (Schmitt T.M.) (32). The color changed at chloroform phase and the color was more sensitive, so the end point was easier to observe.

The detailed procedures for titration using the above different indicators are explained in Appendix A.3.1.

In the experiments, we found that if the concentration of LAS is high, both of the above indicators can be used, and they are good indicator choice (as shown in Figure 4.1 and 4.2). However, if the concentration of LAS is low, using dimethyl yellow as indicator is better than using Mixed Indicator (as shown in Figure 4.3 and 4.4). The experiment results were explained as follows:

<u>Titration of higher concentration of LAS</u>

The concentration of LAS in LAB and LAS mixture was 0.28 mol/l. The color change in the titration, using mixed indicator, is shown in Figure 4.1. From Figure 4.1, we found the color and the end point of titration to be easy to observe.

Figure 4.1: The color changes of the titration of low LAS concentration solution, using mixed indicator as indicator.

The color changes of the titration, using dimethyl yellow indicator, is shown in Figure 4.2. From Figure 4.2, we found the color was and the end point of titration to be easy to observe.

Figure 4.2: The color changes of the titration of high LAS concentration solution, using dimethyl yellow as indicator.

Titration of lower concentration of LAS

The concentration of LAS was 0.008mol/l. The color changes in the titration, using mixed indicator, is shown in Figure 4.3. From Figure 4.3, we found the color to be faint and the end point of titration to be difficult to observe.

Figure 4.3: The color changes of the titration of low LAS concentration solution, using mixed indicator as indicator.

The color change for the titration with low LAS concentration solution, using dimethyl yellow indicator, is shown in Figure 4.4. From Figure 4.4, we found the color to be more sensitive and the end point of titration to be easier to observe than that in Figure 4.3.

Figure 4.4: The color changes of the titration of low LAS concentration solution, using dimethyl yellow as indicator

The yield of LAS is low in this research project, so LAS concentration in LAS/LAB solution is low. In the analytical process with mixed indicator as indicator, the color of chloroform phase was faint-pink, and both LAB and LAS dissolved in chloroform. If the concentration of LAS was lower, the color in the chloroform became fainter, as shown in Figure 4.3. However, if using dimethyl yellow as indicator, the color was more sensitive and the color change was sharper. In the experiments, the concentration of LAS in produced LAS/LAB mixture was less than $\frac{0.006mol}{600ml} \times \frac{1000ml}{l} = 0.01mol/l$. Therefore, dimethyl yellow as indicator was preferred to the Mixed Indicator in this project.

4.3 Analytical method for determining sulfuric acid concentration

The simple acid-base titration using sodium hydroxide as a titrant and phenolphthalein as an indicator was used to analyze the sulfuric acid in the product. The liquid sample had to be blown with N_2 before titration in order to purge off CO_3^{-2} which formed when CO_2(g) dissolved in water. The gaseous CO_2 dissolves rapidly into water and attains equilibrium: (Colbeck, 2003) (33)

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)}$$

Aqueous CO_2 reacts with water to form carbonic acid:

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_{3(aq)}, \qquad k = \frac{[H_2CO_3]}{[CO_{2(aq)}]} = 1.3 \times 10^{-3}$$

H_2CO_3(aq) may loose up to two protons through acid equilibriums:

$$H_2CO_{3(aq)} \Leftrightarrow H^+ + HCO_3^-, \qquad k = \frac{[H^+]\cdot[HCO_3^-]}{[H_2CO_3]} = 2.00 \times 10^{-4}$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}, \qquad k = \frac{[H^+]\cdot[CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

The existing protons would then affect the sulfuric acid analysis. An N_2 purge was therefore used. Therefore, the equilibrium reactions are shifted backward until the ions were all eliminated.

The amount of sulfuric acid was then determined by NaOH solution titration:

$$H_2SO_4 + 2NaOH \Leftrightarrow 2H_2O + 2Na^+ + SO_4^{2-}$$

The detailed procedures for titration are explained in Appendix A.3.2.

Chapter 5

Results and Discussion

In this research project, SO_2 was oxidized to SO_3 and adsorbed on activated carbon (AC). Then the SO_3 adsorbed on AC was desorbed using supercritical carbon dioxide ($SCCO_2$) and reacted with linear alkylbenzene to produce linear alkylbenzene sulfonates, which is one of the main components of detergent. The objectives of the study were to investigate desorption of SO_3 from a packed activated carbon bed using $SCCO_2$ and to study the SO_3 reaction with LAB.

All of the data used in this chapter and Appendix C are average of results of two experiments

5.1 Preloading of SO_2/ SO_3 on an Activated Carbon Bed

Two different sizes of reactors were used for SO_2 adsorption and oxidation. A gas mixture with volumetric compositions of 0.35% SO_2 (3500 ppm) and 5% O_2, with the balance being N_2, was used to simulate the flue gas composition from coal-fired power plants. The simulated flue gas composition and flow rate were controlled by the mass flow controllers. The mass flow meter calibrations are given in Appendix C.

The SO_2 concentration at the reactor exit as a function of time was measured by a SO_2 analyzer. A typical breakthrough curve is S-shaped as shown in Figure 5.1.

At the beginning of the reaction, SO_2 was absorbed on the activated carbon surface and oxidized to SO_3. Thus, the concentration of SO_2 at the reactor exit was zero. As time goes on, more and more active sites of activated carbon were essentially saturated, so more and more SO_2 passed through the bed unreacted. When the reactor bed was saturated completely, no more SO_2 was absorbed and oxidized; therefore, the SO_2 concentration of exit gas did not change and equaled the concentration of exit gas. The SO_2 concentrations shown in Figure 5.1 are the plateau points.

The amount of SO_2 adsorbed and oxidized on AC was measured by integrating the breakthrough curve. The mass of SO_2 adsorbed and oxidized in the smaller reactor was about 6 mmol. The mass of SO_2 adsorbed and oxidized in the larger reactor was about 43 mmol.

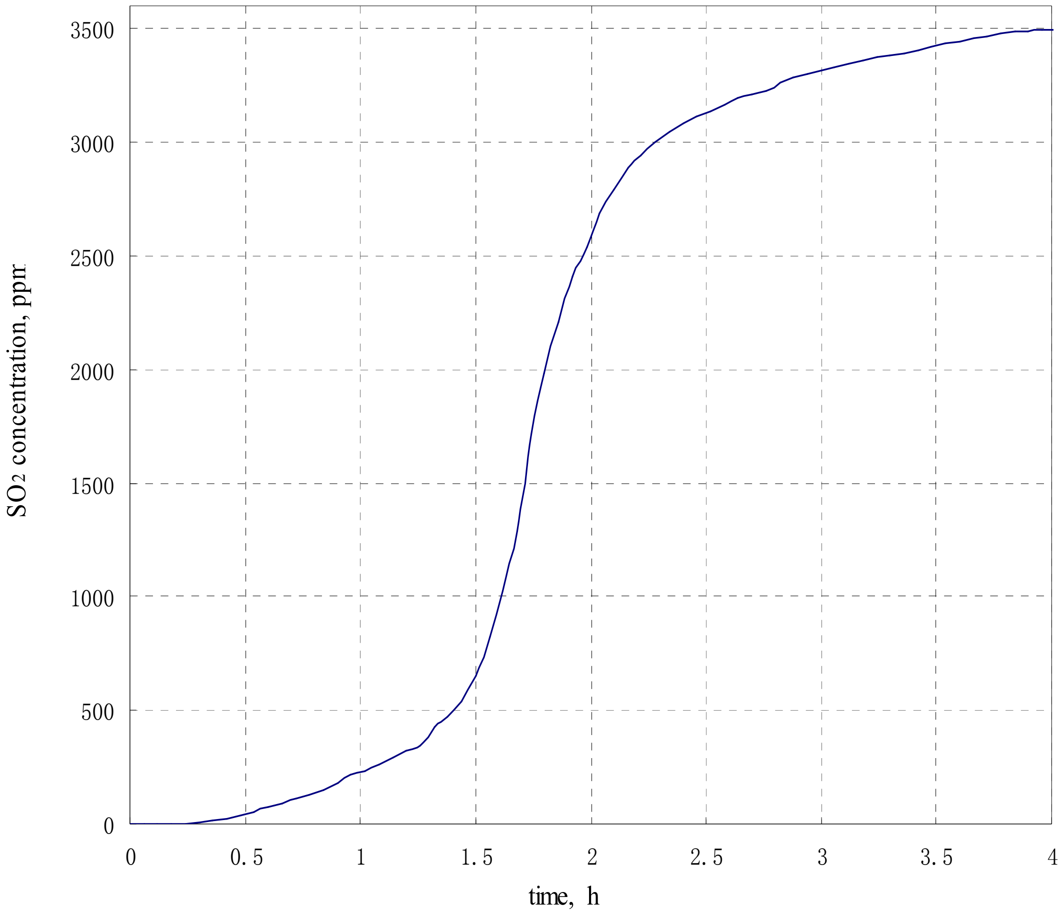


Figure 5.1: SO_2 adsorption and oxidation breakthrough curve for the smaller reactor.

The detailed data are shown in Appendix C.

5.2 SO_3 Desorption Using $SCCO_2$

SO_2 was absorbed and oxidized to SO_3 on activated carbon; SO_3 is strongly adsorbed on AC and thus very difficult to remove from AC. The improvement in SO_3 recovery was one of the objectives of this research project. Therefore, the experiments on desorption are discussed in this section.

In supercritical carbon dioxide desorption experiments, the independent variables are the pressure, temperature and superficial velocity of the pressurized CO_2 in the reactor. The relationship between % sulfur recovery and the pressure, temperature and superficial velocity has previously been demonstrated by Wattanaksemtham, N., (2003). These authors concluded the temperature effect was less than the other two, and lower pressure and lower superficial velocity were better for % sulfur recovery. Lower pressure provides a lower density and a higher diffusivity and leads to an increase in the mass-transfer rates. A lower superficial velocity contributes to higher sulfur recovery, likely because, at low superficial velocity, the retention time (or contact time) between the activated carbon and the fluid is extended, allowing for increased mass transfer.

Given this past work, the effects of pressure, temperature, and superficial velocity were not studied in this experiment. The pressure of $SCCO_2$ was 9 MPa, and its temperature in the reactor was 40°C. Two flushing methods (single-pass flushing and recycle flushing) were used in the experiment, with different flow rates and feed times. As described in section 3.2.2, after SO_3 desorption experiments, water was used to flush the activated carbon bed to determine the amount of SO_2/SO_3 remained by activated carbon as well as to regenerate the activated carbon to zero acid content. The reactor was then heated and purged with N_2 in order to drive off water and prepare for the next run.

5.2.1 $SCCO_2$ Flushing Methods

The $SCCO_2$ flushed the packed activated carbon bed preloading with SO_3. Two flushing methods were used in this research project, and they produced different effects on the sulfur recovery.

The SO_3 recovery as a function of flushing time is shown in Figure 5.2. The square points in Figure 5.2 show the results of single-pass flushing experiments, in which the AC bed has been preheated at 200°C for 3 hours; the triangular and round points show

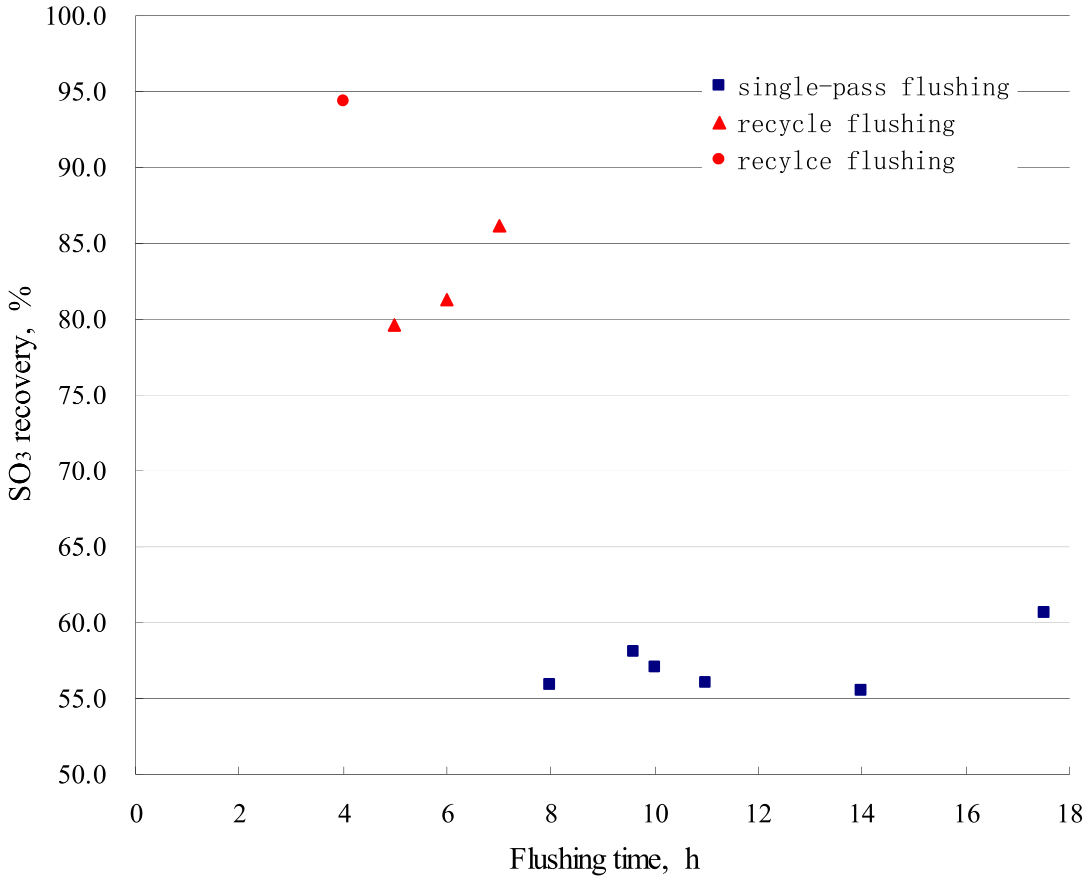


Figure 5.2: SO_3 recovery as a function of flushing time (Data: Table 5.1 and 5.2).

the results of recycle flushing experiments. The round point shows the result of experiment, in which the AC bed has been preheated at 300°C for 6 hours. The SO_3 recovery is defined as:

$$\%, \text{Sulfur recovery} = 100 - \frac{\text{moles of SO2/SO3 remains on AC}}{\text{moles of SO2/SO3 preload on AC}} \times 100$$

Fig.5 shows that the preheating procedures of the AC bed affect the sulfur recovery; this will be discussed in Section 5.2.2.

The square points in Figure 5.2 show that the sulfur recovery increases slowly with flushing time. However, even after 17.5 h, the SO_3 recovery is still low (55-60%). Thus, 40 to 45% of preloaded SO_3 remains in carbon bed. Therefore, long continuous single-pass flushing appears to serve no purpose in sulfur removal.

In contrast, the triangular points in Figure 5.2 shown that the sulfur recovery using recycle flushing increases with flushing duration. Compared to continual single-pass flushing (square points), recycle flushing improved the sulfur recovery rapidly, even at much shorter flushing times and with a smaller feed of $SCCO_2$.

Comparing the two different flushing methods, the recycle flushing is preferred, because it improves the sulfur recovery, shortens the operation time, and reduces the consumption of $SCCO_2$.

The round point in Figure 5.2 shows that if the activated carbon bed was preheated at 300°C for 6 hours, the sulfur recovery increased to 94.3%. Thus, the way the carbon bed is preheated is also important for the sulfur recovery.

5.2.2 Effects of Preheating the Reactor

Activated carbon has a high adsorption capacity because of its large specific surface and is also a catalyst for SO_2 oxidation at room temperature. However, SO_3 is difficult to desorb from AC which inhibits further oxidation. Therefore, water was used in the experiments to flush the packed bed and desorb SO_3 as sulfuric acid. However, water is very difficult to remove completely from a porous material, and it remained in the pores of the activated carbon containing SO_2/SO_3 producing sulfuric and sulfurous acids. The sulfuric acid in the micro-pores is incompletely removed by flushing.

From the above SO_2 absorption and oxidation experiments, about 6 mmol SO_2/SO_3 absorbed on the carbon bed. If 0.108 g (equivalent to 6 mmol) water remained in the bed after water flushing, theoretically, all of the SO_3 would react to form H_2SO_4. That means the sulfur recovery would be zero. Therefore, the packed activated carbon bed must be largely dry.

The independent variables for bed drying are the carbon bed temperature and duration. The four selected experimental temperatures were 200, 230, 250 and 300°C. And the heating duration were 2, 3, 4, 5, and 6 h.

SO_3 recoveries as a function of the heating duration are shown in Table 5.3 of Appendix E. Continuous single-pass flushing was used in these experiments.

The relationship between sulfur recovery and heating duration is shown in Figure 5.3. At a 200°C heating temperature, the sulfur recovery increased from 56.1% to 71.0% as the heating duration increased from 2 to 6 h, as more moisture was removed with time. For a heating duration of up to 6 h, the sulfur recovery was only 71.0%, a value which was unsatisfactory.

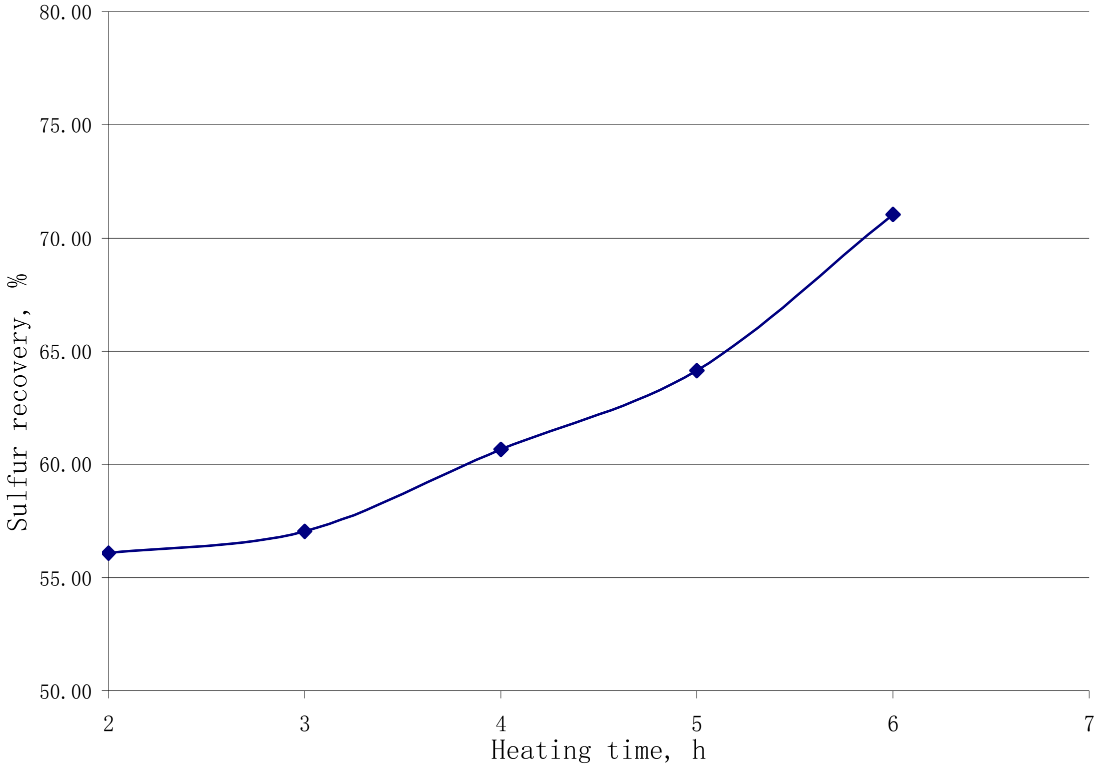


Figure 5.3: Sulfur recovery as a function of heating time at 200°C (Data: Table 5.3).

For this reason, higher preheating temperatures were selected. The results of SO_3 recovery as a function of the heating duration are shown in Table 5.4 of Appendix E. The results were obtained for a heating duration of 6 h.

The relationship between sulfur recovery and heating duration is shown in Figure 5.4.

