Production of Linear Alkybenzene Sulfonic Acid (LAS) at High Pressure in Supercritical Carbon Dioxide Medium

by

Mohammad Basry Attar

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, 2010

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.

I understand that my thesis may be made electronically available to the public.

Abstract

Linear Alkyl benzene Sulfonic Acid (LAS) is the main ingredient of many commercial formulations for industrial and domestic synthetic detergents. The current industrial LAS production method includes sulfonation of linear alkylbenzene (LAB) with sulfur trioxide in tubular falling film reactors. In such reactors a diluted gaseous stream of SO_3 and dry air, feed gas, is contacted with liquid LAB while both reactants flow co-currently downward. The reaction is highly exothermic and product quality is primarily dependent on heat removal efficiency from the reactors, and also contact time.

 This research project investigates a new route for the production of LAS. This new method employs SO_2 oxidation over activated carbon at $25°C$ to SO_3, followed by the extraction of the adsorbed SO_3 from the activated carbon by supercritical carbon dioxide ($SCCO_2$). The condensed phase CO_2-SO_3 mixture after expansion is contacted with LAB where sulfonation of this substrate occurs to yield LAS. The new route should offer lower operating temperatures and lower feed gas SO_3 concentrations in the sulfonation reaction to minimize loss of LAB to side-reactions and reduce LAS contamination (that appears as unacceptable product discoloration).

The laboratory set up was designed, assembled and in total 25 experiments were carried out. Over the course of experiments a number of remedial actions were taken to improve set up functionality and reaction yield. The problems needed to be tackled included feed gas moisture removal, SO_2/SO_3 adsorption/desorption efficiency, homogeneous mixing of reactants and reducing the $SCCO_2$/SO_3 flow rate through LAB columns.
The maximum LAB/LAS conversion obtained was 3.6 % per sulfonation column. The maximum SO_3 removal efficiency from activated carbon obtained was 77%.
It was also found that nitrogen gas in a specific temperature range may be used as the desorbing agent in lieu of supercritical carbon dioxide with satisfactory performance.
As supplementary data, the Brauner-Emmet-Teller surface area of activated carbon type BPL 6x16 from "Calgon Carbon Corporation" was measured.

Acknowledgements

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

The general practice to produce Linear Alkylbenzene Sulfonic acid (LAS) is the sulfonation of Linear Alkylbenzene (LAB) with sulfur trioxide (SO_3). In industry, multi-tube falling film reactors are used for this purpose. In such reactors a diluted gaseous stream of SO_3 in dry air is contacted with liquid LAB while both reactants flow co-currently downward. The reaction is highly exothermic and product quality depends primarily on heat removal efficiency from reactors and contact time.

Throughout this research, the SO_3 required to carry out LAB sulfonation experiments was produced by catalytic oxidation of SO_2 over activated carbon. SO_3 was then extracted by supercritical carbon dioxide ($SCCO_2$) and the $SCCO_2/SO_3$ phase passed through LAB reactors where the main sulfonation reaction occurred.

Activated carbon is known as a SO_2 adsorbent in Environmental Engineering applications. In general, SO_2 emission control is performed using either Scrubbing Throwaway or Regenerative methods, each of which may include wet or dry processes. In regenerative-dry processes SO_2 is adsorbed on catalysts such as activated carbon, copper oxide, etc. In such processes, in the case of activated carbon, the reaction of SO_2 to form H_2SO_4 or oxidation of SO_2 to SO_3 may be catalyzed. If profitable, sulfuric acid may be recovered or SO_3 may be used in a useful sulfonation reaction. Activated carbon could be rejuvenated later for further use. [1]

Previous attempts have been made in Chemical Engineering Department at the University of Waterloo to remove SO_2 from diluted streams using activated carbon. The ability of non-aqueous solvents such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, to remove SO_3 formed on carbon sites was investigated by Panthaky. [2]

Wattanakasemtham [3] used near-critical carbon dioxide as flushing agent to remove SO_3 from activated carbon and achieved 80% removal efficiency.

Yuan [4] used supercritical carbon dioxide as flushing agent to remove SO_3 from activated carbon and achieved 90% removal efficiency. The results obtained by using small size column carrying 8.62 grams of activated carbon. Meanwhile in that work, supercritical CO_2 carrying SO_3, run through linear alkylbenzene (LAB) columns to produce LAS at atmospheric pressure. The reported LAB/LAS Conversion rate was about 25% per sulfonation reactor.

Based on the previous research, the feasibility of the scale up of LAS production process at high pressure in supercritical carbon dioxide medium was intended to be evaluated.

The intended research work scheme included design of, assembling laboratory set up and running sulfonation experiments at high pressure (86 bar) to produce LAS, and finally, upon achieving satisfactory LAS quality, switching from batch to continuous operation.

To proceed with the laboratory work, the first step was to design and assemble experimental set up. Safety criteria were strictly followed as reaction medium involved high pressure and corrosive environment. The laboratory apparatus located under fume hood and surrounded by safety enclosure.

The new route of LAS production includes adsorption (oxidation) and sulfonation processes. Accordingly, a few factors at each process seemed to be crucial to enhance set up functionality. The problems needed to be tackled may be briefed as, 1) feed gas moisture removal, 2) optimizing SO_2/SO_3 adsorption/desorption on activated carbon, 3) homogeneous mixing of the reactants and 4) optimizing flow rate of $SCCO_2/SO_3$ phase through LAB columns.

Chapter 2

Literature Review

2.1 Reactions at High Pressure

2.1.1 Considerations for Reaction at High Pressure:

To predict the effect of high pressure on chemical equilibrium and reaction rate, it is crucial to estimate the volume changes that occur in the overall reaction.

The volume-changes are dependent upon the degree of compression of the reaction system, and may be partly determined by properties such as the dielectric constant, which are also pressure dependent. The quantitative treatment of chemical reactions at high pressure requires the accurate knowledge of the compressibility of dense gases and liquids, of their phase behavior, and of the effects of pressure on diffusion, viscous flow and other physical properties. [5]

Compression of Gases: Pressure-Volume-Temperature relationship for real gases can be predicted by van der Waals, Peng-Robinson and virial equations of state. [5]

Compression of Liquids: Effect of pressure is much less compared with gases but it is appreciable at high pressures. Chemical equilibria, reaction rates, and dielectric constant and viscosity are usually affected by compression. At ordinary temperatures most liquids show a reduction in volume by between 4 to 10 percent when the pressure is increased from 1 to 1000 atm. The molecular structure also plays a role during compression. For example, it is known that a ring-structure introduces a rigidity which decreases the compression. An empirical equation which can be used to estimate high pressure isotherms of liquids is Tait's equation (equation 2.1). [5]

$$\frac{\Delta V}{V^\circ} = k = C * \log\left(\frac{B + P}{B + P^\circ}\right) \qquad (2.1)$$

Here, B and C are constants, k is the compression, or fractional change in volume, when the pressure is changed isothermally from P° to P $(P > P^\circ)$.

Pressure and Viscosity of Gases: At low pressures and temperatures viscosity of a gas is independent of pressure and it is in direct relationship with temperature. As pressure increases, gas behavior becomes more and more liquid-like and viscosity increases with increasing pressure and decreases with increasing temperature. [5]

Pressure and Viscosity of Liquids: The effect of pressure on the viscosities of liquids is notably large. it was found that the viscosities of many organic substances increase by factors of between 10 and 1000 when the pressure is raised from 1 to 11800 bars. This increase in viscosity affects the rate of chemical reactions. Fast reactions with low activation energies may be retarded by increase of viscosity at a few thousand atmosphere pressure. [5]

Pressure and the Dielectric Constant: These effects are important because they have an impact on the volume changes which accompany the reactions of ionically charged species, and these volume-changes in turn determine the effects on the rates or equilibria of the reactions. The dielectric constants of non-polar gases and liquids increase slowly with pressure. [5]

2.1.2 Molecular Theory of Reactions at High Pressure

In transition state theory, a reaction of the general type

$$a \, A + b \, B \; +.... \; \longrightarrow \; X^{\ddagger} \; \longrightarrow \; \ell \, L + m \, M +..... \quad (2.2)$$
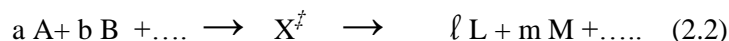
is assumed to proceed through a state of maximum energy $X^{\ddagger}$ that can be considered as a definite molecular species in equilibrium with the reactants and the products.

To discuss experimental data, the following equation was suggested [6]:

$$\frac{\partial(RT\ \ln Kc)}{\partial P} = -\Delta V^{\ddagger} \qquad (2.3)$$

Here, $\Delta V^{\ddagger}$ is the volume change upon formation of activated complex, also called activation volume, and is defined by

$$\Delta V^{\ddagger} = \Delta V_{(1)}^{\ddagger} + \Delta V_{(2)}^{\ddagger} = V_{x}^{\ddagger} - a\ V_{A} - b\ V_{B} \qquad (2.4)$$

Activation volume can be split into two terms $\Delta V_{(1)}^{\ddagger}$ and $\Delta V_{(2)}^{\ddagger}$. $\Delta V_{(1)}^{\ddagger}$ is the change in the volume of the reacting molecules as they form the transition state. Terms contributing to $\Delta V_{(1)}^{\ddagger}$ are those connected with the partial formation of new chemical bonds and with the stretching and partial breaking of existing bonds during the activation process. The breaking of a covalent bond in a molecule causes a large increase in the total molecular volume. Elongation percent of bonds when forming activated complex varies between 10 to 100 percent. The formation of covalent bonds is the reverse of the above phenomenon and leads to shrinkage.

When simultaneous bond formation and breaking happens, the first term predominates, which leads to negative $\Delta V_{(1)}^{\ddagger}$. Some calculated values of $\Delta V_{(1)}^{\ddagger}$ are shown in Table D.1 of Appendix D.

Terms contributing to $\Delta V_{(2)}^{\ddagger}$ deal with the change in volume of solvent during the activation process. It may rise because the solvent molecules rearrange their packing for purely steric reasons, to accommodate the changed shape of the reacting molecules, or because there is tightening or loosening of the electrostatic bonds between the solvent and reactant species. The first effect seems to be quite unimportant in liquid systems. The second effect can be extremely important in reactions in which electrical charges are developed or are neutralized.

It is expected that $\Delta V_{(2)}^{\ddagger}$ to be as important as $\Delta V_{(1)}^{\ddagger}$ in reactions which produce or remove electrical charges. [6, 7]

5

2.2 Supercritical Carbon Dioxide - Properties and Effects on Reactions

The particularity and practicality of carbon dioxide is due to its properties such as, relatively nontoxic, not supporting combustion, exhibiting readily attainable critical parameters, commercial availability, and its environmental friendliness.

2.2.1 Supercritical Carbon Dioxide Properties

The physical state of a substance of fixed composition can be described by a phase (Pressure-Temperature) diagram, Such as the one shown in Figure 2.1.
The critical temperature is the highest temperature at which a gas can be converted to a liquid by increasing pressure. The critical pressure is defined as the highest pressure at which a liquid can be converted to a gas by an increase in the liquid temperature. A fluid is called supercritical when its temperature and pressure are above critical temperature and pressure, respectively. In critical region of the phase diagram there is only one phase and its properties are a mix of both gas and liquid properties.

Properties of supercritical CO_2 that vary with pressure and temperature are density, solvating power, diffusivity, viscosity, thermal conductivity, dielectric constant, partial molar volumes and heat capacity.