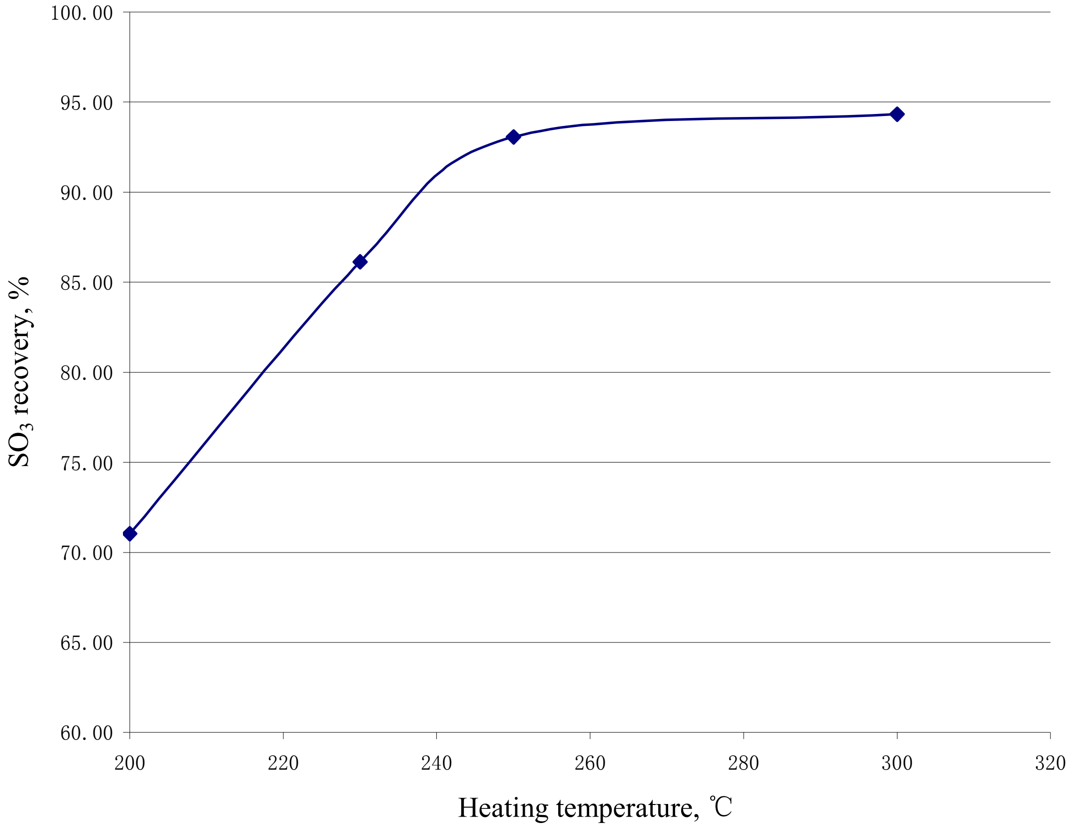


Figure 5.4: SO_3 recovery as a function of heating temperature (Data: Table 5.4).

For bed temperatures lower than 250°C, sulfur recovery increased rapidly with temperature. However above 250°C, sulfur recovery increased only slowly. At a bed temperature of 300°C, and a heating duration of 4.5 h, the sulfur recovery was 94.2%, which was almost the same as the result for heating 6 h.

Therefore, choosing 250°C as the bed temperature and 6 h as the heating duration appeared to be a good choice. Using $SCCO_2$ recycle flushing, the SO_3 recovery could be increased to 95%.

In the course of the experiments, we also found that if activated carbon was preheated at 250°C for 6 h, without a water flush for each run, the sulfur recovery was not affected (see the data in Table 5.5 of Appendix E).

From Table 5.5, the ratio of sulfur remaining to sulfur loaded after one run was 6.05%, and after three runs was 6.18%, i.e. essentially unchanged.

The amount of sulfur remaining in the bed depends on the operating conditions and the characteristics of activated carbon. For the same activated carbon and same operating conditions, the sulfur remaining in the bed was trapped in the smallest pores. Therefore, preheated to 250°C for 6 h, the carbon bed, though not flushed with water, could be used again for the next run. Furthermore, not having to flush the bed meant additional savings in energy and operating time.

5.2.3 The Effect of Bed Size

During experiments, two different bed sizes of reactors were used, the larger one holding about seven times more AC than the smaller. The smaller one filled with 8.6 g activated carbon could adsorb about 6 mmol of sulfur oxides. The larger one filled with 65.4 g activated carbon could adsorb about 43 mmol.

For the same operation conditions, with the same type of activated carbon, the molar ratio of sulfur remaining to sulfur preloaded, i.e. 6.7% for the smaller bed and 8.5% for the larger one, was almost the same for the two reactor sizes. That means the SO_3 recoveries in different sizes of reactor were same. The data are shown in Table 5.6.

These experiments established the proper operating conditions for the desorption step. The activated carbon bed was preheated at 250 for 6 h before the first run and was not flushed with water. The $SCCO_2$ recycle flushing method was used and the sulfur recovery was about 95%.

5.3 SO_3 Absorption/ LAS Production

For the SO_3 desorption and LAS production experiments, the sulfur balance may be considered following each run as consisting of three components: 1) the sulfur remaining in the AC bed; 2) the sulfur transformed to LAS and H_2SO_4 in the absorption columns, and 3) the sulfur losses to the atmosphere. This is shown in Figure 5.5.The sulfur remaining in the AC bed was roughly 5% (see Chapter 5.2).

Because the objective of this study was to remove SO_2/ SO_3 and produce LAS, so the first and third components must be minimized while the second component (the amount of SO_3 reacted with LAB to produce LAS) must be maximized. Of course, increasing the second component would decrease the third.

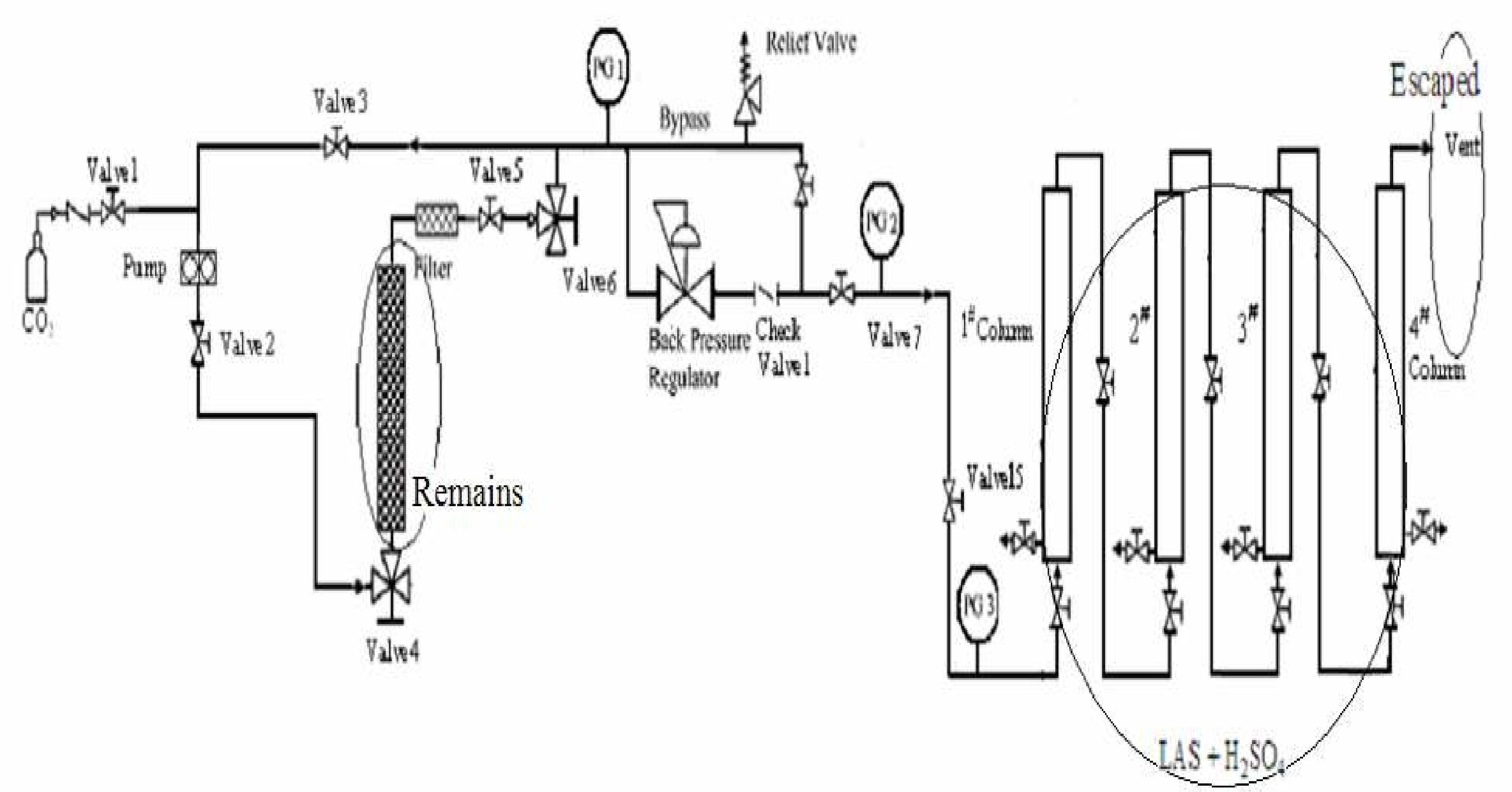


Figure 5.5: Three parts of SO_3, preloaded on the AC bed, in the desorption and absorption experiments.

5.3.1 Effects of Adding Glass Beads

In desorption and absorption experiments, because of the huge change in CO_2 pressure from 9 MPa to atmospheric, the gas flow seemed too large for efficient absorption, despite attempts to control the flow by two needle valves.

In order to improve contact between gas and liquid LAB, glass beads were placed in the absorption columns, the effect of glass beads on absorption is shown in Figure 5.6. In Figure 5.6, the absorbers in the 1st and 2nd column were LAB, and water was in the 3rd column. The 1st and 3rd columns in experiment 2 and the 2nd column in both experiments were filled with glass beads, in contrast to experiment 1 where the 1st and 3rd columns did not contain glass beads.

The effect of glass beads for experiments, in which the absorber in all columns were LAB, is shown in Figure 5.7. In Figure 5.6, all columns in experiment 2 were filled with glass beads, on contrast, only the 1st and 2nd columns in experiment 1 were filled with glass beads.

The Figure 5.6 shows that glass beads improve the yield of LAS, clearly, the glass beads improved the removal of sulfur by about 62%.

Figure 5.7 shows a similar result. The effect of the glass beads in Figure 5.7 with LAS present in the absorption columns, led to a 24% improvement in overall recovery of sulfur.

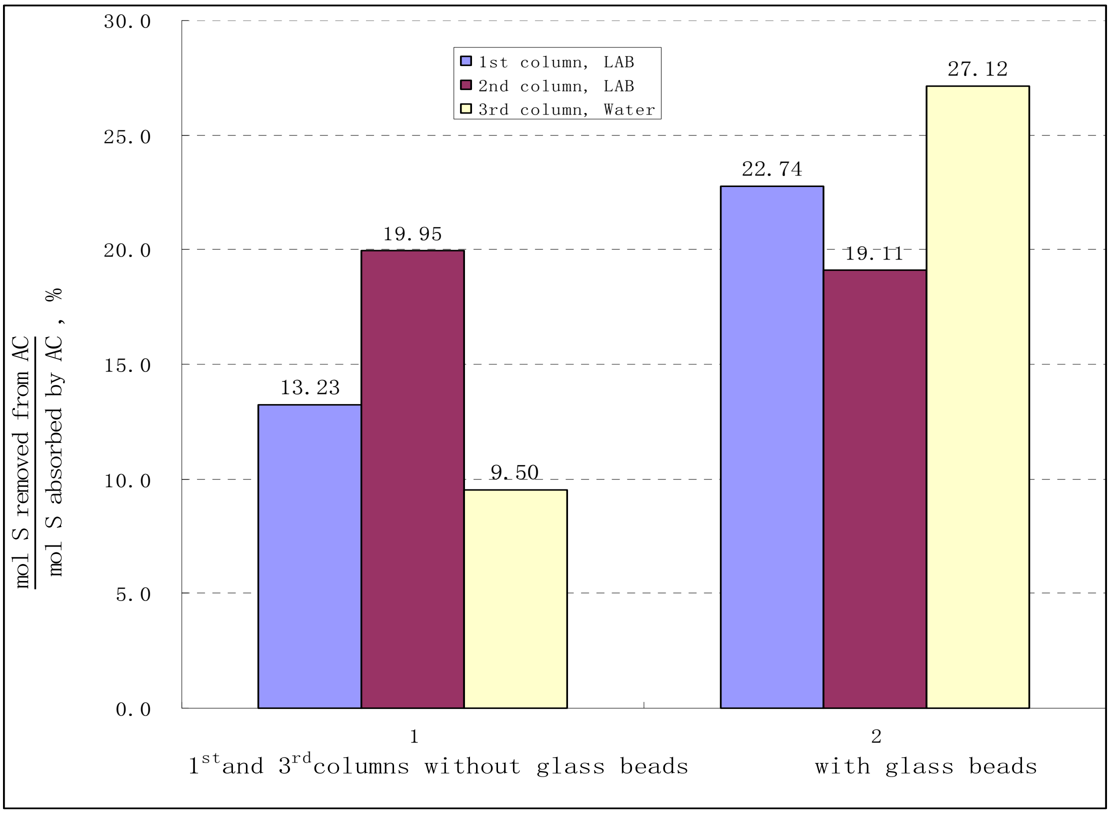


Figure 5.6: Effects of Glass beads on absorption in columns (Data: Table 5.7).

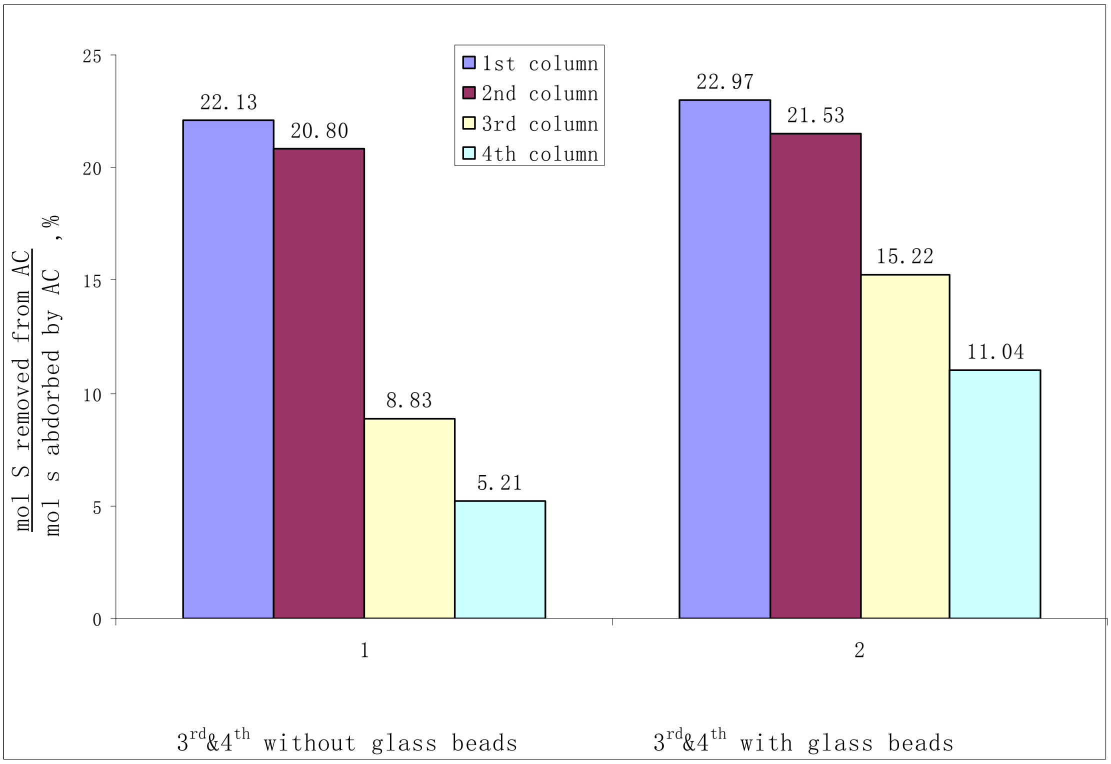


Figure 5.7: Glass beads effect on SO_3 absorption in columns, filled with LAB (Data: Table 5.8).

The glass beads appear to have broken up the bubbles of CO_2 gas, carrying sulfur species to increase the intimacy of gas-liquid contact, and improve mass transfer.

Assuming the bubbles to be spherical and the radius of a bubble to be R, the bubble surface area is:

$$A = 4\pi R^2$$

And the bubble volume is:

$$V = \frac{4}{3}\pi R^3$$

The surface-to-volume ratio is:

$$\frac{A}{V} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{R} \qquad \Rightarrow A = \frac{3}{R}V$$

Therefore, if the same volume of gas (V) passes through the column, the surface area (A) increases as the radius decreases.

At the same time, because of the presence of glass beads and their surface tension, when gas bubbles contact glass beads, they stretch around these beads, and the surface tension make the gas bulbs move more slowly. This increases the contact time, and thereby improves the SO_3 recovery in the absorption columns.

5.3.2 Effect of Different Absorbers

Two absorbers, one filled with LAB and the other filled with water were compared. The ratios of SO_3 trapped by these absorbers to that preloaded were different.

Data from Feb.7, Sep.25 and Nov.8 in Appendix C are shown in Table 5.9 of Appendix E, and plotted in Figure 5.8.

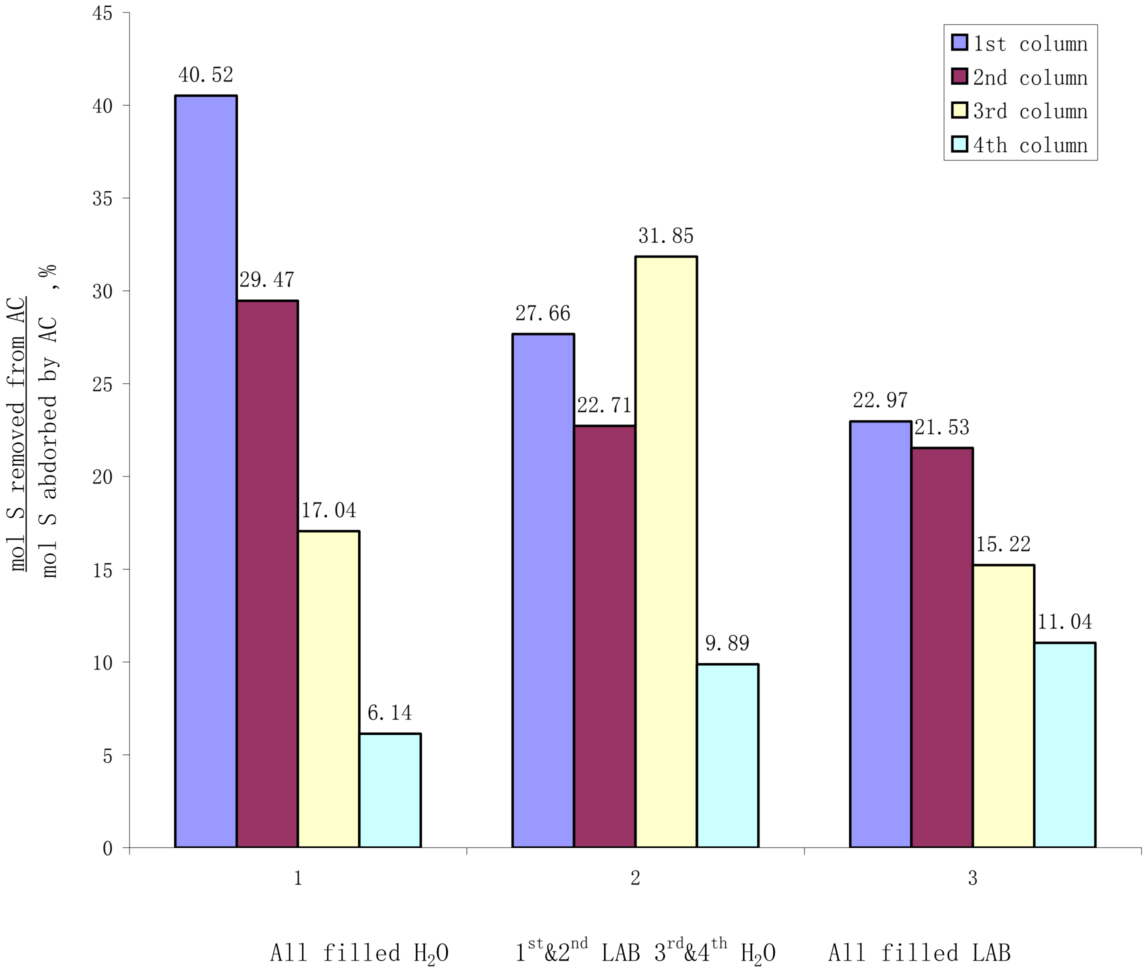


Figure 5.8: Effect of different absorbers on sulfur removal (Data: Table 5.9).

Comparing data for the 1st and 2nd columns in the No.1 and No.2 experiments above and data for the 3rd and 4th columns in above No.2 and No.3 experiments reveals that the ratios of sulfur absorbed by water were 20% greater than that absorbed by LAB, when the volumes of absorbers were the same. For example, the sulfur recovery in 1st and 2nd columns of No.1 experiment was 40.52%+29.47% = 69.99%, while that for 1st and 2nd columns of the No.2 experiment was 27.66%+22.71% = 50.37%.

At room temperature (about 20°C), the SO_3 reaction with water is more rapid than that with LAB. Indeed, SO_3 reacts instantaneously with water to produce sulfuric acid at room temperature. However, the reaction with LAB at room temperature is not so fast. But if the temperature of LAB increases, the reaction becomes faster. The effect of temperature of LAB will be discussed in Section 5.3.3. The best temperature for SO_3 to react with LAB is 40°C (Cross, J., 1998). Under the best reaction conditions, the maximum ratio of SO_3 reacted with LAB to produce LAS with respect to SO_3 preloaded on AC was up to 92-97%.

5.3.3 Effects of LAB Temperature

Four columns were filled with LAB and glass beads in these experiments. In one experiment, no column was heated; in another experiment, the 2nd and 3rd columns were heated to about 40°C, in order to study the effect of LAB temperature. The 1st and 4th columns were not heated in either experiment.

The data from Nov.8 and Dec.4 in Appendix C were chosen to study the effect of the LAB temperature, and they are shown in Table 5.10 in Appendix E. Figure 5.9 plots the data in Table 5.10.

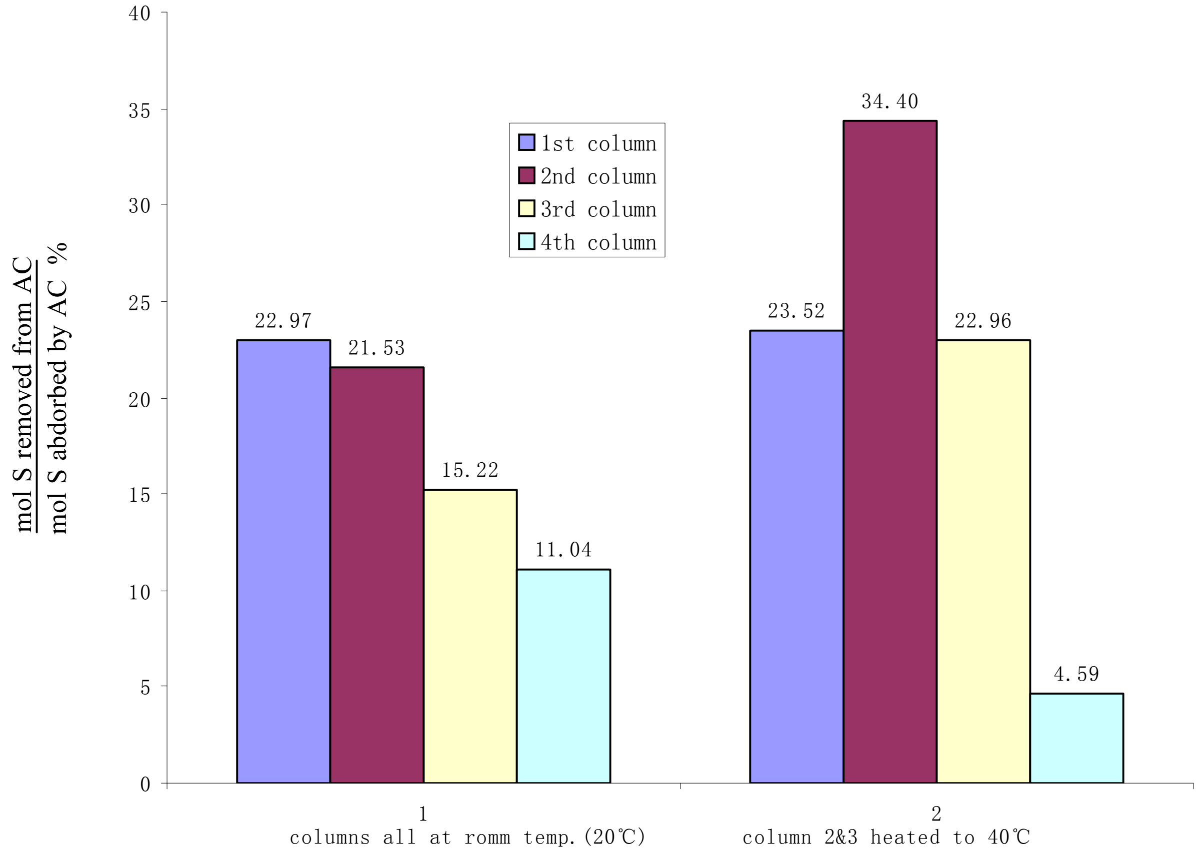


Figure 5.9: Effect of LAB temperature on SO_3 absorption in columns, filled with glass beads and LAB (Data: Table 5.10).

Comparison of the data in Table 5.10 and Figure 5.8 shows that the sulfur recovery of column 2 and 3 increased from 36.75% to 57.36% by heating the columns; heating the columns yields to a 56% higher sulfur recovery than without heating. In the 1st experiment, the total ratio of SO_3 absorbed by LAB in 4 columns was 70.76%. However, in the 2nd experiment, that was 85.47%. The 2nd experiment has 21% better sulfur recovery than the 1st experiment.

We believe that if the 4 columns were heated to about 40°C, the total sulfur recovery will further increase.

5.3.4 Effects of the Staged Pressure Reduction

The pressure changed from 9 MPa to about one atmosphere in the absorption process was discussed in the previous sections. Therefore, it was difficult to achieve very small gas bubble sizes, even though two needle valves, filters and glass beads were used. Two back-pressure regulators were used in order to carry out absorption at an elevated pressure. One of them (Back-Pressure Regulator 1) controlled the operating pressure at 9 MPa, the other one (Back-Pressure Regulator 2) controlled the intermediate pressure at 4.1 MPa.

The schematic flow diagram for the revised absorption system is shown in Figure 5.10.

The data from Dec.4, 2006, Jan. 26, 2007 and Feb.7, 2007 in Appendix C correspond to the study of the effect of the different pressures, and they are shown in Table 5.11 and Figure 5.11.

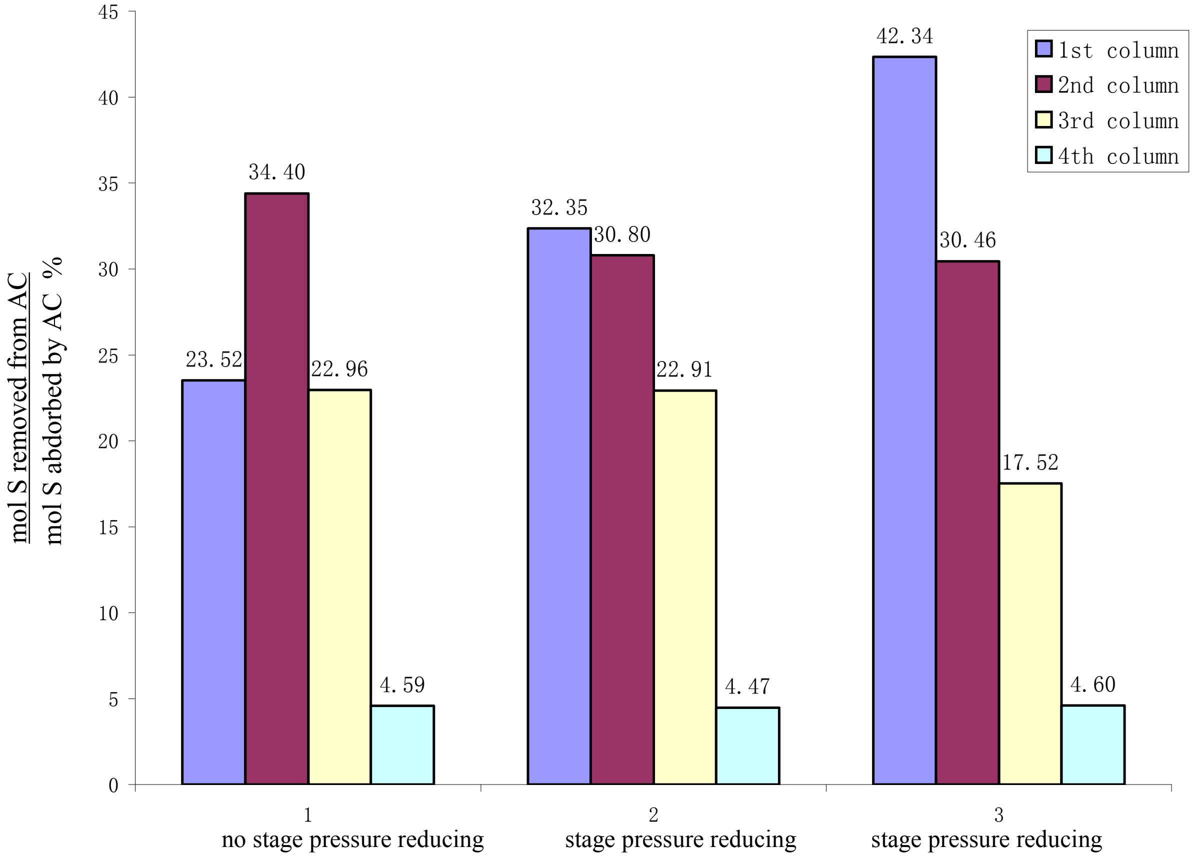


Figure 5.11: Staged pressure reduction effects on SO_3 absorption in columns, filled with glass beads and LAS (Data: Table 5.11).

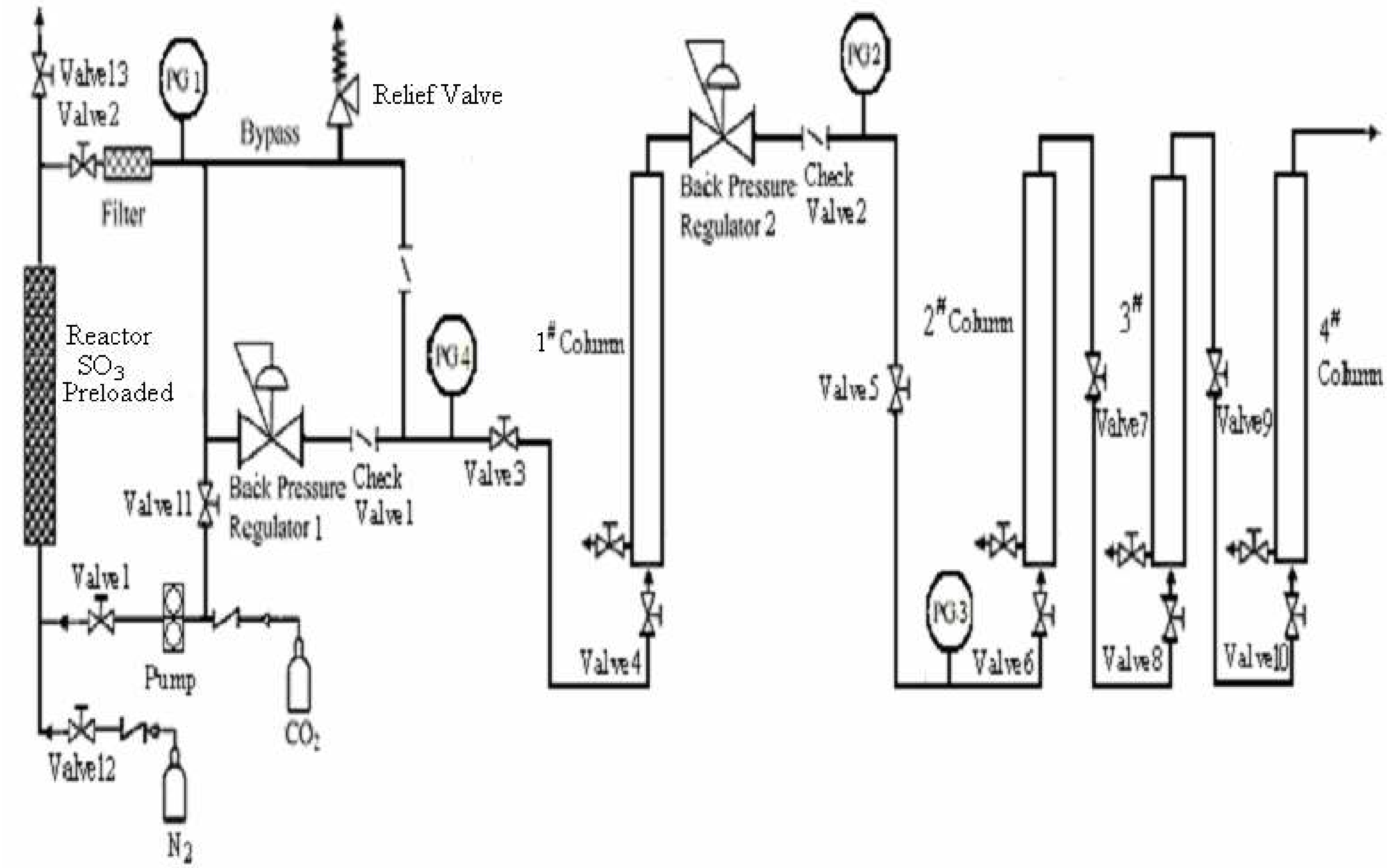


Figure 5.10: The schematic flow diagram of SO_3 desorption and reaction with LAB in staged pressure reduction experiment.

In experiments of Figure 5.11 and Table 5.11, all columns were filled with LAB and glass beads. In the 1st experiment, the staged pressure reduction method was not used, and the pressure changed from 9 MPa to 1 atmosphere. In 2nd and 3rd experiments, the staged pressure reduction method was used; The BPR 2 controlled the pressure in column 1 at 4.1 MPa. In Figure 5.11, the columns 2 and 3 in 1st and 2nd experiments were heated to 40°C, the columns 1 and 2 in the 3rd experiment were heated to 40°C; all other columns were at room temperature.

According to the data for the 1st and 2nd experiments, when the staged pressure reduction method was used, the sulfur recovery of the 1st column increased about 9% (from 23.52% to 32.35%). When the 1st column was heated at the same time (see the data of 3rd experiment), the sulfur recovery increased to 42.34%.

It can also be seen that the total sulfur recovery increased from 85.5% to 90.5%, using staged pressure reduction. When the 1st column was heated, the recovery would increase to 95%.

There is another advantage to using staged pressure reduction. If all of the absorption columns were steel and were located before the second BPR, the CO_2, now vented to atmosphere in the above experiments, could be compressed directly by a syringe pump to the supercritical pressure; thus, the CO_2 could be reused.

Chapter 6.

Conclusions and Recommendations

This project extends the previous research at University of Waterloo on SO_2 removal. The objective of this project is the removal of SO_2 from flue gas and, at the same time, using the removed SO_2 to produce a saleable material. From previous projects done at University of Waterloo (Panthaky, 1998 and Wattanakasemtham, 2003), when SO_2 was adsorbed on AC and oxidized to SO_3, different low-boiling-point solvents were used to flush the AC bed. In the work of Panthaky, acetone and methyl ethyl ketone (MEK) provided high SO_2 removal and H_2SO_4 productivity, but energy was required to separate solvent and SO_3. In the work of Wattanakasemtham, sub-critical and supercritical carbon dioxide were used to separate SO_3 from AC, and it was found that lower temperature, lower pressure, and lower superficial velocity of $SCCO_2$ improved the SO_3 recovery from the AC bed. But the SO_2 removal and the concentration of the sulfuric acid produced were low.

In this project, the SO_2 adsorption and oxidation on AC were not studied, but were based on previous research. This project focused thus on improving SO_3 desorption from AC by flushing with $SCCO_2$ and on improving LAS productivity. It was found:

1) For desorption, activated carbon had to be preheated to 250°C for at least 6 h, in order to remove the moisture in the carbon. After removing moisture, the carbon bed did not need to be reheated again in the next cycle.

2) Recycle flushing is better than single-pass flushing for improving the sulfur recovery. It also reduced the operating time and the consumption of $SCCO_2$. If the carbon bed was dried at 250°C for 6 h prior to use, the sulfur recovery in desorption is about 95% in an appropriate operation.

3) Use of ceramic filters and glass beads in absorption columns improved the sulfur recovery, probably they broke up gas bubbles and increased the contact time between gas and liquid in the absorber.

4) Stage pressure reduction increased the sulfur recovery. For example, if the absorption column pressure changed from one atmosphere to 4.1 MPa, the sulfur recovery in the first column increased from 23.52 to 32.35%. Therefore, the LAS productivity was improved.

5) Heating the absorber to about 40°C also improved sulfur recovery. 94.9% of sulfur was recovered by LAB in 4 columns via the above operation.

In summary, using $SCCO_2$ as the SO_3 desorption agent and allowing the desorbed SO_3 to react with LAB to produce LAS are technically feasible.

Recommendations

In the future, other experiments need to be done. They are as follows:

1. To improve the sulfur recovery in absorption, liquid LAB absorbers were heated to about 40°C. In this project, only two columns were heated to 40°C. Thus, more research should be done to determine if all of the four LAB absorption columns were heated, whether or not the recovery ratios of trapped SO_3 can be improved to close to 100%.

2. In our experiments, one high-pressure adsorption column was placed in between the two back-pressure regulators, so that the sulfur recovery increased. If all of the 4 columns were placed between the BPR, would the amount of trapped SO_3 be increased? Could the CO_2 be reused by re-pumping to supercritical pressure? If the $SCCO_2$ in the system can be kept at high pressure (for example, 4.1 MPa), pumping energy will be saved.

3. The concentrations of LAS in the absorption columns were low. The mixture of LAB and LAS should be reused in order to increase the concentrations of LAS. Can this be done without reducing the sulfur recovery?