At low pressures density of supercritical carbon dioxide decreases dramatically with an increase in temperature. At high pressures, changes in temperature have much less effect on density. Density- temperature- pressure relationships for CO_2 are shown in Table 2.1. As a noticeable example in Table 2.1, at 40°C, by changing the pressure from 70 to 104 bar, density changes from 0.20 to 0.65 g/ml. [8]

Variation of reduced density with reduced pressure (P_r) and temperature (T_r) is shown in Figure 2.2. Between $1 < T_r < 1.2$ small increase in pressure causes dramatic increase in density.
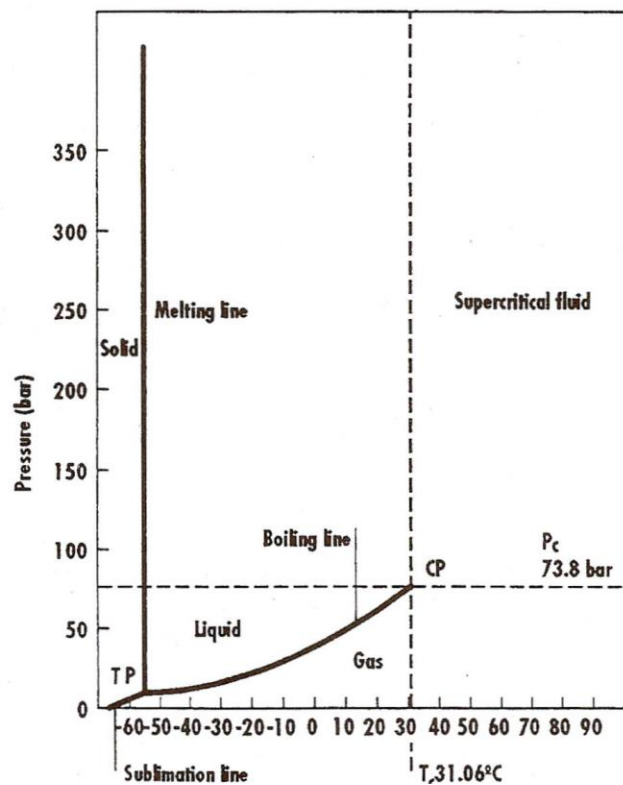
Figure 2.1 P-T diagram of CO_2 ; CP=critical point, TP=triple point, PC=critical pressure , TC= critical temperature. [8]

Supercritical and liquid CO_2 both could be used as solvents. The solvating power of supercritical CO_2 is dependent on its temperature and pressure (or density). Density is a better parameter than pressure when evaluating solubility–temperature relationships. In general, solvent power of a supercritical fluid increases with density at a given temperature. And also, solvent power of a supercritical fluid increases with temperature at a given density.

Solvent strength changes continuously as the material goes from the near critical to the supercritical region. So, it is possible to fine tune the solvating strength of the fluid in a favorite process. Effects of temperature, pressure and density on the solubility of naphthalene in supercritical CO_2 are depicted in Figures E.1 and E.2 of Appendix E.

Density (g/mL)	40°C	50°C	60°C	70°C	80°C	90°C	100°C	110°C	120°C
1.000	526	618							
0.95	383	463	544	644	680				
0.90	281	350	420	489	518				
0.85	211	269	329	401	447				
0.80	164	213	264	314	365	416	467		
0.75	134	175	218	261	305	348	392	436	510
0.70	115	150	187	223	260	297	334	372	425
0.65	104	133	165	196	227	259	290	322	354
0.60	97	122	149	176	203	229	256	284	311
0.55	93	115	138	161	183	206	230	252	276
0.50	91	109	129	148	168	188	207	227	246
0.45	89	104	122	138	155	172	188	205	221
0.40	87	100	115	129	143	157	171	185	197
0.35	84	96	108	120	132	144	155	167	178
0.30	81	90	101	111	121	130	140	149	158
0.25	77	84	93	100	108	116	123	130	137
0.20	70	75	82	88	94	99	105	110	116

Table 2.1 Density, pressure and temperature relation for CO_2. [8]
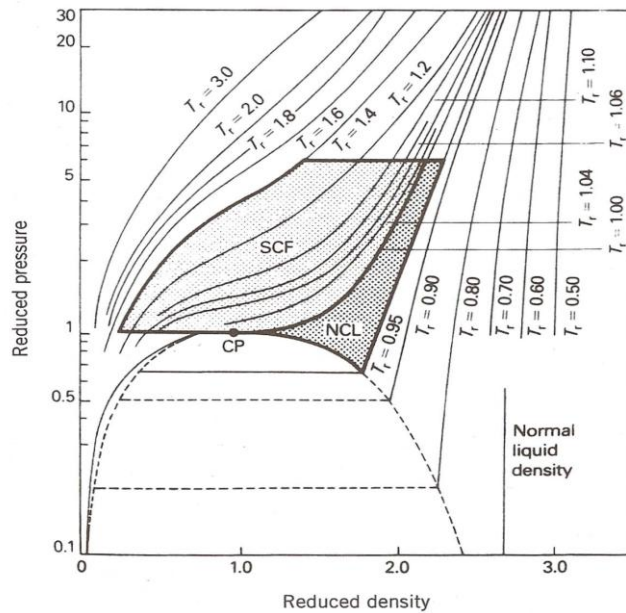
Figure 2.2 Variation of reduced pressure and density of CO_2 with temperature. [8]

8

Viscosity and diffusivity of supercritical fluids are dependent on temperature and pressure. They approach those of liquids as pressure is increased.

Whereas an increase in temperature leads to an increase in gas viscosity, the opposite is true for supercritical fluids. Viscosity behavior of CO_2 is shown in Figure E.3 of Appendix E.

At fixed pressure diffusivity of supercritical carbon dioxide increases with an increase in temperature. Diffusivity variation of carbon dioxide is represented in Figure E.4 of Appendix E.

As Figures E.3 and E.4 show, changes in viscosity and diffusivity are most pronounced in the region around the critical point. [8]

2.2.2-Effects of Supercritical CO_2 on Reactions

It is known that supercritical fluids can affect reaction rates in a variety of ways. The effects can be divided into increased diffusion rates, increased reactant solubilities, elimination of mass transfer resistances, facilitated separation, catalyst life extension, pressure effect on the rate constant, changes in selectivities, and also, effects of local densities and local compositions. For a chemical reaction there could be one or more mechanisms that have a significant effect on the reaction rate. [9]

a) Increased diffusion rates

Supercritical fluids have higher diffusivities compared with liquids because fluid has a lower density and is more gas like. In addition, temperature and pressure have effects on diffusion coefficients. The diffusion coefficient varies considerably in the region around the critical point so one would expect an increase in the rate constant of diffusion controlled reactions.

In modeling the rate constant for a diffusion controlled-bimolecular reaction with the Stokes-Einstein equation (which states that for a bimolecular reaction the rate constant is given by $8KT/3\mu$ where μ is solution viscosity) an increase in the bimolecular rate constant by a factor of 2.5, over a small pressure range at 35°C was reported by Iwasaki

9

and Takahashi [10] . Stokes-Einstein equation predicts that the effect is even more dramatic along isotherms closer to critical temperature, which is 31$°$C for CO_2. [9] Bright et al. [11] showed that in decreasing the pressure from 88 to 75 bar, the diffusion controlled rate constant increased from 1.1 to 1.7 x10^{-11} m^{-1} s^{-1}, which corresponds with that predicted from the Stokes–Einstein equation and experimental solvent viscosity data.

 b) Increased reactant solubility and elimination of mass transfer
Some reactions that normally would be carried out in a multiphase operation may be facilitated by a single phase supercritical process. [9]

c) Facilitated separation
The solubilities of solutes in supercritical fluids are strong functions of temperature in the compressible region near the critical points. Therefore careful selection of operating conditions may allow the easy precipitation of the product if it is less soluble than the reactants. [9]

 d) Pressure effects on rate constants
The most pronounced effect of pressure on reactions in the supercritical region has been attributed to the thermodynamic pressure effect on the reaction rate constant. The effect of pressure is usually shown with activation volumes, as pointed out in Section 2.1.2. At elevated pressures, the changes in the activation volumes of several thousand cc/gmol have been reported for reactants in some chemical reactions, that means order of magnitude changes in the rate constant with small changes in pressure.
Generally, it is difficult to estimate pressure effects with good accuracy since it requires that the values of partial molar volumes of the transition state and the reactants to be known. However, very few experimental values of partial molar volumes of supercritical fluids are available. Also, the characteristics of transition states, especially near critical point, are not exactly known. Using equations of state would be one alternative to calculate partial molar volumes with reasonable estimates. [9]
In the Diels-Alder reaction of isoprene and maleic anhydride in supercritical carbon dioxide, Paulaitis and Alexander [12] reported a two fold increase in the rate constant at

$35^\circ C$, with a 10 bar pressure increase. In their work they also observed an increase in the rate constant with an increase in pressure until it approached that obtainable in liquid solutions at high pressure where the fluid is more liquid like. The pressure effect was found to be less pronounced at higher temperatures, away from the critical temperature of pure CO_2.

In Exciplex formation between naphthalene and triethylamine in carbon dioxide, Brennecke et. al. [13] reported pronounced pressure effects on the rate constant at pressures and temperatures around the critical point. They also estimated the activation volume of -14000 cc/mol by using the Peng-Robinson equation of state.

e) Changes in selectivity

Where several competing or parallel reactions occur, a high pressure reaction medium may help improve selectivity since the thermodynamic pressure effect on each of the individual rate constants could be different. In other words, the activation volumes are not equal for all the reactions. [9]

f) Effects on local densities and local composition

Some spectroscopic and theoretical studies have shown that the local density of supercritical fluid solvent around a dilute solute molecule could be notably greater than the bulk density. This is especially believed to be the case, in the compressible region near the critical point. It was observed that at pressures away from the critical point, the local compositions approached those in the bulk. [14, 15]

In Molecular Dynamics studies of a supercritical mixtures modeled by a simple Lennard-Jones potential, Petsche and Debenedetti [16] pointed out the presence of a dynamic solvent cluster around solute molecules which loses its identity in a few pico-seconds.

It is proposed that the locally dense solvent may affect a reaction in two ways. First, if the reaction is sensitive to a density-dependent property, such as the dielectric constant, the time averaged locally dense medium, which would have a higher dielectric constant than the bulk, might influence that reaction. Second, the solvent around a solute might be considered as a cage, which could prevent the entrance or escape of species. [9]

2.3 Anionic Surfactant Production

The general method to produce anionic surfactants is sulfonation of a fatty hydrocarbon by a sulfonating agent such as SO_3, to produce an organic acid similar to fatty acids and then neutralize it with an alkali, usually sodium or potassium hydroxide.

LAS

$CH_3\text{-}(CH_2)_m\text{-}CH\text{-}(CH_2)_n\text{-}CH_3$

SO_3H

LAB

$CH_3\text{-}(CH_2)_m\text{-}CH\text{-}(CH_2)_n\text{-}CH_3$

- m+n=7-10
- Linear AlkylChain
- Average Molecular Weight=342
- Density 1.2 gr/cc

- m+n=7-10
- Linear AlkylChain
- Average Molecular Weight=240
- Density 0.86 gr/cc
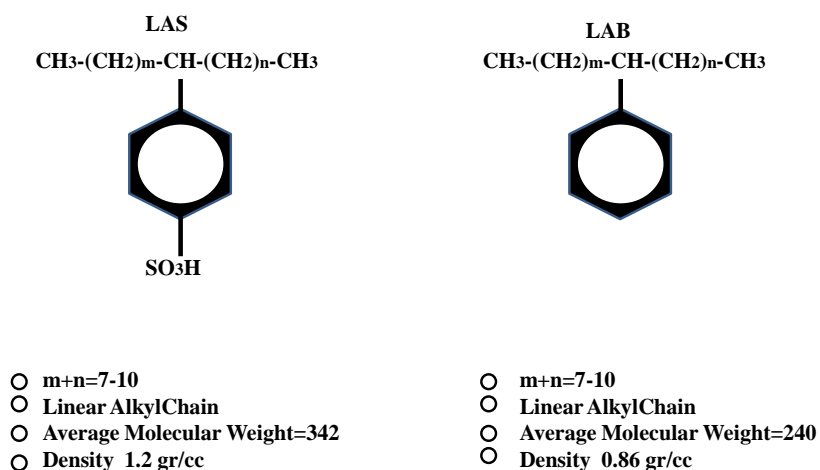
Figure 2.3 The molecular structure of Linear Alkylbenzene and Linear Alkylbenzene Sulfonic Acid

2.3.1 Linear Alkylbenzene (LAB) and Linear Alkylbenzene Sulfonic Acid (LAS)

LAS is an anionic surfactant characterized by a hydrophobic and a hydrophilic group. It is produced by sulfonation of linear alkyl benzene (LAB). LAS is actually a complex mixture of homologues of different alkyl chain lengths and phenyl positional isomers of 2 to 5-phenyl. Homologue proportions are dictated by the starting materials. Each homologue class contains an aromatic ring sulfonated at the "para" position and attached to a linear alkyl chain (C_{10} to C_{13} or C_{14}) at any position with the exception of terminal one (1-phenyl).