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Appendix A Experimental Procedure

A.1 Experimental Procedure for SO_2 Adsorption and Oxidation

The SO_2 adsorption and oxidation operation using the SO_2 analyzer operation were carried out in the following order (Figure A-1 shows the schematic flow diagram for SO_2 oxidation and adsorption):

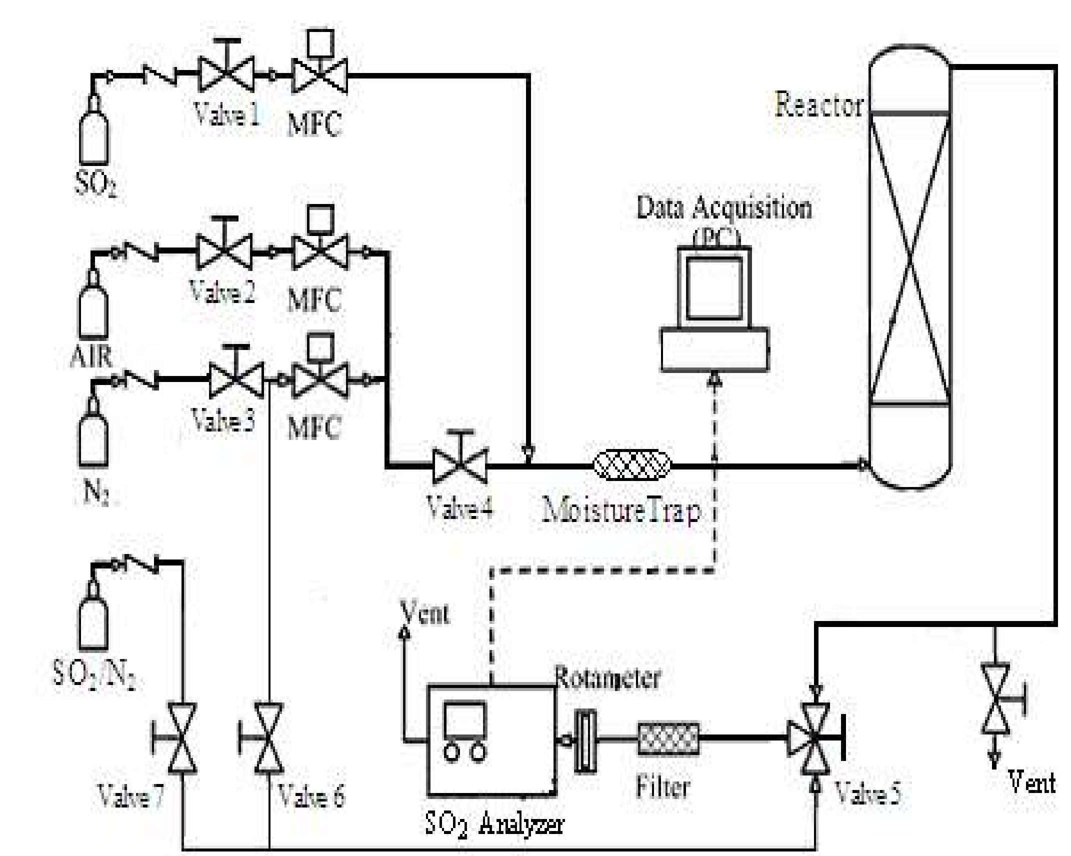


Figure A-1. The schematic flow diagram for SO_2 oxidation and adsorption

A.1.1 SO_2 Analyzer Operation

Zero calibration

Open valve 3 and valve 6.

Turn 3-way valve 5 to the direction of N_2 flow.

Close valve 4.

Check that valves 1, 2 and 7 are closed.

Turn on the N_2 cylinder and adjust the outlet pressure of the regulator to about 30psi.

Adjust the flow rate on the rotameter to 100 or higher.

Wait until the analyzer reading stabilizes on the digital display.

Zero the display by turning the zero knob or adjusting the zero knob on the main board.

Turn off the N_2 cylinder.

Span gas calibration

Open valve 7.

Turn 3-way valve 5 to the direction of SO_2/N_2 flow.

Close valve 6.

Check that valves 1, 2 and 3 are closed.

Turn on the SO_2/N_2 cylinder and adjust the outlet pressure of the regulator to about 30psi.

Adjust the flow rate of the rotameter to 100 or higher.

Wait until the analyzer reading stabilizes on the digital display.

The value should be in the range of 2536±100ppm. If they are in the range, end the span gas calibration. If not, operate as follows:

Adjust the display by turning the span knob or adjusting the span knob on the main board until within the 2536±100ppm.

Turn off the SO_2/N_2 span gas cylinder.

A.1.2 Adsorption and Oxidation Experiment

Open the Excel file: MFCsheet.xls of the PC.

Check flow rate and percentage setting of each gas.

Adjust channels 1, 2, and 3 on the Mass Flow Controller (MFC) to the set points, following the values on file in the MFCsheet.xls (Channel 1 for flow of N_2, Channel 2 for flow of air, Channel 3 for flow of SO_2).

Open Wingen software of PC

Open the file: C:\Gen200\SSTUB2.gen.

Close valves 6, 7 and the vent valve.
Open valves 1, 2, 3, 4.
Turn 3-way valve 5 to the direction of reactor outlet gas flow.
Turn on N_2, Air, and SO_2 gas cylinders.
Press “run” button of Wingen’s window.
Press “view system status” button
In “state status summary”, double click “state”.
A graph of SO_2 concentration will be shown on the screen.

Check all the outlet pressures of regulators (all about 30 psi).
Check all the flow rates of MFC after gas tanks are turned on.
Make sure the moisture trap is put in ice-water before the gas passes through it.

Wait for about 3 h for the saturation process to proceed.
If the graph does not represent that of a S-curve, continue the adsorption until a S-curve is formed.
If after 3 h, the SO_2 adsorption graph shows an S-curve and has stabilized, then perform the following operations:
Press the “stop” and “exit” buttons in Wingen’s window.
Close all gas cylinders.
Close all exits of the reactor.
Take off the fittings.
Remove the reactor and take it to the SO_3 desorption experiment.

A.2 Experimental Procedure for SO_3 Desorption

The SO_3 desorption and reaction with LAB operation and the syringe pump operation are carried out in the following order (Figure A-2 shows the schematic flow diagram of SO_3 desorption and absorption in LAB):

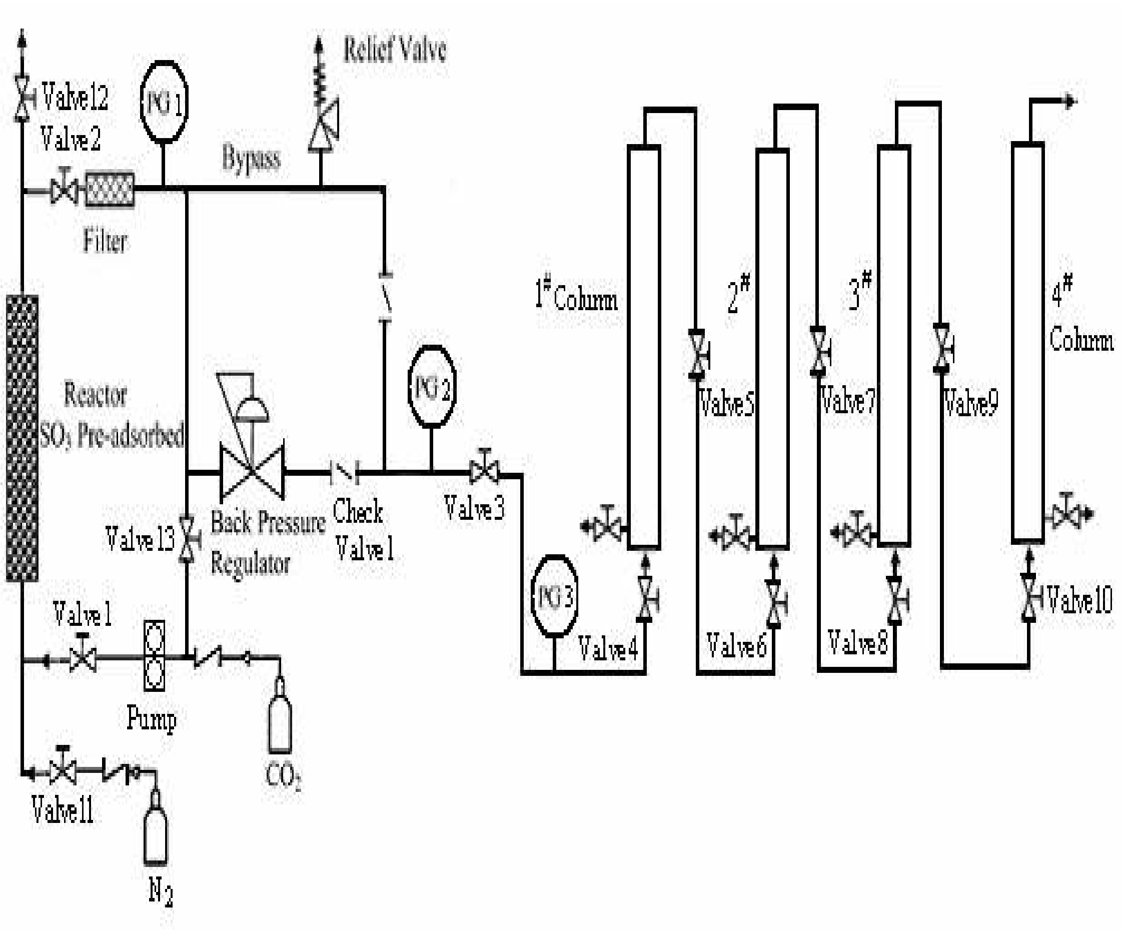


Figure A.2. The schematic flow diagram of SO_3 desorption and absorption in LAB.

A.2.1 Syringe Pump Operation

Open the cooling water valve.

Turn on the pump power.

There are two options of the pump run method that could be used in the experiment: constant pressure and constant flow rate.

Constant pressure operation

Press “menu” key.

Choose “constant pressure” key.

Press number 2 key to set or check the pressure.

Set the desired pressure on the number keyboard and press enter.

Press number 3 key to set or check the refill flow rate.

Set the desired flow rate on the number keyboard and press enter.

Press “previous” key to save and return back to the main menu.

Press “run” key to run the pump at the set constant pressure program.

Constant flow rate operation

Press “menu” key.

Choose “constant flow rate” key.

Press number 3 key to set or check the flow rate.

Set the desired flow rate on the number keyboard and press enter.

Press “previous” key to save and return back to the main menu.

Press “run” key to run the pump at the set constant pressure program.

A.2.2 SO_3 Desorption and LAS Production Experiment

Determine the set point of the Back Pressure Regulator (BPR) at the desired pressure

Turn on the syringe pump and open the cooling water valve.

Turn on CO_2 gas cylinder, and make sure that the outlet pressure of the gas cylinder regulator is lower than the desired pressure of $SCCO_2$.

Turn on the outlet valve of gas cylinder regulator, and let CO_2 feed into the syringe pump.

Set the pressure of the syringe pump at the desired value (for example, 1300 psi).

Press “run” button on the pump screen.

Open all valves from 1 to 10.

Close valves 12 and 13.

Turn the handle of the BPR counter-clockwise little by little to slowly increase the holding pressure of the system before the BPR.

If CO_2 gas escapes, continually turn the handle of the BPR counter-clockwise.

If CO_2 gas no longer escapes turn the handle of the BPR clockwise until the CO_2 gas (at the desired pressure) just does not escape, and if you turn the handle clockwise a little, the CO_2 gas begins to escape. That valve position is the set point for the BPR. Write down the number of turns of the handle.

Operation detail

Set the BPR to the above preset point (for example, 5 and a quarter turns).
Turn on the syringe pump and open the cooling water valve.
Turn on the CO_2 gas cylinder, and make sure that the outlet pressure of the gas cylinder regulator is lower than the desired pressure of $SCCO_2$.
Turn on the outlet valve of the gas cylinder regulator, and let CO_2 feed into the syringe pump.
Close valves 11, 12 and 13.
Open valves 1 and 2.
Set the pressure of the syringe pump at the desired value (for example, 1300 psi).
Press “run” button on the pump screen, and the pump will compress the CO_2 to the set pressure.

When the pressure in the system before the BPR is more than the BPR set point, adjust the needle valves 3 and 4 to control the flow rate.
Open valves 5, 6, 7, 8, 9 and 10 to let $SCCO_2$ flush the carbon bed continually.

Close valve 3 and open valve 13.
Choose “constant flow” mode of the syringe pump, and set the flow rate. Then $SCCO_2$ will flush the carbon bed in the recycled model.
Close valve 13 and open valve 3 to slowly release the $SCCO_2$ carrying SO_3 to the absorption columns.
Feed fresh CO_2 gas into the syringe pump and repeat the above operations.

At the end of the experiment, close the CO_2 gas cylinder.
Adjust the BPR knob to the left little by little to drop the holding pressure.

When the holding pressure dropped to about atmospheric pressure, close all of the valves.

Turn on N_2 gas cylinder.

Open vale 11.

Open valves 2, 3, 4, 5, 6, 7, 8, 9 and 10 to let in the N_2 gas to purge the CO_2 remaining in the absorber and columns (especially, using water as absorber).

After 40min, close all the valves.

Take absorption liquid samples to analyze.

In order to know how much SO_3 remains in the carbon bed, water is used to flush the carbon bed. After this the carbon bed needs to be dried for the next run. The operation is carried out in the order of the following order:

Close valves 1 and 2.

Remove the fittings of the reactor.

Using 500 ml of water flush the carbon bed slowly.

Flush the bed continually for about 30min.

Reattach the reactor back into the system.

Turn on the N_2 gas cylinder.

Open vales 11 and 12, and let N_2 gas flow through the carbon continually.

Heat the reactor to the selected temperature.

When the heating time approaches to the desired duration, stop heating.

Once the temperature of the bed dropped to about room temperature, close N_2 gas cylinder.

Close the valve 12 and 11.

A.3 Experimental of Procedure for SO_3 Liquid Sample Analysis

A.3.1 LAS Analysis

Preparation of indicators

Weight out 0.5±0.005 g Dimidium Bromide (Anionic) and dissolved it in 25 ml of 10 %vol. of hot ethanol solution in water solution.

Weight out 0.25±0.005 g Disulphine Blue (Cationic) and dissolved it in 25 ml of 10 %vol. of hot ethanol solution in water solution.

Mix the above solutions in a 250 ml of volumetric flask and dilute with deionized water.

Mix 10 ml of above mixed acid indicator with 10 ml of 2.5 N H_2SO_4 in a 1000 ml volumetric flask and diluted with deionized water.

Store out of sunlight.

Weight out 0.29±0.002g Dimethyl Yellow indicator and dissolved it in 50 ml chloroform.

Transfer the above solution to a 250 ml of volumetric flask and add chloroform to the full mark.

Tansfer 40 ml of the above solution to a 500 ml of volumetric flask and add chloroform to the full mark.

Preparation of titrant

Weight 1.792±0.005g Hyamine 1622 and put it in a 1-liter flask.

Dissolved it in 1 liter deionized water.

The concentration of Hyamine 1622 is:

$$\frac{W_2}{448.1} = \frac{0.1792}{448.1} 0.004 ml/l$$

W_2 = weight (g) of Hyamine 1622.

Titration

Pipette a 10 ml liquid sample in a 250-ml flask.

To this, add by pipette 10 ml deionized water.

To this, add by pipette 20 ml chloroform.

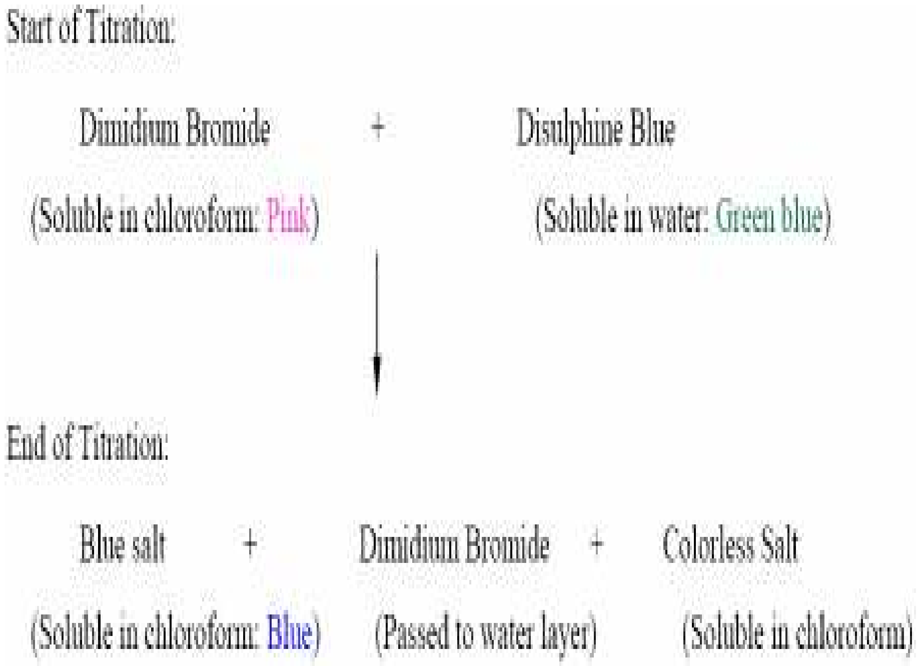
Pipette into the flask10 ml Mixed Indicator (or 5 ml Dimethyl Yellow indicator and add 1 ml 0.01 N H_2SO_4 solution).

Write down the volume of Hyamine 1622 at beginning of the titration.

Add 0.004 M titrant (Hyamine 1622) little by little, and shake well for at least 30 seconds and allow the layers to separate after each addition.

After each addition shake vigorously and permit the layers to separate. As the end is approached, the emulsion formed by shaking tends to break easily. Continue the titration dropwise until the end point is reached.

1) For Mixed Indicator as indicator analysis, the pink color is completely discharged from the chloroform layer; with excess titrant the chloroform layer is blue.



2) For Dimethyl Yellow indicator in the analysis, the color of the chloroform layer changes from red to yellow.

Write down the volume of the titrant at the end of titration.

Record the amount and repeat twice more. Use the conversion for calculations.

A.3.2 Sulfuric Acid Analysis

Use N_2 to purge the sulfuric acid sample for at least 30 min.

Pipette a 10 ml sulfuric acid sample into a 250-ml flask.

Add several drops of phenolphthalein indicator to the flask.

Write down the volume of NaOH solution at the beginning of titration.

Titrate with 0.0100N NaOH, and shake well for at least 30 s. Continue the titration dropwise until the end point is reached.

Write down the volume of titrant at the end of titration.

Record the amount and repeat twice more. Use the average for calculation.

Appendix B

Mass Flow Meter and Rotameter Calibration

1. Gas rotameter calibration

Using N_2 at 25°C

Average value comes from 5 replicate tests.

Reading	Average flow, L/min
0.0	0
10.0	0.08
20.0	0.16
40.0	0.33
50.0	0.41
80.0	0.64
100.0	0.81
150.0	1.18

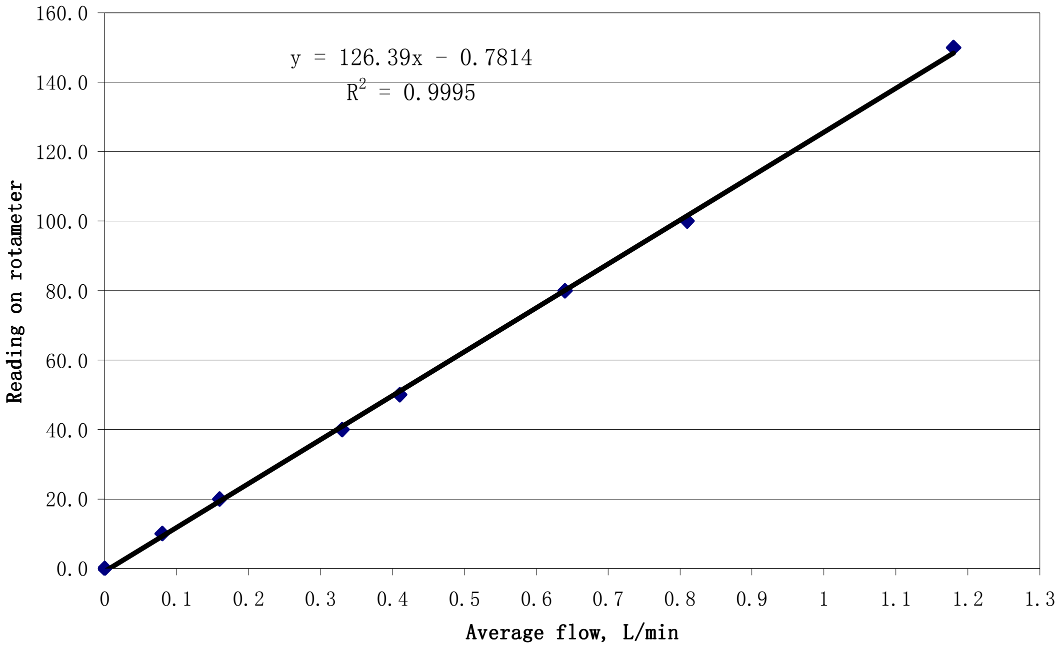


Figure B.1: Calibration curve for the gas rotameter.

2. MFC calibration for N_2.

Using N_2 calibration at 25°C.

Average value comes from 5 replicate tests.

Model: 5.6 SLM Air-MFC

Reading	Average flow rate, L/min
0.0	0
10.0	0.570
20.0	1.144
30.0	1.722
40.0	2.375
50.0	2.950
60.0	3.525
80.0	4.765
100.0	5.875

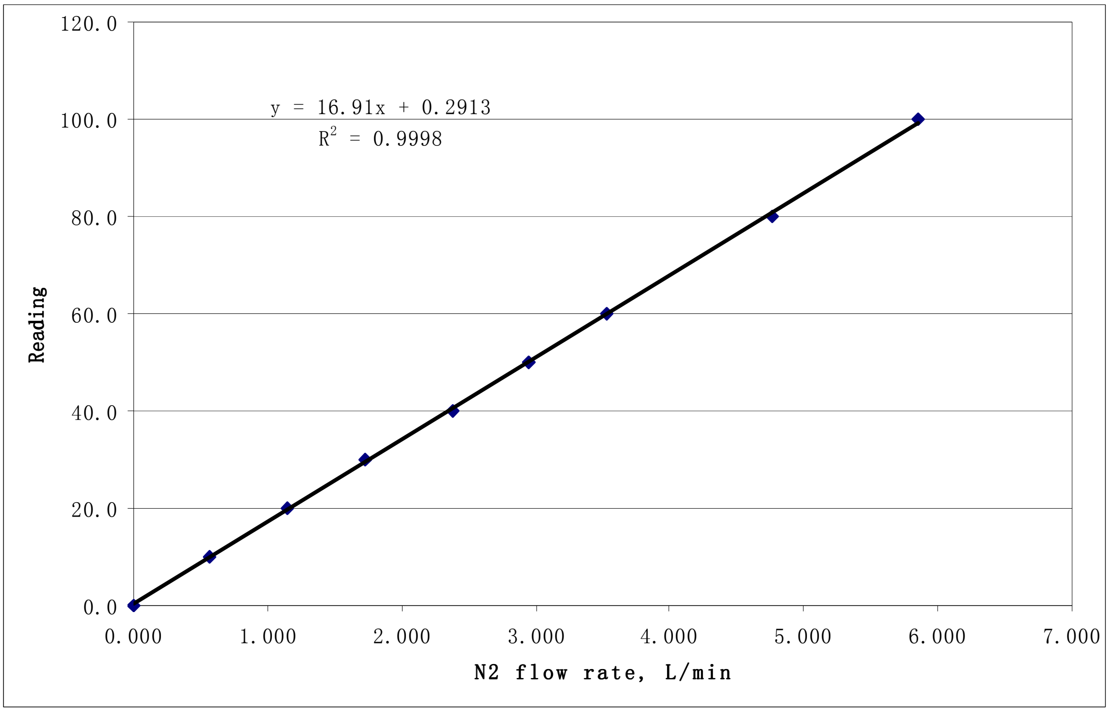


Figure B.2: Mass flow controller calibration for Nitrogen.

3. MFC calibration for Air.

Using N_2 calibration at 25°C.

Average value comes from 5 replicate tests.

Model: 750-SCCMN2-MFC

Reading	Average flow rate, L/min	Corrected to Air, mL/min
0.0	0	0
5.0	0.053	54
10.0	0.099	101
15.0	0.149	152
20.0	0.201	205
30.0	0.293	298
40.0	0.375	382
50.0	0.463	471
80.0	0.708	721
100.0	0.863	878

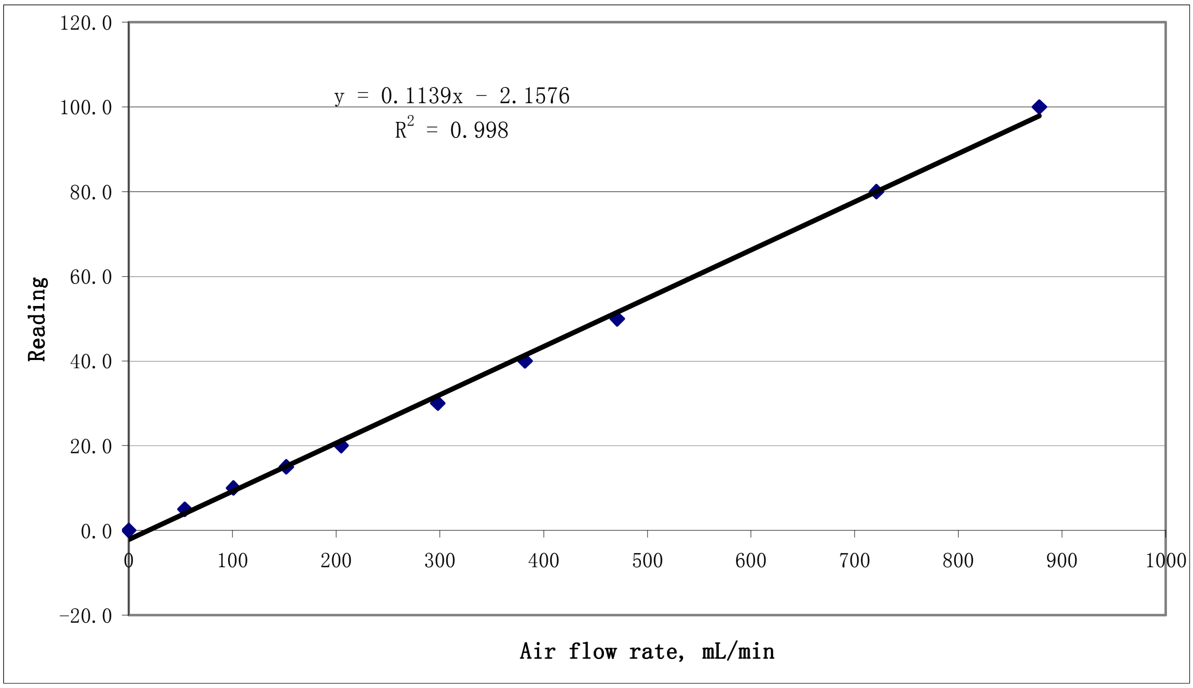


Figure B.3: Mass flow controller calibration for Air.

4. MFC calibration for SO_2.

Using N_2 calibration at 25°C.

Average value comes from 5 replicate tests.

Model: 150 cm^3/min-CO-MFC

Reading	Average flow rate, L/min	Corrected to SO_2, mL/min
0.0	0	0
5.0	0.0070	4.71
7.5	0.0126	8.48
10.0	0.0178	11.98
12.5	0.0238	16.02
15.0	0.0291	19.59
20.0	0.0400	26.93
30.0	0.0615	41.40
40.0	0.0831	55.94
50.0	0.1030	69.33
80.0	0.1624	109.32

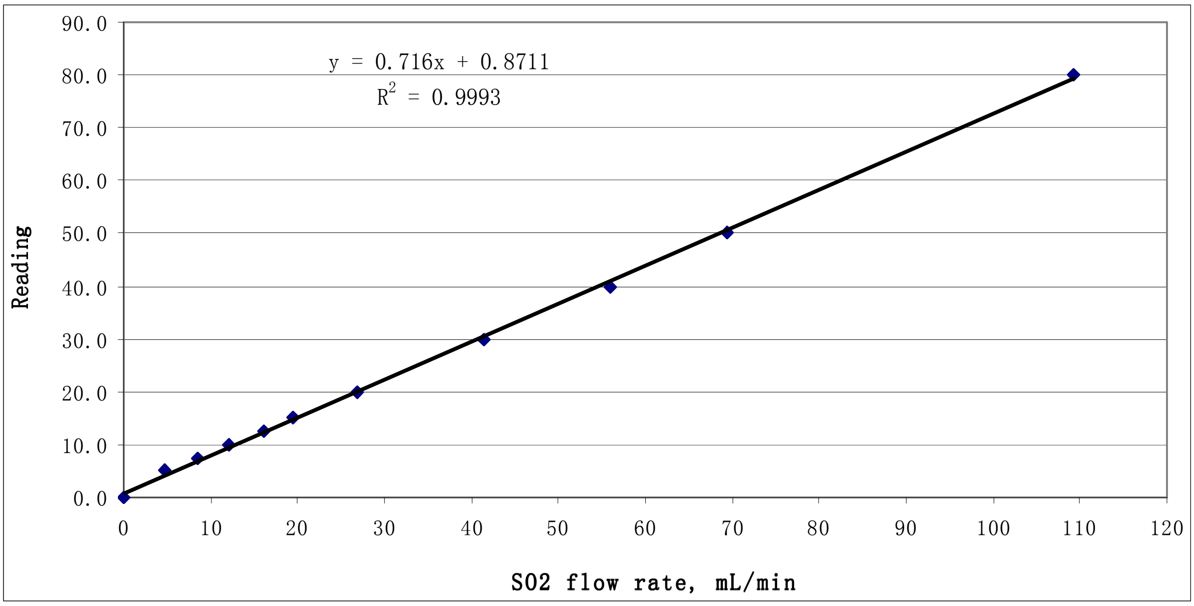


Figure B.4: Mass flow controller calibration for SO_2.

Appendix C Summary of Experimental Data

Date	Mass of SO_2/SO_3 preloaded	SO_3 Remaining in carbon bed		1st column			2nd column			3rd column			4th column		
	,mmol	Mass, mmol	Ratio %	Mass, mmol	Ratio %	note	Mass, mmol	Ratio %	note	Mass, mmol	Ratio %	note	Mass, mmol	Ratio %	note
May 12	6.02	2.6557	44.11	0.2760	4.58	NG,LAB,NH	Reactor preheated at 200℃ for 2hrs, Continually single-pass flushed for 8 hrs								
May 22	6.04	2.5298	41.88	0.3528	5.84	NG,LAB,NH	Reactor preheated at 200℃ for 2hrs, Continually single-pass flushed for 9.6 hrs								
May 31	5.81	2.6557	45.71	0.2360	4.06	NG,LAB,NH	Reactor preheated at 200℃ for 2hrs, Continually single-pass flushed for 10.2 hrs								
Jun. 2	4.66	2.0467	43.92	0.2080	4.46	NG,LAB,NH	Reactor preheated at 200℃ for 2hrs, Continually single-pass flushed for 11 hrs								
Nov. 19	6.21	2.7610	44.46	/	/		Reactor preheated at 200℃ for 2hrs, Continually single-pass flushed for 14 hrs								
Jun. 6	4.89	1.9231	39.33	0.3200	6.54	NG,LAB,NH	Reactor preheated at 200℃ for 4hrs, Continually single-pass flushed for 17.5 hrs								
Jun. 9	4.30	1.8468	42.95	0.2720	6.33	NG,LAB,NH	Reactor preheated at 200℃ for 3hrs, Continually single-pass flushed for 10 hrs								
Dec. 18	6.13	2.1978	35.85	/	/		Reactor preheated at 200℃ for 5hrs, Continually single-pass flushed for 10 hrs								
Jan. 4	6.06	1.7552	28.96	/	/		Reactor preheated at 200℃ for 6hrs, Continually single-pass flushed for 10 hrs								
Jun. 15	5.83	1.1905	20.42	0.5280	9.06	NG,LAB,NH	Reactor preheated at 200℃ for 3hrs, Recycle flush at 10ml/min for 20min for each fresh CO_2 filling of the AC bed								
Nov. 14	6.28	1.1752	18.71	/	/		Reactor preheated at 200℃ for 3hrs, Recycle flush at 20ml/min for 10min for each fresh CO_2 filling of the AC bed								
Jun. 21	5.83	0.8089	13.88	0.6040	10.36	NG,LAB,NH	Reactor preheated at 200℃ for 3hrs, Recycle flush at 20ml/min for 20min for each fresh CO_2 filling of the AC bed								
Jun. 29	6.75	0.4426	6.56	0.8930	13.23	NG,LAB,NH	1.3468	19.95	G,LAB,NH	0.410	9.50	NG,H_2O,NH	250℃ for 6hrs, 20ml/min for 20min		
Jul. 14	5.91	0.3358	5.68	1.2168	20.59	NG,LAB,NH	2.7738	46.93	G,H_2O,NH	0.5418	9.17	G,H_2O,NH	300℃ for 6hrs, 20ml/min for 20min		
Jul. 18	5.96	0.3968	6.66	1.1232	18.85	NG,LAB,NH	2.9048	48.74	G,H_2O,NH	0.4457	7.48	G,H_2O,NH	250℃ for 6hrs, 20ml/min for 20min		
Aug. 9	42.35	3.6935	8.72	6.4584	15.25	NG,LAB,NH	16.6667	39.35	G,H_2O,NH	5.9798	14.12	G,H_2O,NH	From now on same as above		
Aug. 12	41.76	3.4493	8.26	6.9472	16.64	NG,LAB,NH	17.8419	42.72	G,H_2O,NH	4.6758	11.20	G,H_2O,NH			
Sep. 5	6.45	0.3968	6.15	1.4670	22.74	G,LAB,NH	1.23	19.11	G,LAB,NH	1.75	27.12	G,H_2O,NH			
Sep. 25	6.67	0.3816	5.72	1.8450	27.66	G,LAB,H	1.52	22.71	G,LAB NH	2.12	31.85	G,H_2O,NH			

Appendix C Summary of Experimental Data

Continued

Date	Mass of SO_2/SO_3 preloaded	SO_3 Remaining in carbon bed		1st column			2nd column			3rd column			4th column		
	,mmol	Mass, mmol	Ratio %	Mass, mmol	Ratio %	note	Mass, mmol	Ratio %	note	Mass, mmol	Ratio %	note	Mass, mmol	Ratio %	note
Oct. 19	6.62	0.3816	5.76	1.9800	29.91	G,LAB,H	1.85	27.87	G,LAB,H	1.68	25.45	G,H_2O,NH	0.65	9.87	G,H_2O,NH
Oct. 24	6.56	0.3968	6.05	1.9920	30.37	G,LAB,H	1.87	28.45	G,LAB,H	1.58	24.01	G,H_2O,NH	0.63	9.68	G,H_2O,NH
Nov. 3	6.52	0.3510	5.38	1.4430	22.13	G,LAB,NH	1.36	20.80	G,LAB,NH	0.58	8.83	NG,LAB,NH	0.34	5.21	NG,LAB,NH
Nov. 8	6.27	0.3205	5.11	1.4400	22.97	G,LAB,NH	1.35	21.53	G,LAB,NH	0.95	15.22	G,LAB,NH	0.69	11.04	G,LAB,NH
Dec. 4	6.48	/	/	1.5240	23.52	G,LAB,NH	2.23	34.40	G,LAB,H	1.488	22.96	G,LAB,H	0.2976	4.59	G,LAB,NH
Dec. 10	6.67	/	/	1.6710	25.05	G,LAB,NH	2.62	39.27	G,LAB,H	1.597	23.94	G,LAB,H	0.3552	5.33	G,LAB,NH
Dec. 15	6.17	0.3816	6.18	1.6170	26.21	G,LAB,NH	2.55	41.33	G,LAB,H	1.408	22.82	G,LAB,H	0.2448	3.97	G,LAB,NH
Jan. 26	6.01	/	/	1.944	32.35	G,LAB,NH	1.8510	30.80	G,LAB,H	1.38	22.91	G,LAB,H	0.2688	4.47	G,LAB,NH
Feb. 7	6.54	0.4274	6.53	2.769	42.34	G,LAB,H	1.9920	30.46	G,LAB,H	1.15	17.52	G,LAB,NH	0.3008	4.60	G,LAB,NH
Feb. 13	6.34	0.3816	6.02	2.5687	40.52	G,H_2O,NH	1.87	29.47	G,H_2O,NH	1.08	17.04	G,H_2O,NH	0.39	6.14	G,H_2O,NH

Note:

G means this column was filled with glass beads; **NG** means this column was not filled with glass beads.

LAB means this column was filled with LAB; **H_2O** means this column was filled with Water.

H means this column was heated; **NH** means this column was not heated.

“250℃ for 6hrs, 20ml/min for 20min” means the reactor was preheated at 250° C for 6 hours to remove remaining water, and the recycle flush method was used to flush the carbon bed in the desorption experiment; The flow rate of SCCO2 was 20ml/min, with a flushing duration of 20min,

Detailed Data for Each Experiment

Date of Experiment	12-May	22-May	31-May	02-Jun	06-Jun	09-Jun	15-Jun
Room Temperature, ° C	18	20	19	20	18	18	18
Activated Carbon							
Type of carbon used	BPL 6*16 (Calgon Carbon Corp.)						
Weight of carbon in bed, g	8.13	8.13	8.13	8.13	8.13	8.13	8.13
Fresh/Used previously	Fresh	used	used	used	used	used	used
Drying Temperature, ° C	200	200	200	200	200	200	200
N_2 or Air Flow rate, ml/min	50	50	50	50	50	50	50
Drying (Duration (hrs)	2	2	2	2	3	3	3
SO_3 Production							
Reactor (bed) volume, ml	17.7	17.7	17.7	17.7	17.7	17.7	17.7
Weight of Act. Carbon	8.13	8.13	8.13	8.13	8.13	8.13	8.13
Mass Flow Rate of SO_2, mg/min	3.53	3.32	3.13	3.07	2.81	3.21	3.40
Mass Flow Rate of air, g/min	0.453	0.427	0.427	0.440	0.440	0.440	0.440
SO_2 Concentration at end of filling	3530	3520	3320	3160	2900	3300	3500
Moles of SO_2 adsorbed on carbon, mmol	6.02	6.04	5.81	4.66	4.89	4.30	5.83
Moles of SO_2/gm of carbon, mmol/g	0.740	0.743	0.715	0.573	0.601	0.529	0.717
Mass of SO_3/gm of carbon, mg/g	59.24	59.43	57.17	45.85	48.12	42.31	57.37
Extraction of SO_3 with CO_2							
Type of Experiment (Single Pass/Recycle)	single pass	single	single	single	single	recycled	recycled
CO_2 mass flow rate to reactor, ml/min (at the experimental temp.&pres.)	0.45	0.47	0.50	0.51	0.51	0.49	0.58
$SCCO_2$ pressure, psi	1340	1360	1360	1340	1340	1300	1300
$SCCO_2$ temperature, ° C	31	31	31	34	34	34	40
Duration of CO_2 feed, hrs	5	6.6	7.2	8	14.3	7.5	6
Total CO_2 Fed to Reactor, ml	135	186.12	216	244.8	437.58	142	150
Recycle Duration, min	-	-	-	-	-	20	20
Recycle Flow rate, ml/min	-	-	-	-	-	10	10
Duration of CO_2 Release to Absorber, hrs	8	9.6	10.2	11	17.5	10	9
CO_2 Release Flow Rate, ml/min (at room temp.&pres.)	40	47	50	50	50	45	55
Titration of Activated Carbon							
Amount of water used to flush carbon bed, ml	250	250	250	450	500	500	500
Duration of Flush, min	30	30	30	30	30	30	30
NaOH Concentration, mol/l	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221
Beginning Amount of NaOH, ml	13.35	5.90	1.55	24.80	31.20	0.50	12.25
Final Amt. of NaOH, ml	30.75	39.05	18.95	32.25	37.50	6.55	16.15
Volume of NaOH Used, ml	17.40	33.15	17.40	7.45	6.30	6.05	3.90
Moles of H_2SO_4 in bed, mmol	2.6557	2.5298	2.6557	2.0467	1.9231	1.8468	1.1905
Moles of SO_2 (SO_3) Removed by CO_2, mmol	3.364	3.510	3.154	2.613	2.967	2.453	4.640
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	55.89	58.12	54.29	56.08	60.67	57.05	79.58
Absorber (Sulfonation Reactor)							
No. of columns in absorber	1	1	1	1	2	2	2
1st column	not heated	NH	NH	NH	NH	NH	NH
No. of stages containing LAB in 1st contact column	2	2	2	2	2	2	2
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	0	0	0	0	0	0	0
Volume of LAB in column, ml	120	120	200	200	200	200	200