The starting material LAB is produced by the alkylation of benzene with *n*-paraffins in the presence of hydrogen fluoride (HF) or aluminum chloride ($AlCl_3$) as a catalyst. The total world LAB production capacity in 2002 was estimated at 2.5 million tons, virtually all LAB is transformed into LAS.

Quantitatively, LAS is the largest-volume synthetic surfactant produced, because of its relatively low production cost, good performance, the fact that it can be dried to a stable powder and also because of its biodegradable environmental friendliness.
More than 80% of LAS produced worldwide is used in detergent manufacturing. It also has some applications in textile processing, as a wetting or dispersing agent.
LAS can be used in both acidic and alkaline formulations as well as in liquid and powder forms. It is also compatible with other surfactants.

LAS's biodegradability and compatibility with other surfactants make it the best choice for detergent production. It may be used with other non-ionic and cationic surfactants to improve the cleaning ability of detergents. [17]
As a typical example, the components of heavy duty laundry detergent-powder are shown in Table D.2 (Appendix D). As can be seen, anionic and non-ionic surfactants can be used together to improve the cleaning properties of the detergent. [18]

In industry, falling film reactors are used in LAS production processes. Sulfonation of LAB by SO_3 is carried out at ambient pressure. The reaction is heterogeneous with LAB in the liquid phase and SO_3 in the gas phase, usually 5% mixed with dry air, and is exothermic. The reaction exotherm is about -40 Kcal/mol, so cooling plays a major role in product quality control. [19, 20]

2.3.2 LAB Sulfonation in Falling Film Reactors - Reaction Mechanism and Kinetics

R = sec C10-14 alkyl

Figure 2.4 Sulfonation of Linear Alkylbenzene to produce
Linear Alkylbenzene Sulfonic Acid

Sulfonation of linear alkylbenzenes (LAB) is considered to be first order with respect to both SO_3 and LAB. The most widely accepted hypothesis for the reaction pathway is depicted in Figures 2.5 and 2.6. It is believed that sulfonation starts with the reaction of SO_3 with linear alkylbenzene to produce some linear alkylbenzene sulfonic acid (LAS) and pyrosulfonic acid, an intermediate compound, as shown in Figure 2.5. As reactants flow down the reactor the main reaction mechanism takes over. In this step, pyrosulfonic acid reacts with LAB, **1**, to produce 2 mol equiv of LAS, **6,** as shown in Figure 2.6. One of these mole equivalents can be regarded as replacing the one consumed in the first step, and the other can be regarded as contributing to the increase in conversion. [19, 20]

The well-known side reactions are the formation of sulfone (usually considered as an inert by-product), LAS anhydride and sulfuric acid.

  A good quality product typically contains; alkybenzene sulfonic acid, sulfuric acid and neutral oil, with the percentages of 97-98, 0.5 and 1.5-2.5%, respectively. Any dialkyltetralins present are also sulfonated and in the final product will function as hydrotropes. The neutral oil consists mainly of the by-product dialkylsulfone and un-reacted alkylbenzene. The chemical structures of product and by-products of the reaction are shown in Figure E.5 (Appendix E). [19, 21]
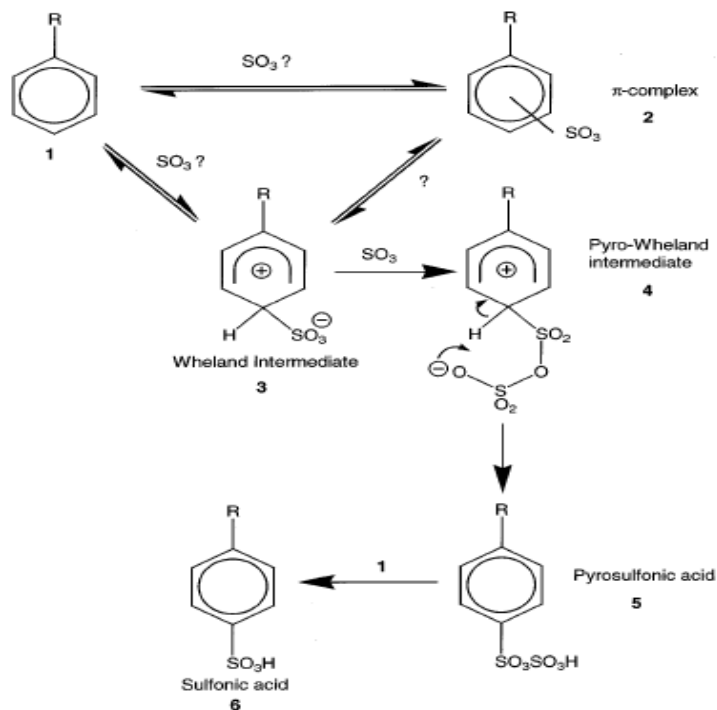
Figure 2.5 Primary reaction pathway - LAB reaction with SO_3.[20]
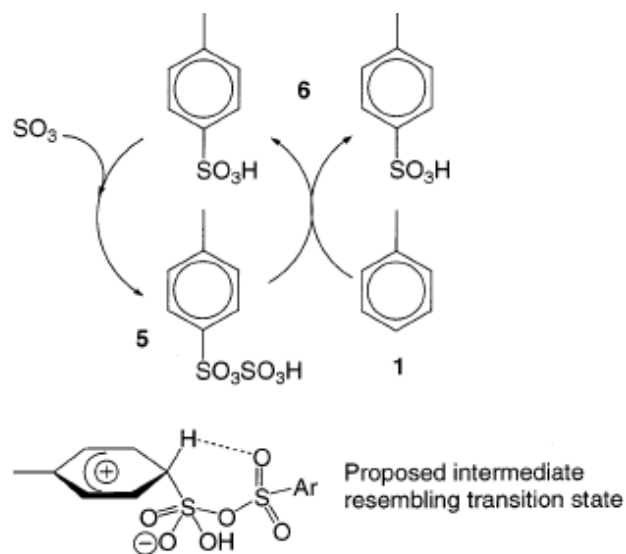
Figure 2.6 Main Reaction Pathway - Pyrosulfonic acid acts as sulfonating agent. [20]

15

The Arrhenius equation for the heterogeneous LAB sulfonation reaction is estimated as:

$$K= (10^{11})\ Exp(-13000/RT)\qquad\qquad(2.5)$$

The calculated enthalpy of reaction is approximated as - 40 kcal/mol. [19, 20]

According to Cross [21], pyrosulfonic acid and sulfonic anhydride function as intermediates, which later react with alkylbenzene or added water to yield the desired sulfonic acid.

2.4 Analytical

The general laboratory practice to measure anionic surfactant concentration is titration. In titration the analyte is determined by a stoichiometric reaction with a reagent having antagonistic properties. In anionic surfactant titration usual antagonists are the quats (or quaternary cationic surfactants).

Different types of quats are shown in Figure E.6 of Appendix E. Throughout the research, a 0.004 molar solution of dimethylbenzylammoniumchloride, also called benzethonium chloride (or Hyamine1622) is used as a titrant. Part-C in Figure E.6 illustrates the structure of Hyamine 1622.

The two oppositely charged surfactant ions combine according to the following equation to produce a hydrophobic salt that is insoluble in water, but soluble in an organic solvent of moderate polarity, such as chloroform. [21, 22]

$$Quat^+\ _{(aq)} + RSO_3^{\ -}\ _{(aq)} \longrightarrow QuateRSO_3(s)\ \ or\ \ QuatRSO_3(org)\qquad\qquad(2.6)$$

The most internationally accepted titrimetric procedure that evolved based on the above reaction is the Mixed Indicator method.

The Mixed Indicator Method

This method is in accordance with ISO-2271. The two indicators involved are the anionic disulfine blue VN (shown by HB in the following text) and the cationic dimidium bromide (DBr). When adding this mixture to an anionic surfactant, a pink complex forms with the D+ ion that is soluble in the chloroform phase according the following equation.

$$D^+ \text{(aq)} + RSO_3^- \text{(aq)} \longrightarrow DRSO_3 \text{(org)} \qquad (2.7)$$
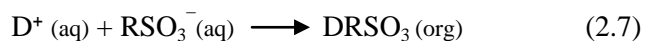
The disulfine blue remains in the aqueous layer and gives a green blue color to it. As the quat (titrant) is added to the reaction, the main reaction, equation 2.7, between the two antagonistic surfactants happens, but as the supply of free anionic surfactant ions becomes exhausted, the pink complex yields its surfactant ion to the titrant and the free dimidium bromide ion returns to the aqueous layer:

$$Quat^+ \text{(aq)} + DRSO3 \text{(org)} \longrightarrow QuatRSO3 \text{(org)} + D^+ \text{(aq)} \qquad (2.8)$$

A slight excess of quat titrant reacts with the disulfine blue anion to form a blue chloroform –soluble complex:

$$Quat^+ \text{(aq)} + B^- \text{(aq)} \longrightarrow QuatB \text{(org)} \qquad (2.9)$$
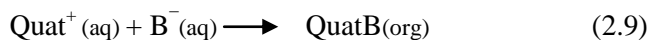
The color change in the chloroform layer at the end point is therefore, from pink to blue. In case the ratio of the two indicators is appropriate, a neutral gray color would be evident at the end point.

In experiments LAB/LAS samples were titrated based on the mixed indicator method. The analytical procedure to prepare indicators, sample aliquots and to perform the titration is explained in Appendix C.

Chapter 3

Experimental Apparatus

Overview

In this research project, production of LAS was intended to be carried out at high pressure in the carbon dioxide medium. SO_3 required for linear Alkylbenzene (LAB) sulfonation was produced by catalytic oxidation of SO_2 over activated carbon (oxidation process), which was later extracted by using supercritical carbon dioxide ($SCCO_2$). $SCCO_2$ carrying SO_3 was then contacted with LAB in reactor columns where the sulfonation reaction happened. In all the experiments, supercritical carbon dioxide at 93 bar pressure and 40°C temperature was used to extract SO_3 from activated carbon.

3.1 Experimental Set Up

The schematic of the experimental set up is shown in Figure 3.1. In the adsorption process the blended feed gas containing about 3000 ppm of SO_2 was passed over activated carbon. Mass flow controllers (MFC) were used to obtain the desired feed gas composition. In the schematic, columns AC1 and AC2 represent activated carbon beds (oxidation stage). A SO_2 gas analyzer, connected to a data acquisition system was used to measure and record the SO_2 concentration of the AC column effluent gas. A flow-meter controlled the volumetric flow rate of gas passing through the gas analyzer.

The SO_3 formed on activated carbon was extracted using supercritical carbon dioxide ($SCCO_2$). The compressed CO_2-SO_3 phase was then contacted with LAB to produce LAS (sulfonation reaction). As shown in Figure 3.1, a high pressure pump, heating circulator and a heat-exchanger were used to pressurize and heat up the carbon dioxide stream to

18
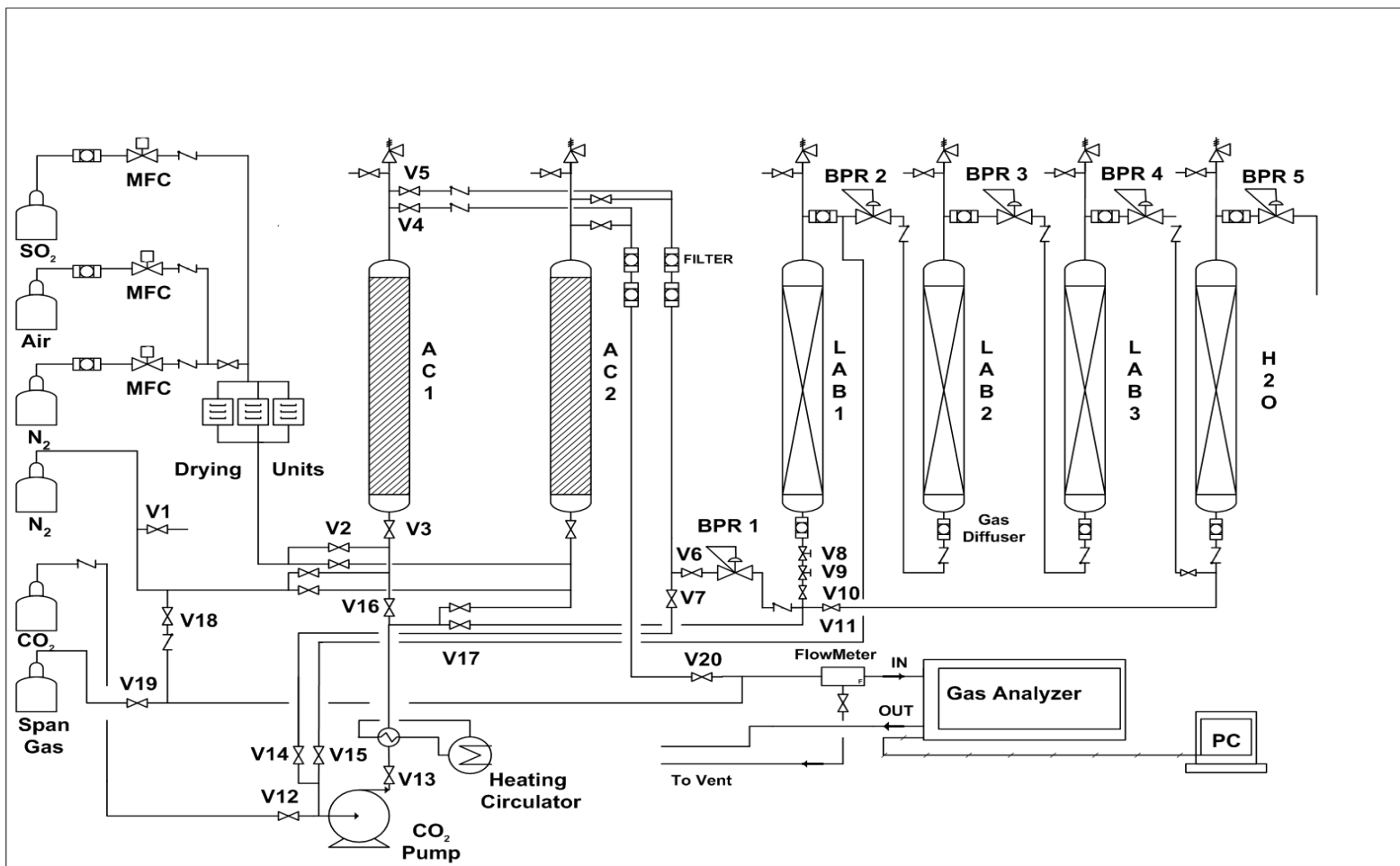
Figure 3.1   Schematic of Laboratory Set Up - LinearAlkylbenzene Sulfonation

reach the supercritical state. LAB1, LAB2, and LAB3 in the schematic represent three LAB columns used in the sulfonation process. Back- Pressure Regulators (BPR) were used to maintain desired pressures in the AC and LAB columns. A water column (H_2O), located downstream of the LAB reactors, captured any un-reacted SO_3 and SO_2.

Filters and strainers were used upstream of mass flow controllers to capture any debris and prevent damage, and similarly were placed upstream of the SO_2 gas analyzer, CO_2 pump and back-pressure regulators.

Columns AC1 and AC2 can be in service alternately, however, the LAB columns operate in series, but in stage-wise reduced pressure.

Different arrangements of valves V1 through V17 were manipulated to fulfill the following experimental requirements;

1. Zero- Span SO_2 gas analyzer (using valves V18 and V19)
2. Carry out the SO_2 oxidation reaction over activated carbon (using valves V2, V3, V4 and V20)
3. Extract SO_3 from activated carbon and re-circulate the $SCCO_2/SO_3$ phase through the AC column (using valves V12, V13, V16, V3, V5, V7 and V14)
4. Carryout LAB sulfonation by releasing the $SCCO_2/SO_3$ phase towards the LAB columns (valves V12, V13, V16, V3, V5, V6, V10, V9 and V8)
5. Bypass LAB reactors (valve V11)
6. Re-circulate CO_2 through LAB1 column (valves V15, V13 and V17)
7. Pressurize LAB columns using CO_2 gas (valves V12, V13 and V17)
8. Pressurize LAB columns using nitrogen through their top vent valves (using valve V1 and a temporary connection made to the vent valve of each LAB column)

All columns, tubing and connections are made of Stainless Steel-316. AC columns are 100 cm long and 1 inch in diameter. In the initial design, the LAB columns were 100 cm

long and ½ inch in diameter. After a few initial experiments the LAB column diameters were increased to 1 inch to prevent LAB loss. All columns are equipped with vent and relief valves.

The specifications of the gases, activated carbon, linear alkylbenzene and equipment used in the experiments are as follows;

Gas Sources

All compressed gas cylinders of nitrogen, air, sulfur dioxide (SO_2), carbon dioxide and span gas (2536 ppm SO_2 in nitrogen) were manufactured and provided by "PraxAir Canada Inc.". Gas specifications are shown in Table D.3 (Appendix D). Data adopted from PraxAir$^{®}$ catalogue. [23]

Mass Flow Controllers

Mass Flow Controllers controlled the flows of nitrogen, air and SO_2, and were manufactured by "Bronkhorst High Tech". The models used were F-202AV-M10-AAD-55-V for the air and nitrogen, and F-201DV-AAD-11-E for SO_2. The measurement span for air and nitrogen mass flow controllers was 0-133 g/min. The SO_2 mass flow controller was calibrated in the range of 0-450 mg/min. The calibration data provided by the manufacturer are shown in Appendix F.

SO_2 Gas Analyzer

The SO_2 gas analyzer, model 721 AT2, was manufactured by "AMETEK Process Instruments-Western Research". It was used to monitor the SO_2 concentration of the AC bed effluent gas. This model uses a dual-wavelength, high resolution, non-dispersive UV methodology. The gas analyzer has the capability of operating with two measurement spans, 0-500 ppm and 0-5000 ppm. The latter was used in this thesis research.

At the beginning of the thesis work, a new source lamp, supplied from the manufacturer, was installed in the gas analyzer. The source lamp alignment was done according to the gas analyzer instruction manual.

The feed gas SO_2 concentration used in the experiments was in the range of 2760 - 3000 ppm.

Back-Pressure Regulators

Back-pressure regulators manufactured by "Tescom Corporation" were used to maintain and control the pressure in the AC column as well as the LAB sulfonation columns. Model 26-1764 was used with a flow coefficient and operating range of 0.1 and 15 – 2500 psig, respectively.

As a remedial action, the back-pressure regulator (BPR) installed at the activated carbon columns was replaced by a BPR manufactured by "Go Regulator", model BP66-1A11CEQ151 with a flow coefficient of 0.04 and maximum control pressure of 10,000 psig.

Temperature Control System

A 7-Zone Temperature Controller, model "CN 1517", along with its associated Relay, model "URM- 800", both manufactured by "OMEGA Engineering" were used to control the process temperature.

Heating tapes, model "FGH051-080", manufactured by "OMEGA Engineering", were used to heat up the AC and LAB columns. This model can be used on conductive surfaces. Heating tapes were wrapped around AC and LAB columns.

Type K thermocouples, manufactured by "OMEGA Engineering", were used to measure temperature of the AC and LAB columns.

Temperature control was done by measuring the temperature of the columns outer surface. In the heating control loop, each thermocouple measures the temperature and sends the signal to the temperature controller. The temperature controller compares the

process temperature with the set point. If the process value is less than the set point, the temperature controller sends a signal to the relay input to activate.

Two profile thermocouples (carrying three sensing points) were also installed inside each activated carbon column to monitor adsorption progress. The profile thermocouples were connected to thermometers (model HH802U manufactured by "OMEGA Engineering").
Throughout the experiments the temperature control was crucial during SO_3 desorption, LAB sulfonation and also activated carbon rejuvenation steps.

High Pressure Pump

A single stage high pressure syringe pump manufactured by "Teledyne ISCO", model "260 D", was used to increase the pressure of carbon dioxide. This model had a 266 ml cylinder capacity with the ability to operate in "Constant Flow" and "Constant Pressure" modes. Pump specifications are listed in Table D.4 (Appendix D). Flow characteristics of the pump are shown in Figure E.7 (Appendix E). [24]

Pressure Relief Valves:

Relief valves were installed at the LAB and AC columns to provide safe operation. ¼ inch relief valves were set to release at pressures over 2000 psig. The maximum operating pressures throughout the experiments were in the activated carbon column. The regular operating pressure in the AC column was 1350 psig.

Gas Diffusers:

In order to provide homogeneous mixing of the $SCCO_2/SO_3$ and LAB phases, gas diffusers were installed at the inlet of each sulfonation (LAB) column. In the initial design, Swagelok® gas filters were used as diffusers. Due to their geometry, filter elements reversed and then installed inside the filter bodies. Initially, ½ inch filters with 60 micron media grade were used in the experiments. The filter element media grade was

later reduced to 15 and finally to 7 micron.

During the experiments, another type of gas diffuser was also used. They were 1 inch and also **½** inch porous discs with 2 micron media grade donated by "Mott Corporation".

New diffuser discs could be placed inside the Swagelok$^{®}$ compression fittings at the bottom of each LAB column.

Filters

Filters and strainers were used to capture any debris in the system to prevent damaging back-pressure regulators, SO_2 gas analyzer, mass flow controllers and pump.

Valves and Fittings

All Compression fittings, ball valves and check valves used, were manufactured by "Swagelok Company".

Refrigerated/Heating Circulating Bath

A heating circulator model "1156 D" manufactured by "VWR International", was used as heating source to provide hot flow for heat exchanger. This model has a 13 liter ethylene glycol reservoir with the capability of controlling temperature in the range of - 30 to 200°C.

Heat Exchanger

A heat exchanger assembly type CPVC 20 ' 6KPSI (model No. 04564), manufactured by "Thar SFC Company", was used to heat up the carbon dioxide stream up to 40°C. The hot flow provided by the circulator. The heat exchanger was located downstream of high pressure pump. Throughout the experiments, supercritical state was achieved when compressed (pressurized) CO_2 passed through heat exchanger. Throughout the research

supercritical carbon dioxide at 1350 psig (93 bar) and 40°C was used to extract SO_3 from activated carbon.

Gas Drying Units (Desiccants)

Gas drying units filled with moisture absorbing material "Drierite" were used to remove moisture from the blended feed gas. Desiccants (model 26800) and drierite are both manufactured by "W.A. Hammond Drierite Company". Desiccants are modeled polycarbonate cylinders with dimensions of 2 5/8 × 11 3/8 inch and the maximum working pressure of the units is 90 psig.

Indicating drierite is composed of 98% calcium sulfate ($CaSO_4$) and 2% cobalt chloride ($CoCl_2$). Its color changes from blue to pink as it absorbs moisture. Each desiccator was filled with 566 g (1¼ lb) of drierite with 8 mesh size granules. [25]

Activated Carbon

Two types of activated carbon were used as catalysts for oxidation of SO_2 to SO_3, "BPL4x6" and "BPL6x16", from "Calgon Carbon Corporation". They are bituminous coal-based products, activated at high pressures in a steam environment designed for gas phase applications. Mean particle diameters are 3.7 and 2.5 mm, respectively. Properties of activated carbon are shown in Tables D.5 and D.6 (Appendix D). [26]

Linear Alkylbenzene (LAB)

LAB was manufactured and provided by "CEPSA Química Bécancour Inc.", Quebec, Canada, a branch of "Petresa Company". Type "P-550-Q" was used in the experiments. Its average density and molecular weight are 0.8596 g/ml (at 15°C) and 240. The "Analysis Certificate" of LAB is shown in Figure E.9 (Appendix E).