Continued

Depth of glass beads in stage, cm	0	0	0	0	0	0	0
Depth of LAB in stage, cm	26	26	44	44	44	44	44
Hyamine Concentration, mol/l	0.004	0.004	0.004	0.004	0.004	0.004	0.004
Amount of Hyamine at start, ml	27.35	12.45	2.10	6.95	13.45	27.85	22.75
Amount of Hyamine at end, ml	34.20	19.80	5.05	9.55	17.45	31.25	15-Jun
Volume of Hyamine used, ml	6.85	7.35	2.95	2.60	4.00	3.40	29.35
Moles of LAS measured in column, mmol	0.3288	0.3528	0.236	0.208	0.32	0.272	6.60
Fraction of Entering SO_2 Captured by LAB in Column, %	9.77	10.05	7.48	7.96	10.79	11.09	0.528
No. of stages filled with water in 1st column	-	-	-	-	-	-	-
Volume of water in column, ml	-	-	-	-	-	-	-
No of stages filled with glass beads	-	-	-	-	-	-	-
Depth of water/stage, cm	-	-	-	-	-	-	-
NaOH Concentration, mol/l	-	-	-	-	-	-	-
Amount of NaOH at start, ml	-	-	-	-	-	-	-
Amount of NaOH at end, ml	-	-	-	-	-	-	-
Volume of NaOH Used, ml	-	-	-	-	-	-	-
Moles of H_2SO_4 captured in column, mmol	-	-	-	-	-	-	-
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	3.04	3.16	2.92	2.41	2.65	2.18	4.11
2nd column					NH	NH	NH
No. of stages containing LAB in 2nd contact column	-	-	-	-	-	-	-
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	-	-	-	-	-	-	-
Volume of LAB in column, ml	-	-	-	-	-	-	-
Depth of glass beads in stage, cm	-	-	-	-	-	-	-
Depth of LAB in stage, cm	-	-	-	-	-	-	-
Hyamine Concentration , mol/l	-	-	-	-	-	-	-
Amount of Hyamine at start, ml	-	-	-	-	-	-	-
Amount of Hyamine at end, ml	-	-	-	-	-	-	-
Volume of Hyamine used, ml	-	-	-	-	-	-	-
Moles of LAS measured in column, mmol	-	-	-	-	-	-	-
Fraction of Entering SO_2 Captured by LAB in Column, %	-	-	-	-	-	-	-
No. of stages filled with water in 2nd column	-	-	-	-	1	1	1
Volume of water in column, ml	-	-	-	-	250	250	300
No. of stages filled with glass beads	-	-	-	-	0	0	0
Depth of glass beads/stage, cm	-	-	-	-	0	0	0
Depth of water/stage, cm	-	-	-	-	45	45	55
NaOH Concentration, mol/l	-	-	-	-	0.01221	0.01221	0.01221
Amount of NaOH at start, ml	-	-	-	-	12.40	18.65	26.25
Amount of NaOH at end, ml	-	-	-	-	15.80	21.75	30.45
Volume of NaOH Used, ml	-	-	-	-	3.40	3.10	4.20
Moles of H_2SO_4 captured in column, mmol					0.5189	0.4731	0.7692
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	-	-	-	-	2.1280	1.7081	3.3423
3rd column							
No. of stages containing LAB in 3rd contact column	-	-	-	-	-	-	-
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	-	-	-	-	-	-	-
Volume of LAB in column, ml	-	-	-	-	-	-	-
Depth of glass beads in stage, cm	-	-	-	-	-	-	-
Depth of LAB in stage, cm	-	-	-	-	-	-	-

Continued

Hyamine Concentration , mol/l	-	-	-	-	-	-	-
Amount of Hyamine at start, ml	-	-	-	-	-	-	-
Amount of Hyamine at end, ml	-	-	-	-	-	-	-
Volume of Hyamine used, ml	-	-	-	-	-	-	-
Moles of LAS measured in column, mmol	-	-	-	-	-	-	-
Fraction of Entering SO_2 Captured by LAB in Column, %	-	-	-	-	-	-	-
No. of stages filled with water in 3rd column	-	-	-	-	-	-	-
Volume of water in column, ml	-	-	-	-	-	-	-
No of stages filled with glass beads	-	-	-	-	-	-	-
Depth of glass beads/stage, cm	-	-	-	-	-	-	-
Depth of water/stage, cm	-	-	-	-	-	-	-
NaOH Concentration, mol/l	-	-	-	-	-	-	-
Amount of NaOH at start, ml	-	-	-	-	-	-	-
Amount of NaOH at end, ml	-	-	-	-	-	-	-
Volume of NaOH Used, ml	-	-	-	-	-	-	-
Moles of H_2SO_4 captured in column, mmol	-	-	-	-	-	-	-
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	-	-	-	-	-	-	-
Total (tubes)							
Total moles of LAS formed, mmol	0.3288	0.3528	0.236	0.208	0.3200	0.2720	0.5280
Fraction of Entering SO_2 (SO_3) Recovered as LAS in Absorber, %	9.77	10.05	7.48	7.96	10.79	11.09	11.38

Date of Experiment	21-Jun	29-Jun	14-Jul	18-Jul	09-Aug	12-Aug	05-Sep
Room Temperature, ° C	21	20	22	21	20	20	22
Activated Carbon							
Type of carbon used							
Weight of carbon in bed, g	8.13	8.62	8.62	8.62	65.24	65.24	8.62
Fresh/Used previously	used	fresh	used	used	used	used	used
Drying Temperature, ° C	230	250	300	300	250	250	250
N_2 or Air Flow rate, ml/min	50	50	50	50	50	50	50
Drying (Duration (hrs)	6	6	6	4.5	6	6	6
SO_3 Production							
Reactor (bed) volume, ml	17.7	17.7	17.7	17.7	135	135	17.7
Weight of Act. Carbon	8.13	8.62	8.62	8.62	65.24	65.24	8.62
Mass Flow Rate of SO_2, mg/min	3.59	3.39	4.20	4.01	17.10	17.10	3.55
Mass Flow Rate of air, g/min	0.440	0.440	0.548	0.531	2.201	2.214	0.453
SO_2 Concentration at end of filling	3700	3490	3500	3420	3520	3500	3550
Moles of SO_2 adsorbed on carbon, mmol	5.83	6.75	5.91	5.96	42.35	41.76	6.45
Moles of SO_2/gm of carbon, mmol/g	0.717	0.783	0.686	0.691	0.656	0.647	0.748
Mass of SO_3/gm of carbon, mg/g	57.37	62.65	54.85	55.31	51.93	51.21	59.86
Extraction of SO_3 with CO_2							
Type of Experiment (Single Pass/Recycle)	recycled	recycled	recycled	recycled	recycled	recycled	recycled
CO_2 mass flow rate to reactor, ml/min (at the experimental temp.&pres.)	0.54	0.58	0.57	0.54	0.51	0.51	0.52
$SCCO_2$ pressure, psi	1300	1300	1300	1300	1300	1300	1300
$SCCO_2$ temperature, ° C	40	40	40	40	40	40	40
Duration of CO_2 feed, hrs	6	4	5	4	18	18	4
Total CO_2 Fed to Reactor, ml	170	83	106	106	317	314	90
Recycle Duration, min	20	20	20	20	20	20	20
Recycle Flow rate, ml/min	20	20	20	20	40	40	20
Duration of CO_2 Release to Absorber, hrs	9	7	8	7	18	18	7
CO_2 Release Flow Rate, ml/min (at room temp.&pres.)	50	55	55	50	50	50	55
Titration of Activated Carbon							
Amount of water used to flush carbon bed, ml	500	500	500	500	1000	1000	500
Duration of Flush, min	30	30	30	30	30	30	30
NaOH Concentration, mol/l	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221
Beginning Amount of NaOH, ml	9.30	9.60	10.25	7.25	1.25	12.35	11.25
Final Amt. of NaOH, ml	11.95	11.05	11.35	8.55	7.30	18.00	12.55
Volume of NaOH Used, ml	2.65	1.45	1.10	1.30	6.05	5.65	1.30
Moles of H_2SO_4 in bed, mmol	0.8089	0.4426	0.3358	0.3968	3.6935	3.4493	0.3968
Moles of SO_2 (SO_3) Removed by CO_2, mmol	5.021	6.307	5.574	5.563	38.656	38.311	6.053
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	86.13	93.44	94.32	93.34	91.28	91.74	93.85
Absorber (Sulfonation Reactor)							
No. of columns in absorber	2	3	3	3	3	3	3
1st column	NH	NH	NH	NH	NH	NH	NH
No. of stages containing LAB in 1st contact column	2	4	4	4	4	4	1
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	0	0	0	0	0	0	1
Volume of LAB in column, ml	200	190	260	260	260	260	150
Depth of glass beads in stage, cm	0	0	0	0	0	0	75
Depth of LAB in stage, cm	44	42	58	58	58	58	78

Continued

Hyamine Concentration, mol/l	0.004	0.004	0.004	0.004	0.004	0.004	0.004
Amount of Hyamine at start, ml	35.25	24.50	13.05	8.05	12.45	8.55	6.80
Amount of Hyamine at end, ml	42.80	36.25	24.75	18.85	43.50	41.95	31.25
Volume of Hyamine used, ml	7.55	11.75	11.70	10.80	31.05	33.40	24.45
Moles of LAS measured in column, mmol	0.604	0.893	1.2168	1.1232	6.4584	6.9472	1.467
Fraction of Entering SO_2 Captured by LAB in Column, %	12.03	14.16	21.83	20.19	16.71	18.13	24.24
No. of stages filled with water in 1st column	-	-	-	-	-	-	-
Volume of water in column, ml	-	-	-	-	-	-	-
No of stages filled with glass beads	-	-	-	-	-	-	-
Depth of water/stage, cm	-	-	-	-	-	-	-
NaOH Concentration, mol/l	-	-	-	-	-	-	-
Amount of NaOH at start, ml	-	-	-	-	-	-	-
Amount of NaOH at end, ml	-	-	-	-	-	-	-
Volume of NaOH Used, ml	-	-	-	-	-	-	-
Moles of H_2SO_4 captured in column, mmol	-	-	-	-	-	-	-
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	4.42	5.41	4.36	4.44	32.20	31.36	4.59
2nd column	NH	NH	NH	NH	NH	NH	NH
No. of stages containing LAB in 2nd contact column	-	1	-	-	-	-	4
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	-	1	-	-	-	-	0
Volume of LAB in column, ml	-	130	-	-	-	-	260
Depth of glass beads in stage, cm	-	72	-	-	-	-	0
Depth of LAB in stage, cm	-	76	-	-	-	-	76
Hyamine Concentration , mol/l	-	0.004	-	-	-	-	0.004
Amount of Hyamine at start, ml	-	21.75	-	-	-	-	2.50
Amount of Hyamine at end, ml	-	47.65	-	-	-	-	14.35
Volume of Hyamine used, ml	-	25.90	-	-	-	-	11.85
Moles of LAS measured in column, mmol	-	1.347	-	-	-	-	1.232
Fraction of Entering SO_2 Captured by LAB in Column, %	-	24.87	-	-	-	-	26.87
No. of stages filled with water in 2nd column	1	-	1	1	1	1	-
Volume of water in column, ml	300	-	130	130	250	250	-
No. of stages filled with glass beads	0	-	1	1	1	1	-
Depth of glass beads/stage, cm	0	-	72	72	72	72	-
Depth of water/stage, cm	55	-	76	76	102	102	-
NaOH Concentration, mol/l	0.01221	-	0.01221	0.01221	0.01221	0.01221	-
Amount of NaOH at start, ml	34.70	-	6.75	3.05	5.00	2.05	-
Amount of NaOH at end, ml	39.50	-	41.70	39.65	59.60	60.50	-
Volume of NaOH Used, ml	4.80	-	34.95	36.60	54.60	58.45	-
Moles of H_2SO_4 captured in column, mmol	0.8791	-	2.7738	2.9048	16.6667	17.8419	-
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	3.5380	4.0676	1.5836	1.5352	15.5314	13.5216	3.3538
3rd column		NH	NH	NH	NH	NH	NH
No. of stages containing LAB in 3rd contact column	-	-	-	-	-	-	-
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	-	-	-	-	-	-	-
Volume of LAB in column, ml	-	-	-	-	-	-	-
Depth of glass beads in stage, cm	-	-	-	-	-	-	-
Depth of LAB in stage, cm	-	-	-	-	-	-	-
Hyamine Concentration , mol/l	-	-	-	-	-	-	-
Amount of Hyamine at start, ml	-	-	-	-	-	-	-

Continued

Amount of Hyamine at end, ml	-	-	-	-	-	-	-
Volume of Hyamine used, ml	-	-	-	-	-	-	-
Moles of LAS measured in column, mmol	-	-	-	-	-	-	-
Fraction of Entering SO_2 Captured by LAB in Column, %	-	-	-	-	-	-	-
No. of stages filled with water in 3rd column	-	3	1	1	1	1	1
Volume of water in column, ml	-	200	250	200	150	150	300
No of stages filled with glass beads	-	0	1	1	1	1	1
Depth of glass beads/stage, cm	-	0	60	60	60	60	26
Depth of water/stage, cm	-	0	85	80	75	75	52
NaOH Concentration, mol/l	-	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221
Amount of NaOH at start, ml	-	21.60	16.00	23.95	3.50	10.25	1.00
Amount of NaOH at end, ml	-	26.85	19.55	27.60	36.15	35.78	10.55
Volume of NaOH Used, ml	-	5.25	3.55	3.65	32.65	25.53	9.55
Moles of H_2SO_4 captured in column, mmol	-	0.6410	0.5418	0.4457	5.9798	4.6758	1.7491
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	-	3.427	1.042	1.090	9.552	8.846	1.605
Total (tubes)							
Total moles of LAS formed, mmol	0.6040	2.240	1.2168	1.1232	6.4584	6.9472	2.699
Fraction of Entering SO_2 (SO_3) Recovered as LAS in Absorber, %	12.03	35.51	21.83	20.19	16.71	18.13	44.59

Date of Experiment	25-Sep	19-Oct	24-Oct	03-Nov	08-Nov	14-Nov	19-Nov
Room Temperature, ° C	20	19	20	20	20	20	20
Activated Carbon							
Type of carbon used							
Weight of carbon in bed, g	8.62	8.62	8.62	8.62	8.62	8.62	8.62
Fresh/Used previously	used	used	used	used	used	used	used
Drying Temperature, ° C	250	250	250	250	250	250	250
N_2 or Air Flow rate, ml/min	50	50	50	50	50	50	50
Drying (Duration (hrs)	6	6	6	6	6	6	6
SO_3 Production							
Reactor (bed) volume, ml	17.7	17.7	17.7	17.7	17.7	17.7	17.7
Weight of Act. Carbon	8.62	8.62	8.62	8.62	8.62	8.62	8.62
Mass Flow Rate of SO_2, mg/min	3.80	3.70	3.70	3.60	3.50	3.50	3.50
Mass Flow Rate of air, g/min	0.485	0.479	0.479	0.466	0.453	0.453	0.453
SO_2 Concentration at end of filling	3550	3500	3500	3500	3500	3500	3500
Moles of SO_2 adsorbed on carbon, mmol	6.67	6.62	6.56	6.52	6.27	6.28	6.21
Moles of SO_2/gm of carbon, mmol/g	0.774	0.768	0.761	0.756	0.727	0.729	0.720
Mass of SO_3/gm of carbon, mg/g	61.90	61.44	60.88	60.51	58.19	58.28	57.63
Extraction of SO_3 with CO_2							
Type of Experiment (Single Pass/Recycle)	recycled	recycled	recycled	recycled	recycled	recycled	single
CO_2 mass flow rate to reactor, ml/min (at the experimental temp.&pres.)	0.62	0.42	0.42	0.51	0.50	0.54	0.53
$SCCO_2$ pressure, psi	1300	1300	1300	1300	1300	1300	1300
$SCCO_2$ temperature, ° C	40	40	40	40	40	40	40
Duration of CO_2 feed, hrs	4	4	4	4	4	4	11
Total CO_2 Fed to Reactor, ml	85	93	88	94	84	154	349.8
Recycle Duration, min	20	20	20	20	20	10	-
Recycle Flow rate, ml/min	20	20	20	20	20	20	-
Duration of CO_2 Release to Absorber, hrs	7	7	7	7	7	7	14
CO_2 Release Flow Rate, ml/min (at room temp.&pres.)	60	55	55	60	60	60	60
Titration of Activated Carbon							
Amount of water used to flush carbon bed, ml	500	500	500	500	500	500	450
Duration of Flush, min	30	30	30	30	30	30	30
NaOH Concentration, mol/l	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221	0.01221
Beginning Amount of NaOH, ml	24.55	12.30	6.50	2.00	3.75	2.00	18.35
Final Amt. of NaOH, ml	25.80	13.55	7.80	3.15	4.80	5.85	28.40
Volume of NaOH Used, ml	1.25	1.25	1.30	1.15	1.05	3.85	10.05
Moles of H_2SO_4 in bed, mmol	0.3816	0.3816	0.3968	0.3510	0.3205	1.1752	2.7610
Moles of SO_2 (SO_3) Removed by CO_2, mmol	6.288	6.238	6.163	6.169	5.949	5.105	3.449
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	94.28	94.24	93.95	94.62	94.89	81.29	55.54
Absorber (Sulfonation Reactor)							
No. of columns in absorber	4	4	4	4	4	/	/
1st column	H	H	H	NH	NH	/	/
No. of stages containing LAB in 1st contact column	1	1	1	1	1	/	/
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	1	1	1	1	1	/	/
Volume of LAB in column, ml	150	150	150	150	150	/	/
Depth of glass beads in stage, cm	75	75	75	75	75	/	/
Depth of LAB in stage, cm	78	78	78	78	78	/	/

Continued

Hyamine Concentration, mol/l	0.004	0.004	0.004	0.004	0.004	/	/
Amount of Hyamine at start, ml	2.50	3.85	7.20	2.45	3.80	/	/
Amount of Hyamine at end, ml	33.25	36.85	40.40	26.50	27.80	/	/
Volume of Hyamine used, ml	30.75	33.00	33.20	24.05	24.00	/	/
Moles of LAS measured in column, mmol	1.845	1.98	1.992	1.443	1.44	/	/
Fraction of Entering SO_2 Captured by LAB in Column, %	29.34	31.74	32.32	23.39	24.20	/	/
No. of stages filled with water in 1st column	-	-	-	-	-	/	/
Volume of water in column, ml	-	-	-	-	-	/	/
No of stages filled with glass beads	-	-	-	-	-		
Depth of water/stage, cm	-	-	-	-	-		
NaOH Concentration, mol/l	-	-	-	-	-		
Amount of NaOH at start, ml	-	-	-	-	-		
Amount of NaOH at end, ml	-	-	-	-	-		
Volume of NaOH Used, ml	-	-	-	-	-		
Moles of H_2SO_4 captured in column, mmol	-	-	-	-	-		
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	4.44	4.26	4.17	4.73	4.51		
2nd column	NH	H	H	NH	NH		
No. of stages containing LAB in 2nd contact column	4	4	4	4	4		
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	4	4	4	4	4		
Volume of LAB in column, ml	150	150	150	150	150		
Depth of glass beads in stage, cm	76	76	76	76	76		
Depth of LAB in stage, cm	79	79	79	79	79		
Hyamine Concentration , mol/l	0.004	0.004	0.004	0.004	0.004		
Amount of Hyamine at start, ml	8.55	15.00	9.75	12.85	5.45		
Amount of Hyamine at end, ml	31.80	45.75	40.85	35.45	27.95		
Volume of Hyamine used, ml	23.25	30.75	31.10	22.60	22.50		
Moles of LAS measured in column, mmol	1.395	1.845	1.866	1.356	1.350		
Fraction of Entering SO_2 Captured by LAB in Column, %	31.39	43.33	44.74	28.69	29.94		
No. of stages filled with water in 2nd column	-	-	-	-	-		
Volume of water in column, ml	-	-	-	-	-		
No. of stages filled with glass beads	-	-	-	-	-		
Depth of glass beads/stage, cm	-	-	-	-	-		
Depth of water/stage, cm	-	-	-	-	-		
NaOH Concentration, mol/l	-	-	-	-	-		
Amount of NaOH at start, ml	-	-	-	-	-		
Amount of NaOH at end, ml	-	-	-	-	-		
Volume of NaOH Used, ml	-	-	-	-	-		
Moles of H_2SO_4 captured in column, mmol	-	-	-	-	-		
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	3.0484	2.4134	2.3052	3.3700	3.1595		
3rd column	NH	NH	NH	NH	NH		
No. of stages containing LAB in 3rd contact column	-	-	-	1	1		
(Note: a stage is when the gas is dispersed as bubbles in the liquid)							
No. of stages containing Glass Beads	-	-	-	0	1		
Volume of LAB in column, ml	-	-	-	300	300		
Depth of glass beads in stage, cm	-	-	-	34	34		
Depth of LAB in stage, cm	-	-	-	52	52		
Hyamine Concentration , mol/l	-	-	-	0.004	0.004		
Amount of Hyamine at start, ml	-	-	-	5.50	8.90		
Amount of Hyamine at end, ml	-	-	-	10.30	16.85		

Continued

Volume of Hyamine used, ml	-	-	-	4.80	7.95		
Moles of LAS measured in column, mmol	-	-	-	0.576	0.954		
Fraction of Entering SO_2 Captured by LAB in Column, %	-	-	-	17.09	30.19		
No. of stages filled with water in 3rd column	1	1	1	-	-		
Volume of water in column, ml	300	300	300	-	-		
No of stages filled with glass beads	1	1	1	-	-		
Depth of glass beads/stage, cm	26	26	26	-	-		
Depth of water/stage, cm	52	52	52	-	-		
NaOH Concentration, mol/l	0.01221	0.01221	0.01221	-	-		
Amount of NaOH at start, ml	2.50	8.05	2.00	-	-		
Amount of NaOH at end, ml	14.10	17.25	10.60	-	-		
Volume of NaOH Used, ml	11.60	9.20	8.60	-	-		
Moles of H_2SO_4 captured in column, mmol	2.1245	1.6850	1.5751	-	-		
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	0.924	0.728	0.730	2.794	2.205		
4th column	NH	NH	NH	NH	NH		
No. of stages containing LAB in 4th contact column	-	-	-	1	1		
No. of stages containing Glass Beads	-	-	-	0	1		
Volume of LAB in column, ml	-	-	-	200	200		
Depth of glass beads in stage, cm	-	-	-	36	36		
Depth of LAB in stage, cm	-	-	-	42	42		
Hyamine Concentration , mol/l	-	-	-	0.004	0.004		
Amount of Hyamine at start, ml	-	-	-	21.95	23.55		
Amount of Hyamine at end, ml	-	-	-	26.20	32.20		
Volume of Hyamine used, ml	-	-	-	4.25	8.65		
Moles of LAS measured in column, mmol	-	-	-	0.3400	0.6920		
Fraction of Entering SO_2 Captured by LAB in Column, %	-	-	-	12.17	31.38		
No. of stages filled with water in 4th column	1	1	1	-	-		
Volume of water in column, ml	200	200	200	-	-		
No. of stages filled with glass beads	1	1	1	-	-		
Depth of glass beads/stage, cm	36	36	36	-	-		
Depth of water/stage, cm	42	42	42	-	-		
NaOH Concentration, mol/l	0.01221	0.01221	0.01221	-	-		
Amount of NaOH at start, ml	15.85	32.90	28.25	-	-		
Amount of NaOH at end, ml	22.75	38.25	33.45	-	-		
Volume of NaOH Used, ml	6.90	5.35	5.20	-	-		
Moles of H_2SO_4 captured in column, mmol	0.84	0.65	0.63	-	-		
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	0.0814	0.0752	0.0952	2.4540	1.5135		
Total (tubes)							
Total moles of LAS formed, mmol	3.240	3.825	3.858	3.715	4.436		
Fraction of Entering SO_2 (SO_3) Recovered as LAS in Absorber, %	51.52	61.31	62.60	60.22	74.56		
Fraction of Entering SO_2 (SO_3) Recovered in Absorber, %	98.71	98.79	98.46	60.22	74.56		
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	94.28	94.24	93.95	94.62	94.89		

Date of Experiment	04-Dec	10-Dec	15-Dec	18-Dec	04-Jan	26-Jan	07-Feb	13-Feb
Room Temperature, ° C	18	18	19	19	18	20	20	20
Activated Carbon								
Type of carbon used								
Weight of carbon in bed, g	8.62	8.62	8.62	8.62	8.62	8.62	8.62	9.62
Fresh/Used previously	used	used	used	used	used	used	used	used
Drying Temperature, ° C	250	/	/	250	250	250	/	250
N_2 or Air Flow rate, ml/min	50	/	/	50	50	50	/	50
Drying (Duration (hrs)	6	/	/	6	6	6	/	6
SO_3 Production								
Reactor (bed) volume, ml	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7
Weight of Act. Carbon	8.62	8.62	8.62	8.62	8.62	8.62	8.62	8.62
Mass Flow Rate of SO_2, mg/min	3.60	3.60	3.50	3.70	3.50	3.50	3.50	3.50
Mass Flow Rate of air, g/min	0.466	0.466	0.453	0.479	0.453	0.453	0.453	0.453
SO_2 Concentration at end of filling	3500	3500	3500	3500	3500	3500	3500	3500
Moles of SO_2 adsorbed on carbon, mmol	6.48	6.67	6.17	6.13	6.06	6.01	6.54	6.34
Moles of SO_2/gm of carbon, mmol/g	0.752	0.774	0.716	0.711	0.703	0.697	0.759	0.735
Mass of SO_3/gm of carbon, mg/g	60.14	61.90	57.26	56.89	56.24	55.78	60.70	58.84
Extraction of SO_3 with CO_2								
Type of Experiment (Single Pass/Recycle)	recycled	recycled	recycled	single	single	recycled	recycled	recycled
CO_2 mass flow rate to reactor, ml/min (at the experimental temp.&pres.)	0.48	0.56	0.52	0.54	0.50	0.49	0.50	0.49
$SCCO_2$ pressure, psi	1300	1300	1300	1300	1300	1300	1300	1300
$SCCO_2$ temperature, ° C	40	40	40	40	40	40	40	40
Duration of CO_2 feed, hrs	4	4	4	7	7	4	4	4
Total CO_2 Fed to Reactor, ml	81	82	85	226.8	210	83	91	94
Recycle Duration, min	20	20	20	20	-	20	20	20
Recycle Flow rate, ml/min	20	20	20	20	-	20	20	20
Duration of CO_2 Release to Absorber, hrs	7	7	7	10	10	7	7	7
CO_2 Release Flow Rate, ml/min (at room temp.&pres.)	60	60	60	60	60	55	55	55
Titration of Activated Carbon								
Amount of water used to flush carbon bed, ml	/	/	500	500	500	/	500	500
Duration of Flush, min	/	/	30	30	30	/	30	30
NaOH Concentration, mol/l	/	/	0.01221	0.01221	0.01221	/	0.01221	0.01221
Beginning Amount of NaOH, ml	/	/	2.50	7.20	1.50	/	5.50	12.00
Final Amt. of NaOH, ml	/	/	3.75	14.40	7.25	/	6.90	13.25
Volume of NaOH Used, ml	/	/	1.25	7.20	5.75	/	1.40	1.25
Moles of H_2SO_4 in bed, mmol	/	/	0.3816	2.1978	1.7552	/	0.4274	0.3816
Moles of SO_2 (SO_3) Removed by CO_2, mmol	/	/	5.788	3.932	4.305	/	6.113	5.958
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	/	/	93.82	64.15	71.04	/	93.47	93.98
Absorber (Sulfonation Reactor)								
No. of columns in absorber	4	4	4	/	/	4	4	4
1st column	NH	NH	NH	/	/	NH	H	NH
No. of stages containing LAB in 1st contact column	1	1	1	/	/	1	1	1
(Note: a stage is when the gas is dispersed as bubbles in the liquid)								
No. of stages containing Glass Beads	1	1	1	/	/	1	1	-
Volume of LAB in column, ml	150	150	150	/	/	150	150	-
Depth of glass beads in stage, cm	75	75	75	/	/	47	47	-

Continued

Depth of LAB in stage, cm	78	78	78	/	/	59	59	-
Hyamine Concentration, mol/l	0.004	0.004	0.004	/	/	0.004	0.004	-
Amount of Hyamine at start, ml	2.85	12.00	3.85	/	/	10.45	1.25	-
Amount of Hyamine at end, ml	28.25	39.85	30.80	/	/	42.85	47.40	-
Volume of Hyamine used, ml	25.40	27.85	26.95	/	/	32.40	46.15	-
Moles of LAS measured in column, mmol	1.524	1.671	1.617	/	/	1.944	2.769	-
Fraction of Entering SO_2 Captured by LAB in Column, %	23.52	25.05	26.21	/	/	32.35	42.34	-
No. of stages filled with water in 1st column	-	-	-	/	/	-	-	1
Volume of water in column, ml	-	-	-	/	/	-	-	150
No of stages filled with glass beads	-	-	-			-	-	75
Depth of water/stage, cm	-	-	-			-	-	78
NaOH Concentration, mol/l	-	-	-			-	-	0.01221
Amount of NaOH at start, ml	-	-	-			-	-	3.20
Amount of NaOH at end, ml	-	-	-			-	-	31.25
Volume of NaOH Used, ml	-	-	-			-	-	28.05
Moles of H_2SO_4 captured in column, mmol	-	-	-			-	-	2.5687
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	4.96	5.00	4.17			4.07	3.34	3.39
2nd column	H	H	H			H	H	NH
No. of stages containing LAB in 2nd contact column	4	4	4			1	1	-
(Note: a stage is when the gas is dispersed as bubbles in the liquid)								
No. of stages containing Glass Beads	4	4	4			1	1	-
Volume of LAB in column, ml	150	150	150			150	150	-
Depth of glass beads in stage, cm	76	76	76			75	75	-
Depth of LAB in stage, cm	79	79	79			78	78	-
Hyamine Concentration , mol/l	0.004	0.004	0.004			0.004	0.004	-
Amount of Hyamine at start, ml	7.50	3.55	3.25			13.00	10.05	-
Amount of Hyamine at end, ml	44.65	47.20	45.75			43.85	43.25	-
Volume of Hyamine used, ml	37.15	43.65	42.50			30.85	33.20	-
Moles of LAS measured in column, mmol	2.229	2.619	2.550			1.851	1.992	-
Fraction of Entering SO_2 Captured by LAB in Column, %	44.98	52.39	56.01			45.52	52.82	-
No. of stages filled with water in 2nd column	-	-	-			-	-	4
Volume of water in column, ml	-	-	-			-	-	150
No. of stages filled with glass beads	-	-	-			-	-	4
Depth of glass beads/stage, cm	-	-	-			-	-	76
Depth of water/stage, cm	-	-	-			-	-	79
NaOH Concentration, mol/l	-	-	-			-	-	0.01221
Amount of NaOH at start, ml	-	-	-			-	-	12.35
Amount of NaOH at end, ml	-	-	-			-	-	32.75
Volume of NaOH Used, ml	-	-	-			-	-	20.40
Moles of H_2SO_4 captured in column, mmol	-	-	-			-	-	1.8681
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	2.7270	2.3800	1.6214			2.2150	1.3517	1.5216
3rd column	H	H	H			H	NH	NH
No. of stages containing LAB in 3rd contact column	1	1	1			4	4	-
(Note: a stage is when the gas is dispersed as bubbles in the liquid)								
No. of stages containing Glass Beads	1	1	1			4	4	-
Volume of LAB in column, ml	160	160	160			150	150	-
Depth of glass beads in stage, cm	34	34	34			76	76	-
Depth of LAB in stage, cm	52	52	52			79	79	-
Hyamine Concentration , mol/l	0.004	0.004	0.004			0.004	0.004	-

Continued

Amount of Hyamine at start, ml	17.00	4.85	23.75			1.50	11.55	-
Amount of Hyamine at end, ml	40.25	29.80	45.75			24.45	30.65	-
Volume of Hyamine used, ml	23.25	24.95	22.00			22.95	19.10	-
Moles of LAS measured in column, mmol	1.488	1.5968	1.408			1.377	1.146	-
Fraction of Entering SO_2 Captured by LAB in Column, %	54.57	67.09	70.29			62.17	64.42	-
No. of stages filled with water in 3rd column	-	-	-			-	-	1
Volume of water in column, ml	-	-	-			-	-	300
No of stages filled with glass beads	-	-	-			-	-	1
Depth of glass beads/stage, cm	-	-	-			-	-	34
Depth of water/stage, cm	-	-	-			-	-	52
NaOH Concentration, mol/l	-	-	-			-	-	0.01221
Amount of NaOH at start, ml	-	-	-			-	-	5.75
Amount of NaOH at end, ml	-	-	-			-	-	11.65
Volume of NaOH Used, ml	-	-	-			-	-	5.90
Moles of H_2SO_4 captured in column, mmol	-	-	-			-	-	1.0806
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	1.239	0.783	0.213			0.838	0.206	0.441
4th column	NH	NH	NH			NH	NH	NH
No. of stages containing LAB in 4th contact column	1	1	1			1	1	-
No. of stages containing Glass Beads	1	1	1			1	1	-
Volume of LAB in column, ml	240	240	240			160	160	-
Depth of glass beads in stage, cm	36	36	36			34	34	-
Depth of LAB in stage, cm	42	42	42			52	52	-
Hyamine Concentration , mol/l	0.004	0.004	0.004			0.004	0.004	-
Amount of Hyamine at start, ml	3.95	31.95	15.50			11.65	3.75	-
Amount of Hyamine at end, ml	7.05	35.65	18.05			15.85	8.45	-
Volume of Hyamine used, ml	3.10	3.70	2.55			4.20	4.70	-
Moles of LAS measured in column, mmol	0.2976	0.3552	0.2448			0.2688	0.3008	-
Fraction of Entering SO_2 Captured by LAB in Column, %	24.02	45.35	41.14			32.08	47.52	-
No. of stages filled with water in 4th column	-	-	-			-	-	1
Volume of water in column, ml	-	-	-			-	-	200
No. of stages filled with glass beads	-	-	-			-	-	1
Depth of glass beads/stage, cm	-	-	-			-	-	36
Depth of water/stage, cm	-	-	-			-	-	42
NaOH Concentration, mol/l	-	-	-			-	-	0.01221
Amount of NaOH at start, ml	-	-	-			-	-	7.05
Amount of NaOH at end, ml	-	-	-			-	-	10.25
Volume of NaOH Used, ml	-	-	-			-	-	3.20
Moles of H_2SO_4 captured in column, mmol	-	-	-			-	-	0.39
Moles of SO_2 (SO_3) Removed out the column by CO_2, mmol	0.9414	0.4280	-0.0314			0.5692	-0.0951	0.0503
Total (tubes)								
Total moles of LAS formed, mmol	5.539	6.242	5.820			5.441	6.208	0.000
Fraction of Entering SO_2 (SO_3) Recovered as LAS in Absorber, %	85.47	93.58	94.32			90.53	94.92	0.00
Fraction of Entering SO_2 (SO_3) Recovered in Absorber, %	85.47	93.58	100.54			90.53	101.56	99.16
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	/	/	93.82			/	93.47	93.98

Appendix D

Sample of Data Calculation

Table D.1. The data of experiment on November 8, 2006.

Date of Experiment	8-Nov
Room Temperature, ° C	20
Activated Carbon	
Weight of carbon in bed, g	8.62
Drying Temperature, ° C	250
N_2 or Air Flow rate, ml/min	50
Drying (Duration (hrs)	6
SO_3 Production	
Reactor (bed) volume, ml	17.7
Weight of Act. Carbon	8.62
Mass Flow Rate of SO_2, mg/min	3.50
Mass Flow Rate of air, g/min	0.453
SO_2 Concentration at end of filling	3500
Moles of SO_2 adsorbed on carbon, mmol	6.27
Moles of SO_2/gm of carbon, mmol/g	0.727
Mass of SO_3/gm of carbon, mg/g	58.19
Extraction of SO_3 with CO_2	
Type of Experiment (Single Pass/Recycle)	recycle
CO_2 mass flow rate to reactor, ml/min (at the experimental temp.&pres.)	0.50
$SCCO_2$ pressure, psi	1300
$SCCO_2$ temperature, ° C	40
Duration of CO_2 feed, hrs	4
Total CO_2 Fed to Reactor, ml	84
Recycle Duration, min	20
Recycle Flow rate, ml/min	20
Duration of CO_2 Release to Absorber, hrs	7
Titration of Activated Carbon	
Amount of water used to flush carbon bed, ml	500
Duration of Flush, min	30
NaOH Concentration, mol/l	0.01221
Beginning Amount of NaOH, ml	3.75
Final Amt. of NaOH, ml	4.80
Volume of NaOH Used, ml	1.05
Moles of H_2SO_4 in bed, mmol	0.3205
Moles of SO_2 (SO_3) Removed by CO_2, mmol	5.949
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	94.89
Absorber (Sulfonation Reactor)	
No. of columns in absorber	4
1st column	
No. of stages containing LAB in 1st contact column	1
(Note: a stage is when the gas is dispersed as bubbles in the liquid)	

Continued

No. of stages containing Glass Beads	1
Volume of LAB in column, ml	150
Depth of glass beads in stage, cm	75
Depth of LAB in stage, cm	78
Hyamine Concentration, mol/l	0.004
Amount of Hyamine at start, ml	3.80
Amount of Hyamine at end, ml	27.80
Volume of Hyamine used, ml	24.00
Moles of LAS measured in column, mmol	1.44
Fraction of Entering SO_2 Captured by LAB in Column, %	24.20
2nd column	
No. of stages containing LAB in 2nd contact column	4
(Note: a stage is when the gas is dispersed as bubbles in the liquid)	
No. of stages containing Glass Beads	4
Volume of LAB in column, ml	150
Depth of glass beads in stage, cm	76
Depth of LAB in stage, cm	79
Hyamine Concentration , mol/l	0.004
Amount of Hyamine at start, ml	5.45
Amount of Hyamine at end, ml	27.95
Volume of Hyamine used, ml	22.50
Moles of LAS measured in column, mmol	1.350
Fraction of Entering SO_2 Captured by LAB in Column, %	29.94
3rd column	
No. of stages containing LAB in 3rd contact column	1
(Note: a stage is when the gas is dispersed as bubbles in the liquid)	
No. of stages containing Glass Beads	1
Volume of LAB in column, ml	300
Depth of glass beads in stage, cm	34
Depth of LAB in stage, cm	52
Hyamine Concentration , mol/l	0.004
Amount of Hyamine at start, ml	8.90
Amount of Hyamine at end, ml	16.85
Volume of Hyamine used, ml	7.95
Moles of LAS measured in column, mmol	0.954
Fraction of Entering SO_2 Captured by LAB in Column, %	30.19
4th column	
No. of stages containing LAB in 4th contact column	1
No. of stages containing Glass Beads	1
Volume of LAB in column, ml	200
Depth of glass beads in stage, cm	36
Depth of LAB in stage, cm	42
Hyamine Concentration , mol/l	0.004
Amount of Hyamine at start, ml	23.55
Amount of Hyamine at end, ml	32.20

Continued

Volume of Hyamine used, ml	8.65
Moles of LAS measured in column, mmol	0.6920
Fraction of Entering SO_2 Captured by LAB in Column, %	31.38
Total (tubes)	
Total moles of LAS formed, mmol	4.436
Fraction of Entering SO_2 (SO_3) Recovered as LAS in Absorber, %	74.56
Fraction of Entering SO_2 (SO_3) Recovered in Absorber, %	74.56
% Recovery of adsorbed SO_2 (SO_3)) by CO_2	94.89

1. SO_2 adsorption and oxidation

The outer diameter of the reactor was 12.7 mm and the wall thickness was 1.5 mm.

The Area of carbon bed

$$=\frac{\pi}{4}(12.7-1.5\times 2)^2 = 73.898mm^2 = 0.79898cm^2$$

The volume of the bed

$$= 0.79898\times 24 = 17.7cm^3 = 17.7ml\,.$$

SO_2 feed concentration was 0.35% and feed duration was 178.8 min=2.98 h.