Glass Beads

Glass beads were used in LAB columns to break large gas bubbles and dampen agitation

in the liquid phase. Initially glass beads with 3mm diameter were used to fill LAB columns. In the course of the experiments the beads grain size was reduced down to 2 mm and finally to 1 mm. LAB columns were filled with glass beads up to ¾ of their total (100 cm) height.

Data Acquisition

The data acquisition system includes a USB model NI 6008, manufactured by "National Instruments" and LabView$^{®}$ software. The SO_2 gas analyzer was connected to the data acquisition system and was used to monitor and record SO_2 concentration data of the AC column effluent gas.

3.2 Operational Procedures

LAS production experiments consisted of adsorption (oxidation) and sulfonation processes.

3.2.1 Oxidation Process:

Throughout this step SO_2 was converted to SO_3 catalytically over activated carbon. Figure 3.2 illustrates the flow diagram of the oxidation process. In an adsorption run, an activated carbon column, span gas cylinder (2536 ppm SO_2 in nitrogen), feed gas components (air, nitrogen and SO_2 cylinders), mass flow controllers, SO_2 gas analyzer, flow-meter and data acquisition system were in service.

The gas analyzer was zero-spanned before each adsorption run. A span gas cylinder and a nitrogen source were used for that purpose. For accurate and reliable measurements it is necessary to zero-span the gas analyzer at conditions similar to experimental conditions,
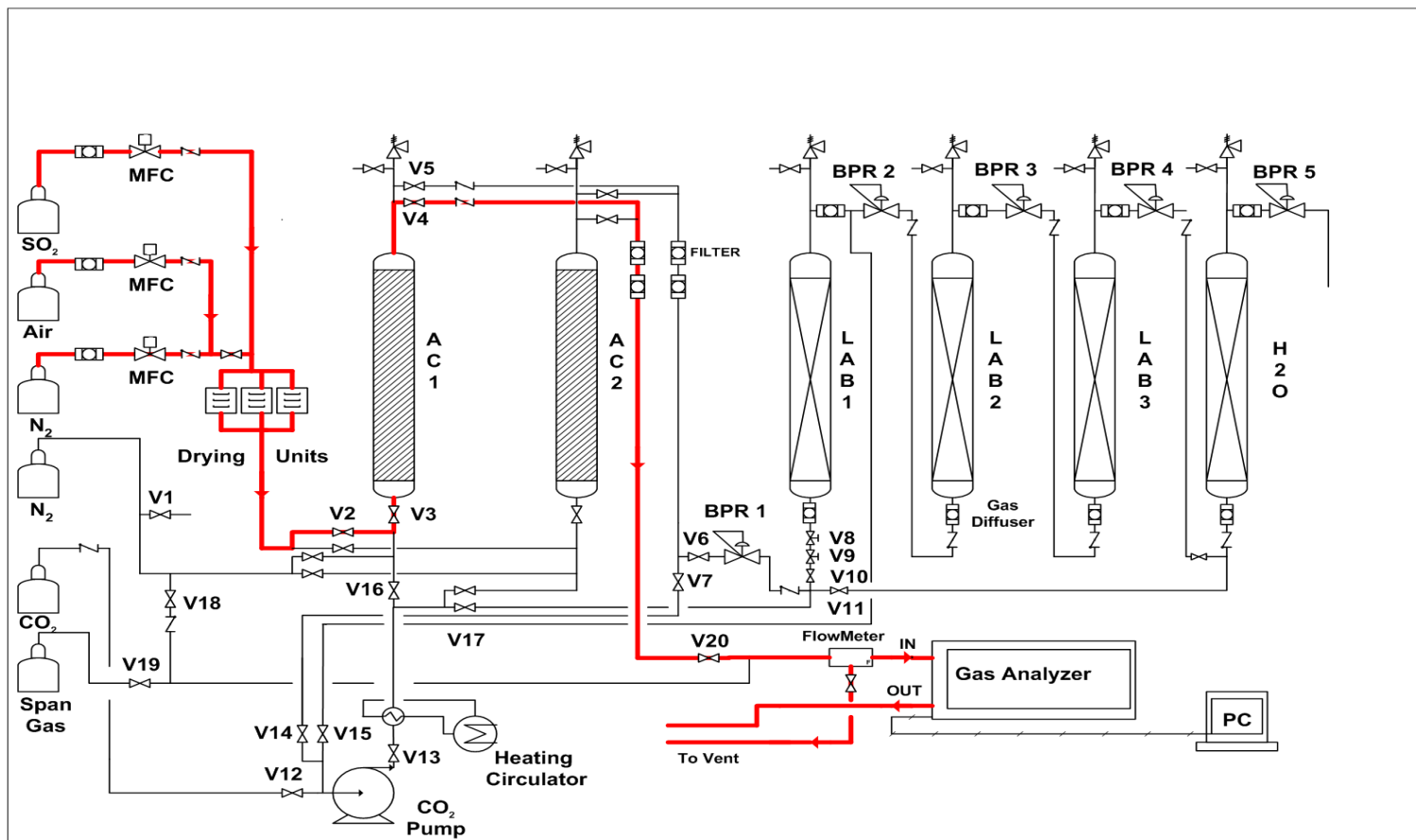
Figure 3.2 SO$_2$ Oxidation Flow Diagram – LinearAlkylbenzene Sulfonation

i.e.: operating gas flow rate passing through and also analyzer cell pressure must be the same during calibration and experiment runs. To fulfill this requirement a flow-meter was installed at the inlet of the gas analyzer to control the flow rate of gas passing through. During zero-span of the gas analyzer, the pressure was maintained at 15 psig by means of gas cylinder regulators.

The optimal design flow rate for the gas analyzer is 1-2 lit/min. In all the experiments the above mentioned flow-meter controlled the flow rate of gas passing through the analyzer at 1 lit/min. Connections were made to direct the bypassed gas to vent.

The outlet pressure of the mass flow controllers is 15 psig provided that MFC inlet pressures are controlled at 40 psig for air and nitrogen flows, and 30 psig for the SO_2 stream.

To carry out the oxidation process, SO_2, air and nitrogen flows were mixed to obtain the required feed gas composition. The criteria to control the mass flow rates was to maintain the feed gas SO_2 concentration and oxygen content at around 3000 ppm and 5% by volume, respectively. Feed gas was then passed through the activated carbon bed to get oxidized and form SO_3.

The SO_2 gas analyzer monitored SO_2 concentration of the AC bed effluent gas. Obtaining the SO_2 concentration at the outlet of AC column equal to that of at the inlet shows the end of the adsorption step. SO_2 concentration–time data was used to obtain the SO_2 adsorption break-through curve. Figure 3.3 depicts a typical adsorption break-through curve. Using this curve, the total mass of SO_2 fed to and mass of SO_2 left in the AC bed during adsorption run can be calculated. A sample calculation is shown in Appendix B.

The adsorption process was carried out at ambient temperature (25°C). Feed gas entered the AC bed at 15 psig pressure.

Different feed gas flow rates were used throughout the experiments, depending on the size of activated carbon column and the purpose of the experiment.
In experiments No. 1, 2, 3, 4, 5, 9, 10, 11, 13, 14, 15, 16, 17, 18 and 19 (Appendix A), the
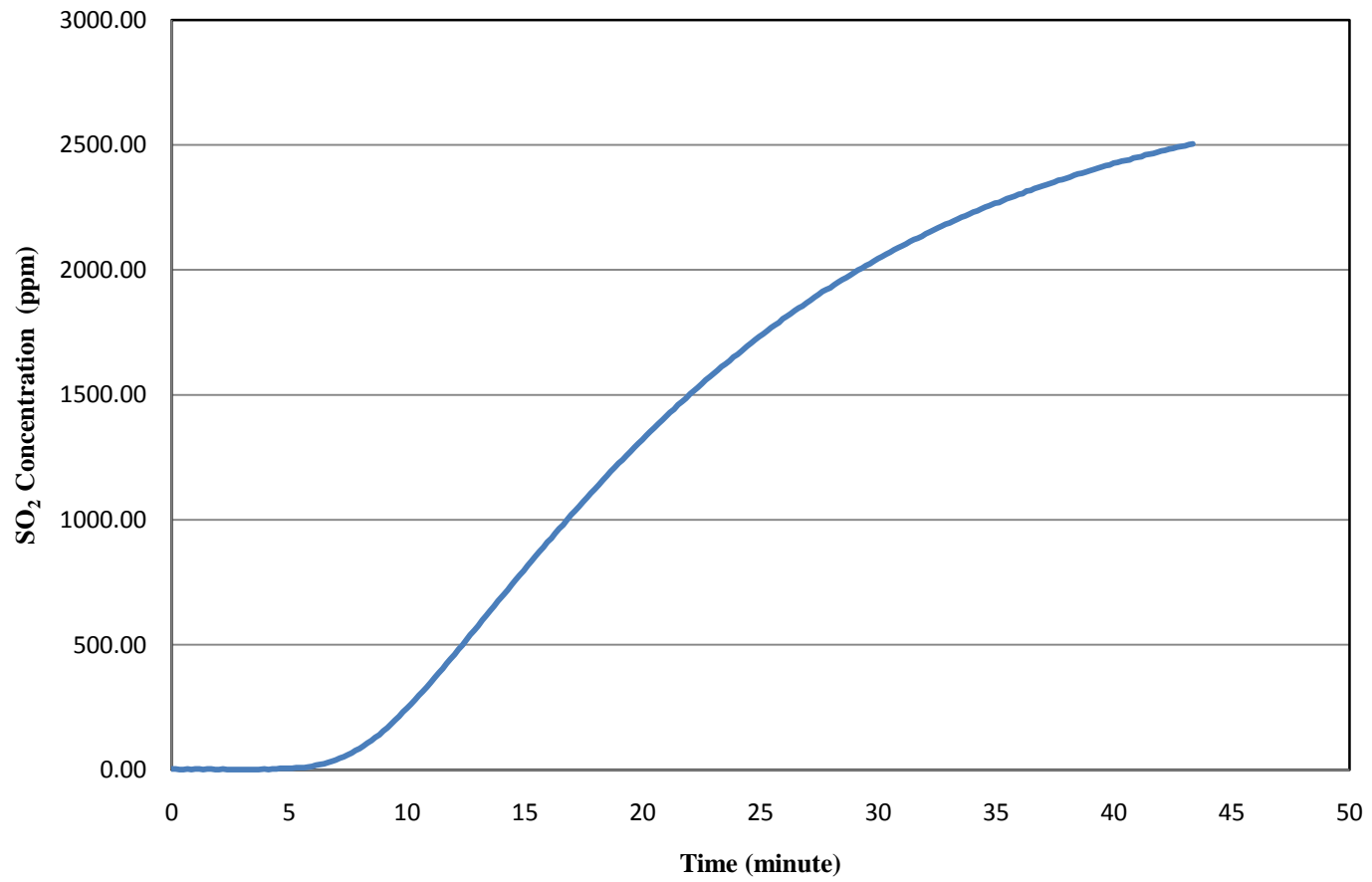
Figure 3.3 Typical SO$_2$ adsorption break-through curve

operating feed gas flow rate was 33.5 lit/min. Mass flow rates of SO_2, air and nitrogen were controlled at 250.8 mg/min, 9.3 g/min and 30.1 g/min, respectively. These mass flow rates provide feed gas SO_2 concentration as high as 2800 ppm as well as 4.6 % by volume oxygen content.

In experiments No. 6, 7, 8 and 12, the feed gas oxygen content was raised from 4.6 to 15.3% by volume. In order to obtain this composition, the mass flow rate of SO_2, air and nitrogen were maintained at 240 mg/min, 30.1 g/min and 8.9 g/min, respectively. The total feed gas flow rate was 32.6 lit/min carrying 2760 ppm of SO_2.

The AC columns length was reduced from 100 to 45 cm after experiment No.19. In experiments No. 20 to 22 (Appendix A) the operating feed gas flow rate was 11.18 lit/min containing 2845 ppm SO_2 and 5.5 % by volume oxygen. The corresponding mass flow rates of SO_2, air and nitrogen applied were 85 mg/min, 3.7 g/min and 9.4 g/min.