Total SO_2 fed $=\frac{PVt}{RT}$

$$=\frac{0.0035\times 0.35l/\min\times 178.8\min}{0.8026\frac{l.atm}{mol.k}\times 293.15K}$$

=0.009309 mole =9.309 mmole

From integration using polymath software, the under curve area

$$=2.12\times 10^5\ ppm.\min$$

Total SO_2 left in bed $= ppm.\min\times 10^{-6} 1/ppm\times SO_2 density, g/ml\times V, ml/\min$

$$= 2.120\times 10^5\times 10^{-6}\times 0.002620\times 350$$

=0.1944g

$$=\frac{0.1944g}{64.06g/mol} = 0.003035mole = 3.035mmole$$

The mass of SO_2 absorbed = 9.309-3.035 = 6.27 mmol

Moles of SO_2 per gram of carbon

$$= \frac{6.27}{8.62} = 0.727 mmol/g$$

2. Titration analysis of carbon bed flushing solution

Total acid determination

The volume of flushing water was 500 ml = 0.5 liter. The concentration of NaOH titrant was 0.01221 mol/l.

The concentration of total acid $= \frac{C_{NaOH}, mol/l \times V_{NaOH}, ml}{2 \times V_{sample}, ml}$

$$= \frac{0.01221 \times (4.80 - 3.75)}{2 \times 10} = 0.641 mmol/l$$

The total mass of SO_3 remaining in AC bed $= 0.641 mmol/l \times 0.5 = 0.3205 mmol$

Moles of SO_2/SO_3 removed by CO_2 $= 6.27 - 0.3205 = 5.949$

Recovery of adsorbed SO_2/SO_3 by CO_2 $= \frac{5.949}{6.27} \times 100\% = 94.89\%$.

3. Titration analysis of absorbers

If the absorber was water, the product was a H_2SO_4 solution. The method of total acid determination was the same as in 2. The differences were the water volume and the volume of NaOH consumed.

If the absorber was LAB, The mixture of LAS and LAB had to be titrated to know how much LAS was produced.

1st column

The volume of this absorber is 150 ml = 0.15 liter, and we assumed the volume did not change because the LAS production was small in this process. The volume of the sample was 10 ml.

The concentration of titrant, Hyamine 1622, was 0.004 mol/l.

Concentration of LAS measured in the 1st column

$$= \frac{C_{Hyamine}, mol/l \times V_{Hyamine}, ml}{V_{sample}, ml}$$

$$= \frac{0.004 \times (27.80 - 3.80)}{10}$$

$$= 0.0096 mol/l$$

Moles of LAS measured in the 1st column

$$= 0.0096 mol/l \times 0.15 l$$

$$= 0.00144 mol$$

$$= 1.44 mmol$$

Fraction of Entering SO_3 Captured by LAB in this Column

$$= \frac{1.44 mmol}{6.27 - 0.3205 mmol} \times 100\%$$

$$= 24.20\%$$

2nd column

The volume of this absorber is 150 ml = 0.15 liter, and the volume of sample was 10 ml.

Concentration of LAS measured in the 2nd column

$$= \frac{C_{Hyamine}, mol/l \times V_{Hyamine}, ml}{V_{sample}, ml}$$

$$= \frac{0.004 \times (27.95 - 5.45)}{10}$$

$$= 0.009 mol/l$$

Moles of LAS measured in the 2nd column

$$= 0.009 mol/l \times 0.15 l$$

$$= 0.00135 mol$$

$$= 1.35 mmol$$

Fraction of Entering SO_3 Captured by LAB in this Column

$$= \frac{1.35 mmol}{6.27 - 0.3205 - 1.44 mmol} \times 100\%$$

$$= 29.94\%$$

3rd column

The volume of this absorber is 300 ml = 0.3 liter, and the volume of sample was 10 ml.

Concentration of LAS measured in the 3rd column

$$= \frac{C_{Hya\min e}, mol/l \times V_{Hya\min e}, ml}{V_{sample}, ml}$$

$$= \frac{0.004 \times (16.85 - 8.90)}{10}$$

$$= 0.00318 mol/l$$

Moles of LAS measured in the 3rd column

$$= 0.00318 mol/l \times 0.3l$$

$$= 0.000954 mol$$

$$= 0.954 mmol$$

Fraction of Entering SO_3 Captured by LAB in this Column

$$= \frac{0.954 mmol}{6.27 - 0.3205 - 1.44 - 1.35 mmol} \times 100\%$$

$$= 30.19\%$$

4th column

The volume of this absorber is 200 ml = 0.2 liter, and the volume of sample was 10 ml.

Concentration of LAS measured in the 4th column

$$= \frac{C_{Hya\min e}, mol/l \times V_{Hya\min e}, ml}{V_{sample}, ml}$$

$$= \frac{0.004 \times (32.20 - 23.55)}{10}$$

$$= 0.00346 mol/l$$

Moles of LAS measured in the 4th column

$$= 0.00346 mol/l \times 0.2l$$

$$= 0.000692 mol$$

$$= 0.692 mmol$$

Fraction of Entering SO_3 Captured by LAB in this Column

$$= \frac{0.692 mmol}{6.27 - 0.3205 - 1.44 - 1.35 - 0.954 mmol} \times 100\%$$

$$= 31.38\%$$

Total moles of LAS formed in 4 columns

$$= 1.44 + 1.35 + 0.954 + 0.692$$

$$= 4.436 mmol$$

Fraction of entering SO_2/ SO_3 recovered as LAS in absorber

$$= \frac{4.436}{6.27 - 0.3205} \times 100\%$$
$$= 74.56\%$$

Because there was no water in these absorption columns, fraction of entering SO_2/ SO_3 recovered in the absorber was same as the fraction of entering SO_2/ SO_3 recovered as LAS, 74.56%. If there was water as absorber in the columns, the fraction equaled the sum of the fraction of entering SO_2/ SO_3 recovered as LAS and the fraction of entering SO_2/ SO_3 recovered as H_2SO_4.

The recovery of adsorbed SO_2/ SO_3 by CO_2

= 1- fraction of SO_2/ SO_3 remaining in the AC bed

$$= (1 - \frac{0.3205}{6.27}) \times 100\%$$
$$= 94.89\%$$

Appendix E

Data Tables

Table 2.1: SO_2 Emission Trends in Ontario (kilotonnes) (9)

	Source	Sulfur Dioxide (SO_2)			
		1990	1999	2010 (estimate)	2015 (estimate)
Industry Sources	Iron and Steel	27	23	20	19
	Cement	21	23	24	24
	Petroleum Refining	63	55	59	60
	Chemical	8	10	10	10
	Pulp and Paper	17	8	8	8
	Non-Ferrous Smelting	693	264	245	245
	Other Manufacturing	67	17	18	19
	Electricity	197	144	131	131
	Industry Total	1093	545	516	517
Non-industry Sources	Transportation	21	15	4	4
	Off-Road/Rail/Air/Marine	30	21	18-23	17-25
	Residential/ Commercial	13	7	6-8	6-8
	Other	0	0	0	0
	Ontario Total	1158	588	544-551	544-554
	Ontario Target	442			
	Gap	102-112			

Table3.1: The characteristics of activated carbon (BPL6×16) (4)

Properties	Value
Brunauer-Emmett-Teller surface area, m^2/g	1200
Average pore radius, nm	1.184
Pore volume, mL/g	0.710
Apparent density, g/mL	0.43
Average diameter, mm	2.18

Table 5.1. The results of SO_3 desorption experiments using continuous single-pass flushing

SO_2/SO_3 preloaded on AC, mmol	$SCCO_2$ flow rate, ml/min	$SCCO_2$ feed duration, h	Total $SCCO_2$ feed into reactor, ml	Mass of H_2SO_4 in flush water, mmol	SO_2/SO_3 remaining on AC, mmol	Sulfur recovery, %
6.02	0.45	8	216	2.656	2.656	55.89
6.04	0.47	9.6	271	2.530	2.530	58.12
5.81	0.50	10	306	2.656	2.656	54.29
4.66	0.51	11	337	2.047	2.047	56.08
6.21	0.53	14	445	2.761	2.761	55.54
4.89	0.51	17.5	536	1.923	1.923	60.67

Note: the temperature of $SCCO_2$ was 40°C, the pressure of $SCCO_2$ was 1300psi, and the heating duration was 3 h at a bed temperature of 200°C

$$\%,\text{Sulfur recovery} = 100 - \frac{\text{moles of } SO_2/SO_3 \text{ remaining on AC}}{\text{moles of } SO_{2/}SO_3 \text{ preloaded on AC}} \times 100$$

Table 5.2. The results of SO_3 desorption experiment using recycle flushing

SO_2/SO_3 preloaded on AC, mmol	$SCCO_2$ flow rate, ml/min	Flush duration of each recycle, min	Total $SCCO_2$ feed into reactor, ml	Mass of H_2SO_4 in flush water, mmol	SO_2/SO_3 remaining on AC, mmol	Sulfur recovery, %
5.83	10	20	150	1.191	1.191	79.58
6.28	20	10	154	1.175	1.175	81.29
5.83	20	20	170	0.809	0.809	86.13
*5.91	20	20	106	0.336	0.336	94.32

Note: the temperature of $SCCO_2$ was 40°C, the pressure of SCCO2 was 1300 psi, the heating duration was 4 h, at a heating temperature of 200°C. The total feed and recycle duration was 6 hours.

* For this experiment the heating duration was 6 h, at a temperature of 300°C.

Table 5.3. SO_3 recovery as a function of the heating duration.

Heating duration, h	2	3	4	5	6
% Sulfur recovery, %	56.08	57.05	60.67	64.15	71.04

Note: The temperature of $SCCO_2$ was 40°C, pressure was 1300 psi, and carbon bed temperature was 200°C, continuous single-pass flushing was employed.

Table 5.4. SO_3 recovery as a function of the bed temperature.

Heating temperature, °C	200	230	250	300
SO_3 recovery, %	71.04	86.13	93.06	94.32

Note: The temperature of $SCCO_2$ was 40°C, pressure was 1300 psi, the heating duration was 6 h, recycled flushing was employed, except for the 200°C experiment.

Table 5.5 Comparison of ratio of sulfur remaining to preloaded for experiments of flushing the bed after one run and after three runs.

Date	Oct.24	Dec.4	Dec.10	Dec.15
Moles of SO_3 preloaded, mmol	6.56	6.48	6.67	6.17
Sulfur remaining in bed, mmol	0.3968	/	/	0.3816
Ratio of S remaining to preloaded, %	6.05	/	/	6.18
S recovery, %	93.95	/	/	93.82

Table 5.6. Comparison of results using different sizes of reactors

Date	Jul.18, 06	Aug.9, 06	Aug.12, 06
Moles of SO_3 preloaded, mmol	5.96	42.35	41.76
Sulfur remaining in bed, mmol	0.3968	3.6935	3.4493
Ratio of S remaining to preloaded, %	6.66	8.72	8.26
S recovery, %	93.34	91.28	91.74

Table 5.7. Comparison of ratios of SO_3 absorbed in columns filled with glass beads or unfilled.

1st & 3rd column	Mass of SO_3 preload, mmol	Mass of SO_3 absorbed in columns					
		1st column, mmol	Ratio, %	2nd column, mmol	Ratio, %	3rd column, mmol	Ratio, %
Without glass beads	6.75	0.8930	13.23	1.3468*	19.95*	0.6410	9.50
With glass beads	6.45	1.4670	22.74	1.2300	19.11	1.7500	27.12

Note:

1. The absorbers in the 1st and 2nd columns contained LAB, while the 3rd column contained water
2. Ratios are the mass of SO_3 absorbed by the column to the total mass of SO_3 preloaded on AC.
3. 2nd column in the two experiments were filled with glass beads.

Table 5.8 Comparison of ratios of SO_3 absorbed in columns filled with glass beads or unfilled.

3rd and 4th column	Mass of SO_3 preload, mmol	Mass of SO_3 absorbed in columns							
		1st column, mmol	Ratio, %	2nd colum, mmol	Ratio, %	3rd column, mmol	Ratio, %	4th column, mmol	Ratio, %
Without glass beads	6.52	1.443	22.13	1.36	20.80	0.58	8.83	0.34	5.21
With glass beads	6.27	1.440	22.97	1.35	21.53	0.95	15.22	0.69	11.04

Note:

1. All columns were filled with LAB.
2. Ratios are the mass of SO_3 absorbed by the column to the total mass of SO_3 preloaded on AC.
3. 1st and 2nd columns in the two experiments were filled with glass beads.

Table 5.9. Effect of different absorbers in the 3rd and 4th columns on SO_3 absorption.

Experiment Number	Mass of SO_3 preload, mmol	Mass of SO_3 absorbed in columns							
		1st column, mmol	Ratio, %	2nd column, mmol	Ratio, %	3rd column, mmol	Ratio, %	4th column, mmol	Ratio, %
1	6.34	2.569	40.52	1.87	29.47	1.08	17.04	0.39	6.14
2	6.67	1.845	27.66	1.52	22.71	2.12	31.85	0.66	9.89
3	6.27	1.44	22.97	1.35	21.53	0.95	15.22	0.69	11.04

Note: 1. In the 1st experiment, all columns were filled with water; in the 2nd, the 1st and 2nd column were filled with LAB, and the 3rd and 4th columns were filled with water; in the 3rd, all columns filled with LAB.

2. Ratios are the mass of SO_3 absorbed by the column to the total mass of SO_3 preloaded on AC.

3. All columns in three experiments were filled with glass beads.

Table 5.10. The comparison of ratio of SO3 absorbed in columns, which were heated or not.

2nd & 3rd column	Mass of SO3 preload, mmol	Mass of SO_3 absorbed in columns							
		1st column, mmol	Ratio, %	2nd column, mmol	Ratio, %	3rd column, mmol	Ratio, %	4th column, mmol	Ratio, %
Not heated	6.27	1.443	22.97	1.36	21.53	0.58	15.22	0.34	11.04
Heated	6.48	1.440	23.52	1.35	34.40	0.95	22.96	0.69	4.59

Note:

1. All of the columns were filled with LAB.
2. Ratios are the mass of SO_3 absorbed by the column to the total mass of SO_3 preloaded on AC.
3. All columns in the two experiments were filled with glass beads, and the 1st and 4th columns were not heated.

Table 5.11 Ratio of SO_3 absorbed in columns at stage pressure reducing experiments.

Experiment Number	Mass of SO_3 preload, mmol	Mass of SO_3 absorbed in columns							
		1st column, mmol	Ratio, %	2nd column, mmol	Ratio, %	3rd column, mmol	Ratio, %	4th column, mmol	Ratio, %
1	6.48	1.440	23.52	1.35	34.40	0.95	22.96	0.69	4.59
2	6.01	1.944	32.35	1.851	30.80	1.38	22.91	0.269	4.47
3	6.54	2.769	42.34	1.992	30.46	1.15	17.52	0.301	4.60

Note:

1. All of columns were filled with LAB and glass beads.
2. Ratios are the mass of SO_3 absorbed by the column to the total mass of SO_3 preloaded on AC.
3. In 1st experiment, pressure change directly from1300psi to about 1 atmosphere pressure. In the 2nd and 3rd experiments, the pressure changes from1300 psi to 600 psi, then from 600 psi to about 1 atmosphere pressure.
4. The 1st and 2nd columns in 3rd experiment were heated. The 2nd and 3rd columns in 1st and 2nd experiment s were heated

Appendix F

LAS Analysis Experiments Using Different Indicator

LAS/LAB Solution Preparation:

Weight 17.3g LAS, equal to 17.3/321 = 0.0539 mol

Weight 149.0g LAB, equal to 149.0/241 = 0.618 mol

Mix them.

The volume of above LAS/LAB solution is 193 ml.

The concentration of LAS is:

$$\frac{0.0539mol}{193ml} \times \frac{1000ml}{l} = 0.28mol/l$$

Case 1: Take 0.3ml above LAS/LAB solution.

Take 0.3ml LAS/LAB solution, add 20ml H_2O, 15ml chloroform and 10ml **MI**.

The mass of LAS is:

$$\frac{0.3}{193} \times 0.0539 = 8.378 \times 10^{-5} mol$$

The volume of Hyamine 1622 solution (C=0.004M) used in the titration:

Experiment 1: 20.65ml

Experiment 2: 20.70ml

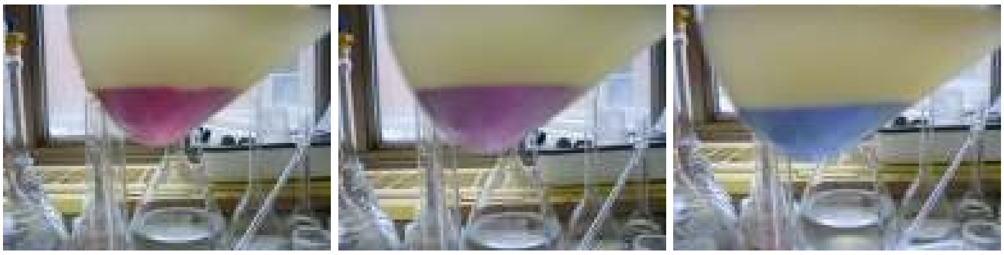
the average volume is 20.68ml

The mass of LAS we get it from titration is:

$$\frac{20.68}{1000} \times 0.004 = 8.27 \times 10^{-5} mol$$

So the veracity of this experiment is $\frac{8.27 \times 10^{-5}}{8.378 \times 10^{-5}} \times 100\% = 98.7\%$

The color changes (close to the end point) in the this Experiment are shown as follows:



Take 0.3ml LAS/LAB solution, add 20ml H_2O, 15ml chloroform , 1ml 0.01N H_2SO_4 and 5ml **DY**.

The volume of Hyamine 1622 solution (C=0.004M) used in the titration:

Experiment 1: 20.20ml

Experiment 1: 20.40ml

the average volume is 20.30ml

The mass of LAS we get it from titration is:

$$\frac{20.30}{1000} \times 0.004 = 8.12 \times 10^{-5} mol$$

So the veracity of this experiment is $\frac{8.12 \times 10^{-5}}{8.378 \times 10^{-5}} \times 100\% = 96.9\%$

The color changes (close to the end point) in the this Experiment are shown as follows:

The colors of the chloroform are sensitive in both of above experiments, and the end points are easy to observe.

Diluted LAS/LAB Solution Preparation:

Take 3ml above prepared LAS/LAB solution and dilute it with LAB to 100ml. So the concentration of LAS is:

$$0.0539mol \times \frac{3ml}{193ml} \times \frac{1000ml/l}{100ml} = 0.008378mol/l$$

Case 2: Take 10ml diluted LAS/LAB solution.

Take 10ml above diluted LAS/LAB solution, add 20ml H_2O, 15ml chloroform and 10ml MI.

The mass of LAS is:

$$\frac{10ml}{1000ml/l} \times 0.008378mol/l = 8.378 \times 10^{-5} mol$$

The volume of hyamine 1622 solution (C=0.004M) used in the titration:

Experiment 1: 20.10ml

Experiment 2: 20.00ml

the average volume is 20.05ml

The mass of LAS we get it from titration is:

$$\frac{20.05}{1000} \times 0.004 = 8.02 \times 10^{-5} mol$$

So the veracity of this experiment is $\frac{8.02 \times 10^{-5}}{8.378 \times 10^{-5}} \times 100\% = 95.7\%$

The color changes (close to the end point) in the this Experiment are shown as follows:

Take 10ml above LAS/LAB solution, add 20ml H_2O, 15ml chloroform , 1ml 0.01N H_2SO_4 and 5ml DY.

The volume of hyamine 1622 solution (C=0.004M) used in the titration:

the average volume is 20.00ml

The mass of LAS we get it from titration is:

$$\frac{20.00}{1000} \times 0.004 = 8.00 \times 10^{-5} mol$$

So the veracity of this experiment is $\frac{8.00 \times 10^{-5}}{8.378 \times 10^{-5}} \times 100\% = 95.5\%$

The colors of the chloroform is feint in experiment, in which mixed indicator is used as indicator, and the end points are easy to observe.

Conclusions

1. The veracities of these experiments are all more than 95%. Therefore, both above indicators could be used as indicator in LAS analysis.

2. If the concentration of LAS is high (e.g. 0.28 mol/l), both of above indicators can be used, and they are good indicator choice. However, if the concentration of LAS is low (e.g. 0.008 mol/l), using dimethyl yellow as indicator is better than using Mixed Indicator.