Through experiments No. 22 to 25, gas drying units (desiccants) were used to remove feed gas moisture content. Accordingly, in experiments No. 23 to 25 (Appendix A) the operating feed gas flow rate was maintained at 6.3 lit/ min, carrying 3000 ppm of SO_2 and 20% (by volume) oxygen. Mass flow rates of SO_2 and air were maintained at 50.4 mg/min and 7.6 g/min. There was no separate nitrogen flow in experiments No. 23 to 25.

The experimental procedure for SO_2 oxidation in column AC1 is as follows;

1. Warm up Gas Analyzer and Mass Flow Controllers for at least 30 minutes

2. Gas Analyzer Zero-Span by using nitrogen and span gas (using valves V18 and V19)

3. AC1 column outlet valve towards LAB columns (V6) closed

4. AC1 column inlet valves (V2 and V3) and outlet valves towards gas analyzer (V4 and V20) opened

5. Pre-determined mass flow rates set for SO_2, air and nitrogen mass flow controllers

6. Data acquisition program enabled

7. Feed gas directed towards AC1 column by through valves V2, V3, V4, V20, to start adsorption

8. Monitor and record SO_2 concentration of AC1 bed effluent gas

9. Stop feed gas flow (gradually) upon observing equal SO_2 concentration at AC1 column outlet and inlet flows

10. SO_2, air and nitrogen gas cylinder valves closed

11. Data acquisition program closed

12. AC1 column inlet/outlet valves (V2, V3, V4 and V20) closed

13. Purging gas analyzer by nitrogen gas (from 2nd source) for 20 minutes (using valve V18)

14. Stop purging and close valve V18

15. Transfer acquired SO_2 concentration – time data to PolyMath® software for integration

16. Calculate the area under the SO_2 concentration vs. time curve (that shows the amount of SO_2 left in the AC bed during adsorption run)

17. Calculate total mass of SO_2 fed during adsorption run, total mass of SO_2 adsorbed and mass SO_2 adsorbed per unit weight of activated carbon in AC column

3.2.2 SO₃ Desorption from Activated Carbon:

SO_3 was extracted from the activated carbon and carried through LAB columns by supercritical carbon dioxide (SCCO₂). In order to reduce CO_2 consumption and also

increase SO_3 concentration in the carbon dioxide phase, the $SCCO_2$ was re-circulated through the AC bed for a certain time and then released towards the LAB columns. This section explains the $SCCO_2$ recirculation process. The release of the $SCCO_2/SO_3$ phase towards the LAB columns (sulfonation reaction) is discussed in section 3.2.3.

Figure 3.4 illustrates the flow diagram of the SO_3 desorption process. As shown in the Figure, by opening/closing valves V6 and V7, the AC column outlet flow can be re-circulated or released towards the LAB columns. In the experiments, each re-circulation run continued for 10-15 minutes and was repeated after each injection of fresh supercritical CO_2 to the AC column.

As mentioned before, In all experiments supercritical CO_2 at 1350 psig (93 bar) and $40^{\circ}C$ was used to strip SO_3 from activated carbon. The temperature of the CO_2 stream was controlled using a heating circulator and heat exchanger.

Throughout the SO_3 desorption and re-circulation process, the AC column temperature was maintained at $40^{\circ}C$. The AC columns were also insulated to reduce heat loss and minimize slight pressure surges that could occur when the temperature controller turns on.

The SO_3 desorption procedure is as follows;

1. Temperature controller is set to maintain $40^{\circ}C$ at AC1, LAB1, LAB2, LAB3 columns

2. Heating circulator turned on. Temperature set at $40\ ^{\circ}C$

3. Back-pressure regulators adjusted to their maximum setting (BPR1, BPR2, BPR3 and BPR4)

4. Close valve V6 (AC columns outlet toward LAB1 reactor)

5. Close valve V7 (AC column re-circulation valve)

6. Open pump inlet and outlet valves (V12 and V13)
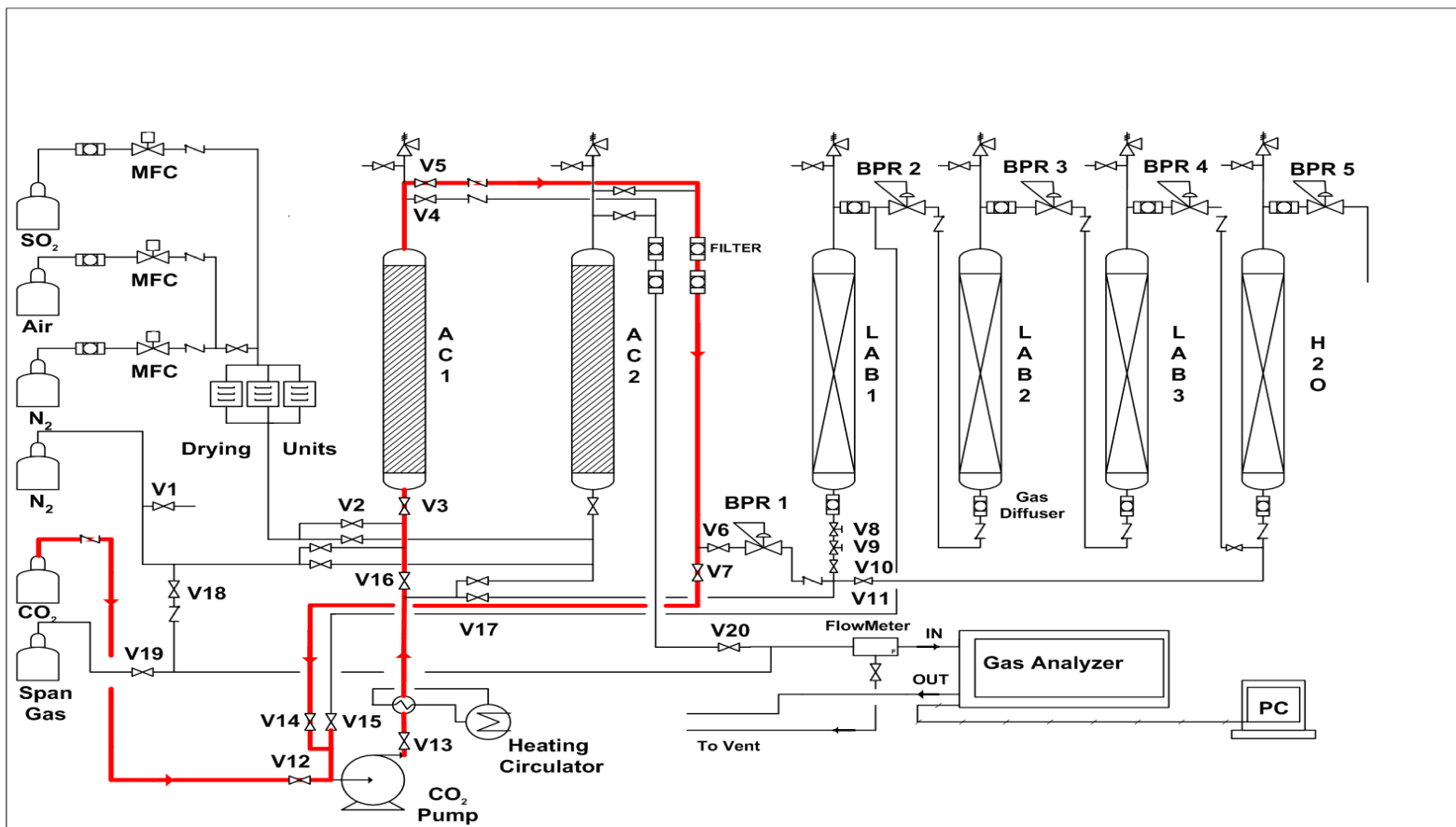
Figure 3.4   SO$_3$ Desorption Flow Diagram - Linear Alkylbenzene Sulfonation

33

7. CO$_2$ cylinder opened very slowly until pressure in the AC column reaches 1350 psig. At this step CO$_2$ passes through the pump while the inlet/outlet valves of the pump are open. Pump is not pumping any fluid yet.

8. Upon gaining 1350 psig at AC1, the pump inlet and outlet valves are closed (V12 and V13)

9. Pressurize LAB columns using nitrogen (from 2nd source) to pre-determined experimental pressure (Appendix A)

10. Open re-circulation valve (V7)

11. Open pump re-fill inlet valve (V14)

12. Start pump re-fill. At this step, the pump sucks the fluid content of the AC column in (through valves V5 and V14). The refill rate throughout the experiments is set at 20 ml/min.

13. Stop refill upon collecting 10-15 ml of fluid in the pump cylinder

14. Close re-circulation valve (V7)

15. Close pump refill inlet valve (V14)

16. Open pump outlet valve (V13)

17. Start pumping the above fluid back to AC1 column. Injection rate was maintained at 20 ml/min (through valves V13, V16 and V3)

18. Close pump outlet valve (V13)

19. Open valve V7 to repeat pump refill and injection (steps 11 through 18)

20. Stop SCCO2 re-circulation after 10-15 minutes

21. Reduce BPR1 setting to 1350 psig by turning its knob

22. Open the pump inlet valve (V12) to load fresh CO_2 to the pump

23. Flow the $SCCO_2/SO_3$ phase towards the LAB columns by pumping fresh $SCCO_2$ into the AC bed as described in the following section.

3.2.3 Sulfonation reaction

The sulfonation reaction immediately follows SO_3 desorption. The flow diagram of the sulfonation process is depicted in Figure 3.5.

Before releasing $SCCO_2/SO_3$, the LAB columns were pressurized to pre-determined experimental pressures (step 9 of the desorption procedure) and back- pressure regulators BPR2, BPR3 and BPR4 set at the desired pressure (Appendix A). After 10-15 minutes re-circulating $SCCO_2$ through AC bed, re-circulation valve (V7) is closed, fresh CO_2 is pumped to reach its supercritical state (CO_2 compressed by pump and passed through heat exchanger). Needle valve (V9) and metering valve (V8) at the inlet of LAB1 column are set to manipulate the desired flow coefficient (Appendix A). Valve V6 is then opened to direct the flow of $SCCO_2/SO_3$ phase towards the LAB columns.

Having back-pressure regulator No. 1 set at 1350 psig (93 bar), the $SCCO_2$ (at 1350 psig and 40°C) flow rate was controlled at 0.25-0.40 ml/min. A slight and slow increase in column pressure eventually causes the AC bed pressure to exceed the BPR1 setting and $SCCO_2/SO_3$ is released to the LAB1 column. When running experiments with three LAB columns in operation, fluid released to the LAB1 is also passed through the LAB2 and LAB3 columns. The LAB columns operated in a stage-wise reduced pressure. The highest pressure at which the sulfonation process was carried out was 1250 psig (86bar).

Throughout the experiments the minimum pressure difference between the AC and LAB1 columns was about 100 psig which could cause expansion of the compressed CO_2 phase. In addition, the LAB columns operating pressure was reduced in a stage-wise pattern that could also cause more expansion of the CO_2 phase. Expansion of the $SCCO_2/SO_3$
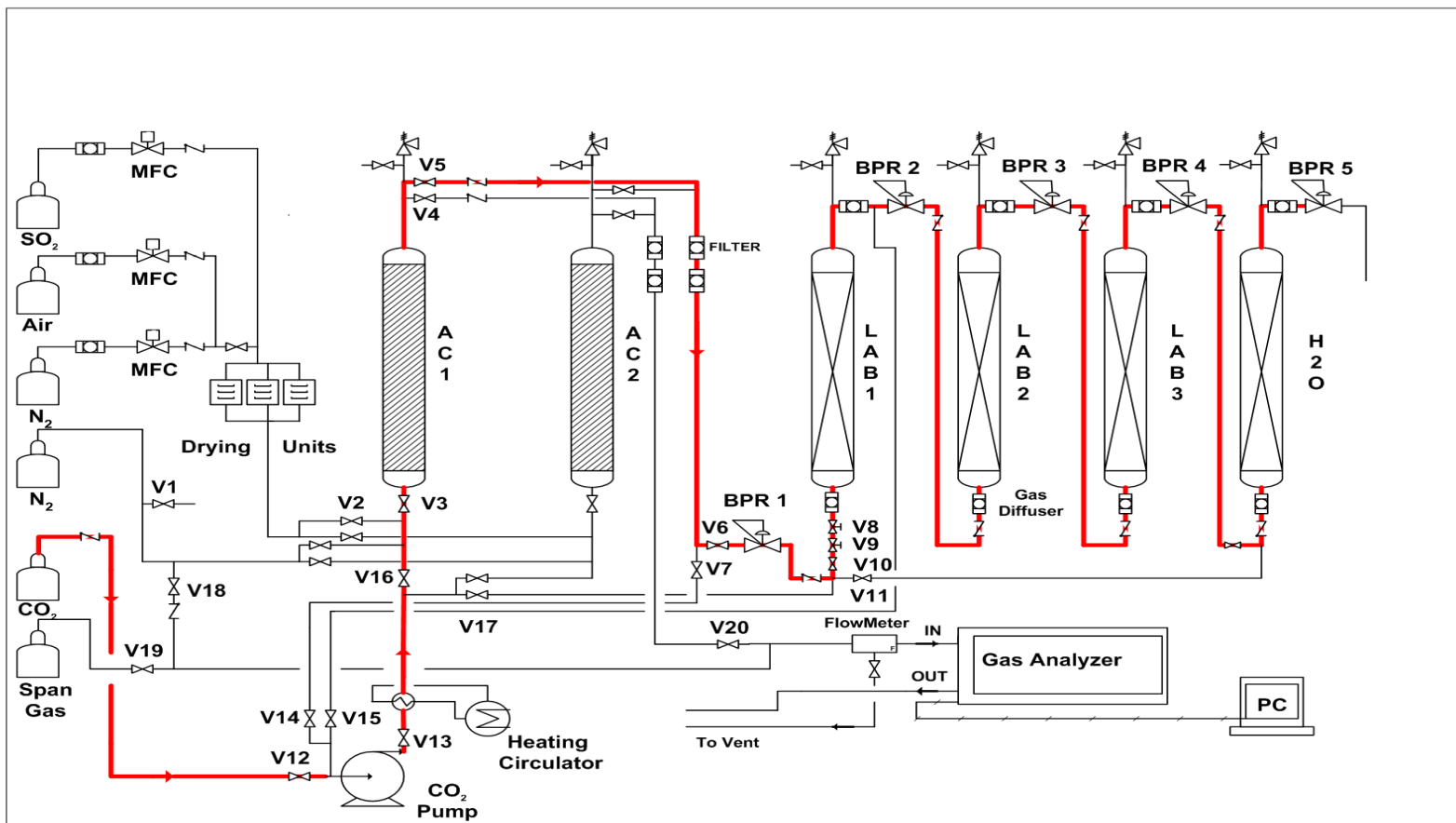
Figure 3.5   LAB Sulfonation Flow Diagram - Linear Alkylbenzene Sulfonation

mixture when flowing through the liquid LAB phase led to severe agitation in columns and in some cases to the loss of LAB (transferred to the downstream H_2O column). In order to dampen agitations and prevent LAB loss, column diameters were increased from ½ to 1inch. Glass beads were also used to fill the LAB columns up to 75 cm in height.

As mentioned above, pumping fresh $SCCO_2$ causes the $SCCO_2/SO_3$ phase to flow towards LAB reactors. High pressure pump may operate either in "Constant Pressure" or "Constant Flow" modes.

In Constant-Pressure mode, the pump adjusts the outlet pressure with pump set-pressure. If the pressure downstream of the pump is lower than the pump setting, pumping continues until either the fluid in the pump cylinder runs out, or the downstream pressure increases to the upstream pressure. In the case where the pressure downstream of the pump exceeds the set-pressure, pump starts sucking fluids from downstream system in, to adjust outlet pressure. This situation happens when the pressure in the AC column increases slightly at the moment that the heating system goes on.

In Constant-Flow mode, pumping continues at a fixed (set) flow rate until the pump cylinder contents run out, regardless of the downstream system pressure. In re-circulation and sulfonation processes, the pump operated in a Constant-Flow mode.

The sulfonation process procedure is as follows;

1. LAB columns are pressurized by nitrogen to a pre-determined pressure (Appendix A) using valve V1 and a temporary connection made to the vent valve at the top of each LAB column.

2. Back-pressure regulators BPR2, BPR3 and BPR4 are set to maintain the predetermined experimental pressure in the LAB columns (Appendix A)

3. The temperature controller is set to maintain 40ºC at AC1, LAB1, LAB2, LAB3 columns

4. $SCCO_2$ re-circulation is stopped

5. Re-circulation valve (V7), pump re-fill inlet valve (V14) and pump inlet/outlet valves (V12 and V13) are closed at this step

6. Needle valve and metering valve are set by turning their knob

7. Open the pump inlet valve (V12) to fill the pump by fresh CO_2 (about 10 ml)

8. Close the pump inlet valve (V12)

9. Open the pump outlet valve (V13)

10. Open valve V6 (AC column outlet towards LAB reactors)

11. Pump fresh $SCCO_2$ to AC1 column at a very low flow rate, 0.2- 0.4 ml/min, ($SCCO_2$ pressure and temperature maintained at 1350 psig and 40°C, respectively)

12. Monitor the operation and wait until all fresh $SCCO_2$ is injected

13. Record Injection data

14. Starting next re-circulation run (by closing valve V6 and opening V7 & V14). Steps 11 through 17 of desorption procedure repeated

15. Repeat re-circulation step and continue until pre-determined $SCCO_2$ volume for experiment is injected

16. Close valves V7 & V14 and open V12 to load fresh CO_2 to the pump

17. Repeat steps 5 through 12

18. Stop injection of fresh CO_2 upon injecting desired amount of $SCCO_2$ to the reactors

19. De-Pressurize the reactors by reducing the set-points of back-pressure regulators slowly, in sequence LAB3, LAB2, LAB1, AC column

20. Draining LAB reactors

21. Purge columns with nitrogen

3.2.4 Rejuvenation step

Activated carbon is rejuvenated at the end of each experiment. The AC column is heated up to 200°C and nitrogen (from 2nd source) is passed through for 1 hour. The effluent flow is directed to vent.

3.2.5 Sample titration

Titrate LAB/LAS samples after one hour. The mixed indicator method was used to titrate the LAB/LAS samples. Sample calculations and analytical procedures are shown in Appendices B and C, respectively.

Chapter 4

Methodology and Results Evaluation

4.1 Methodology

In order to enhance the reaction yield, few key factors needed to be improved for each process.

In the sulfonation reaction, controlled (minimized) flow of $SCCO_2$ towards LAB columns and homogeneous mixing of LAB and $SCCO_2/SO_3$ phases are the main challenges. In addition, the effects of pressure on sulfonation reaction are not exactly known.

In the oxidation process, improving SO_3 desorption efficiency and feed gas moisture removal were known to be the main obstacles.

Some experiments were also run to evaluate the feasibility of SO_3 removal from activated carbon using nitrogen gas and carrying it through the LAB reactors.

Brauner-Emmet-Teller surface area of activated carbon type BPL 6x16 from "Calgon Carbon Corp." was measured. The active surface area was estimated to be 1400 m^2 /g.

Laboratory work started with a focus on the sulfonation process. In order to improve the sulfonation reaction, the following steps were taken;

1. The glass beads used in the LAB columns, were switched from 3 to 1 mm diameter (experiments No.1 to 9 Appendix A).

2. The LAB column diameter was increased from $\frac{1}{2}$ to 1 inch (through experiments No. 1 to 5 Appendix A).

3. The back-pressure regulator installed at the AC columns was swapped to reduce the flow rate of $SCCO_2/SO_3$ in the LAB columns. The flow coefficient, C_v, decreased from

0.1 to 0.04 (experiment No. 9 Appendix A).

4. The gas diffusers at the inlet of the LAB columns were replaced to increase the diameter and reduce media grade.

5. A needle valve at the inlet of LAB1 column was used to reduce the $SCCO_2/SO_3$ flow rate through the sulfonation columns (experiment No. 19 Appendix A).

6. A metering valve, with a maximum flow coefficient of 0.004, was installed at the inlet of the LAB1 column (experiment No. 21 Appendix A).

A schematic of modified LAB1 column is illustrated in Figure 4.1. After applying each modification, experiments were run to observe the effects on reaction yield. Steps 1, 2, 3, 5 and 6 were taken to minimize the flow rate of the $SCCO_2/SO_3$ phase when released from the activated carbon bed to the LAB columns. The purpose of step 4 was to provide a better dispersion of $SCCO_2/SO_3$ phase through LAB (homogeneous mixing), therefore, increasing the contact surface area of SO_3 and LAB.

In order to evaluate the effect of pressure on LAS production, the sulfonation reaction was carried out at high and low pressures in some experiments. In total, in 11 experiments (No. 4, 5, 6, 8, 9, 10, 20, 21, 22, 24, 25 in appendix A) sulfonation was carried out when LAB1 column pressure maintained in the range of 1000-1250 psig. In experiments having 2 or 3 LAB columns in service, pressure was reduced in a stage-wise pattern. In 8 experiments (No. 13, 14, 15, 16, 17, 18, 19 and 23 Appendix A) sulfonation was conducted at 15 psig.

Evaluating pressure effect seemed to be important from two aspects. First, by running sulfonation reaction at elevated pressures, close to the critical pressure of carbon dioxide, the flow of $SCCO_2/SO_3$ towards the LAB columns could be under better control due to smaller ΔP. Second, the effect of high pressure that could contribute to the effects on reaction rate constant is not known.

In order to improve homogeneous mixing of LAB and $SCCO_2/SO_3$ phases, the gas diffuser diameter and media grade were changed in the course of the research. In the initial design, ½ inch "Swagelok[®]" gas filters, with 60 micron media grade, were used as gas diffusers.

41
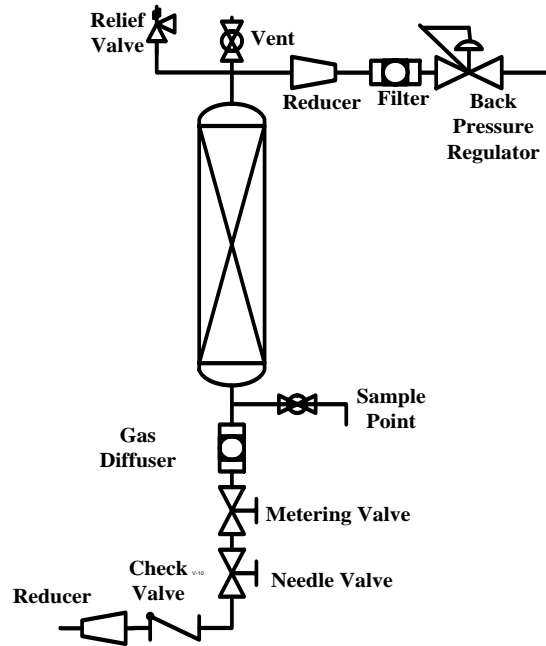
Figure 4.1 Schematic of modified LAB1 column

During the research, $\frac{1}{2}$ inch filters with 15 and 7 micron media grades were also examined. As the final step to optimize $SCCO_2/SO_3$ dispersion through LAB, filter-element type diffusers were replaced by thin stainless-steel porous discs, 1 inch in diameter and 2 micron media grade.

To improve adsorption/desorption efficiency, the following steps were taken;

 1. Using activated carbon with smaller pellet size (experiments No. 20 to 25 Appendix A).

2. Changing the feed gas Oxygen content from about 5 to 15% by volume and vice versa (experiments No. 6, 7, 8, 12 Appendix A).

3. Using gas de-humidifier units and varying the feed gas flow rate (experiments No. 22 to 25 Appendix A).

Two sizes of activated carbon column were used in adsorption stage throughout the research. In experiments No. 1 to 18 (Appendix A), a 100 cm long column (containing 151 g activated carbon) was used as AC bed. In experiments No. 19 to 25 (Appendix A) a 45 cm long AC column with 46.7 g activated carbon was in service.

4.2 Results Evaluation

Due to the rather large difference between the mass of SO_3 adsorbed on the activated carbon and mass of SO_3 extracted from activated carbon in the majority of the experiments, the LAB/LAS conversion percentage in the data tables (Appendix A) is calculated based on following criteria;

1. Mass SO_3 reacted to form LAS/mass SO_3 adsorbed over activated carbon in the experiment
2. Mass SO_3 reacted to from LAS/mass SO_3 extracted from activated carbon in the experiment

Because the number of sulfonation columns was not the same in all the experiments, each of the above calculations is also shown as;

a. Total LAB/LAS conversion percentage in all sulfonation columns in the experiment
b. Average LAB/LAS conversion percentage per sulfonation column

The criterion to compare and report experimental results is based on "mass SO_3 reacted to form LAS/mass SO_3 adsorbed (on activated carbon) in the experiment, per sulfonation column".

4.2.1 Sulfonation Process

With the listed modifications, the percentage of SO_3 reacted to form LAS improved from 0.06 to 3.6% per sulfonation column. Those figures represent the fraction of the mass SO_3 reacted to form LAS to mass SO_3 adsorbed. The maximum conversion was obtained under conditions where the pressure difference between the activated carbon column and the LAB1 column was maintained at about 100 psig (1350 and 1250 psig for columns, respectively).

The final SO_3 mass balance obtained in experiment No. 25 is shown in Table 4.1.

Table 4.1 Final SO_3 mass balance -Summary of the results of experiment No. 25

Mass SO_3 adsorbed/reacted	mmol	Percentage
Mass SO_3 adsorbed on activated carbon	30.636	
Mass SO_3 reacted to form LAS	1.104	3.604
Mass SO_3 extracted by $SCCO_2$ (as LAS &H_2SO_4)	19.824	64.7
Mass SO_3 extracted by N_2 flow after releasing CO_2 (passed through LAB column)	3.66	11.95
Mass SO_3 extracted by water flushing the activated carbon column	2.99	9.76
Total SO_3 extracted	26.474	86.41

4.2.1.1 LAB column size increase

As the results of experiments No.1 to 8 show, increasing the LAB column diameter from ½ to 1 inch increased the percentage of SO_3 reacted to form LAS from 0.2 to 0.85%, on average (0.07% to 0.28% per sulfonation column). After applying this change, the volumetric flow rate of $SCCO_2$/SO_3 phase through LAB reactors was reduced from 61 to 27 scfm (standard cubic feet per minute) under 100 psi pressure difference between AC and LAB columns.

4.2.1.2 Using Back-Pressure Regulator with lower flow coefficient

As the results of experiments No. 9 to 13 show, by swapping back-pressure regulator installed at the activated carbon column along with reducing glass bead size down to 1 mm, the reaction yield increased to 1.24% on average (0.41% per sulfonation column). Via this change, the BPR flow coefficient decreased from 0.1 to 0.04. The flow rate of the $SCCO_2/SO_3$ phase through the LAB columns reduced from 27 to about 10 scfm (under 100 psig ΔP between AC and LAB columns).

4.2.1.3 Using needle valve

A needle valve was installed at the inlet of the LAB1 column as shown in Figure 4.1. The operating flow coefficient manipulated was 0.02, which was half of that of the new back-pressure regulator. In the experiments, the flow rate of the $SCCO_2/SO_3$ phase through LAB1 column could be maintained at 10 scfm (under 350 psig ΔP between AC and LAB columns). The maximum LAB/LAS conversion obtained was 0.74 % per LAB column. The sulfonation column pressure was maintained at 1000 psig in the experiment.

4.2.1.4 Using metering valve

A metering valve was installed at the inlet of LAB1 column between the needle valve and gas diffuser. It had maximum flow coefficient of 0.004. By using the metering valve, the flow rate of the $SCCO_2/SO_3$ through the LAB column was reduced from 1.8 to 1.1 scfm with 100 psi pressure difference between AC bed and LAB reactor. Experiments No. 21 to 25 have a metering valve in service. The percentage of SO_3 reacted to form LAS increased from 0.74% to 1.4% per sulfonation column.

4.2.2 Oxidation Process

4.2.2.1 Using different types of activated carbon

Activated carbon types "BPL 4×6" and "BPL 6×16" were used as catalysts in the oxidation process. Their average granule diameters are 3.7 and 2.5 mm, respectively. In terms of SO_2/SO_3 adsorption/desorption capacity, both types showed similar performance. The comparison made was based on the results of the first 6 adsorption runs

for both types. The average mass of SO_2 adsorbed per unit weight of activated carbon was 0.663 and 0.667 mmol SO_2/g activated carbon for BPL 4×6 and BPL 6×16, respectively.

4.2.2.2 Feed gas oxygen content

The feed gas oxygen content during SO_2 oxidation was changed from 4.6 to 15.3% by volume and vice versa to make sure that SO_2 oxidation occurred in oxygen enriched environment. Observing no change in SO_3 desorption efficiency shows that feed gas containing 4.6% by volume oxygen can provide enough oxygen for optimal SO_2/SO_3 conversion (experiments No. 6, 7, 8 and 12 Appendix A).

4.2.2.3 Using de-humidifying units (desiccants)

Using gas drying units (desiccants) improved the total SO_3 removal from 18% to 77% without water-flushing of the activated carbon bed, as the results of experiments No. 22 to 25 show. Although moisture transferred to the activated carbon bed in each adsorption run was about 1.5 ml (without using desiccants), it most probably led to the reaction of SO_3 with H_2O to form minor amounts of sulfuric acid. Sulfuric acid could have been removed later during activated carbon rejuvenation. A sample calculation of feed gas moisture content is shown in section B.3 (Appendix B).

Each drying unit had maximum design flow rate of 200 lit/hr (3.3 lit/min) for optimal performance. In total 3 units were brought into service in the course of experiments. The feed gas flow rate during adsorption process had to be reduced down to 6.3 lit/min for proper moisture removal (2.1 lit/min passed through each drying unit).

By continual water-flushing of the AC bed, the total percentage of SO_3 extracted increased up to 86% as shown in Table 4.1.

Having more SO_3 in the $SCCO_2$ phase boosted LAB/LAS conversion. As the results of experiments No. 22 to 25 show, the LAB/LAS conversion increased from 1.4 to 3.6% per sulfonation column.

4.2.2.4 Different sizes of activated carbon column

Two sizes of activated carbon bed were used in the adsorption process. In experiments No. 1 to 18, a 100 cm – long AC bed was used that could hold 151 g of activated carbon.

In experiments No. 19 to 25, a 45 cm-long AC bed was used. The mass of activated carbon loaded in this column was 46.7 g. Both AC beds are 1 inch in diameter.

Considering the unsatisfactory desorption results obtained from experiment No. 1 to 18, the next remedial action was to remove the moisture content of the feed gas .There were two facts to be considered. First, in order to shorten adsorption period, higher feed gas flow rates could be used. The applied feed gas flow rate at the start was 33 lit/min. Second, de-humidifying units (desiccants) were known to be efficient up to 3.3 lit/min. As a tradeoff between AC column length (mass SO_3 adsorbed), adsorption run time (feed gas flow rate) and desiccants moisture removal efficiency, the length of activated carbon column was reduced from 100 to 45 cm.

As the results of experiments No. 18, 19, 20 and 21 show, when using the 45 cm long AC column, a slight decrease in product LAS molarity (LAS in LAB/LAS mixture) was observed that was due to less amounts of SO_3 in the $SCCO_2/SO_3$ phase. LAS molarity decreased from 0.0048 to 0.0028 M. Adding a metering valve with very low flow coefficient, C_v of 0.004, improved the LAS molarity later on. The maximum amounts of SO_3 extracted from the 45 and 100 cm AC columns without using desiccants were 9.756 and 18.685 mmol, respectively. Those amounts correspond to 31.25% and 19.93% desorption efficiencies.

4.3 Using Nitrogen gas as desorbing agent and SO_3 carrier

In total four experiments were run to evaluate the feasibility of SO_3 removal from activated carbon and carrying it through the LAB reactors by using nitrogen gas. The results show that nitrogen gas, instead of supercritical carbon dioxide, may be used to remove SO_3 from the pre-heated activated carbon bed. According to the results, nitrogen gas can remove SO_3 from activated carbon with up to 80 % of the removal efficiency achievable by supercritical carbon dioxide. Pre-heating the carbon bed up to 65°C is necessary, as the SO_3 boiling point at atmospheric pressure is 44.5°C (experiments No. 14, 15, 16, 23 Appendix A). A summary of the results of nitrogen tests is shown in

Table 4.2.

In experiment No. 23, the removal efficiency obtained by using nitrogen was as high as that of supercritical carbon dioxide, which is because of the longer desorption run and also having two drying units in service.

In experiments No. 13, 24 and 25, nitrogen gas was run after supercritical carbon dioxide for 1, 2 and 11 hours, respectively. The corresponding increases in SO_3 removal efficiencies were 1.8%, 6.52% and 11.95%.

Table 4.2 Summary of the results of Nitrogen experiments

Experiment No.	14	15	16	23
Desorption agent	N_2	N_2	N_2	N_2
Mass SO_3 adsorbed (mmol)	92.891	94.719	92.625	31.008
N_2 flow duration (hr)	6.5	14.5	14	103
N_2 pressure (psig)	40	20	20	20
AC bed temperature (ºC)	65	65	65	65
Mass LAS formed in LAB columns (mmol)	1.23	1.248	1.278	
mmol SO_3 extracted by N_2 flow (passed through LAB columns)	10.17	12.108	12.978	10.016
Total SO_3 extracted (mmol)	10.17	12.108	12.978	10.018
Percent SO_3 reacted to form LAS	1.32	1.318	1.38	2.515
Percent SO_3 captured as H_2SO_4	9.63	11.48	12.62	29.786
Total SO_3 extracted (%)	10.95	12.8	14	32.302

4.4 BET Results

Brauner-Emmet-Teller surface area of activated carbon type BPL 6x16 from "Calgon Carbon Corporation" was measured by a surface active analyzer model "Gemini2375" manufactured by "Micromeritics Instrument Corporation". The estimated active surface area is 1400 m^2/g activated carbon. The detailed results are shown in appendix G.

Chapter 5

Conclusions and Recommendations

In this research, the production of linear alkylbenzene sulfonic acid (LAS) at high pressure in a supercritical carbon dioxide medium was investigated. The possibility of running the above reaction at high pressures (above critical pressure of carbon dioxide) and at temperatures lower than that of the current industrial method, was examined.

5.1 Conclusions

1. Through this research, the percentage of SO_3 reacted to form LAS improved from 0.06 to 3.6 % per sulfonation column. Those figures represent the fraction of mass SO_3 reacted to form LAS to mass SO_3 adsorbed on activated carbon. The maximum conversion was obtained under condition where the pressure difference between the activated carbon and LAB columns was maintained at about 100 psig (1350 and 1250 psig for columns, respectively).

A number of factors may contribute to low LAS production yield. For a sulfonation reaction to occur, SO_3 needs to be transferred from the supercritical CO_2 phase to the LAB phase and react with it. Basically, three problems could inhibit the reaction;
a) mass transfer i.e.: SO_3 is not delivered from $SCCO_2$ to the LAB phase. It is known that in some supercritical fluid systems solute molecules are surrounded tightly by supercritical fluid molecules. In this case there could be clusters of supercritical CO_2 molecules around SO_3 molecules that act like a cage and prohibit their reactivity.
b) SO_3 is exposed to LAB, however reaction does not happen due to thermodynamic pressure effects on the reaction rate constant. The effect of pressure on the sulfonation reaction rate constant is not known. The effect of pressure is usually shown with

activation volumes. Activation volumes of several thousand cc/gmol have been reported for some supercritical fluid systems that mean order of magnitude changes in the rate constant with changes in pressure.

c) SO_3/ LAB contact time is not enough at the experimental conditions.

2. In the SO_2/SO_3 adsorption/desorption process on activated carbon, complete feed gas moisture removal is necessary. As the results show, the presence of minor amounts of H_2O as moisture, even less than 1.5 ml, led to maximum SO_3 removal efficiency of about 20%.

 3. Upon perfect feed gas drying, SO_3 recovery efficiency of 77% was achieved without water-flushing of activated carbon bed.

4. Nitrogen gas, instead of supercritical carbon dioxide, may be used to remove SO_2/SO_3 from pre-heated activated carbon. According to the results, nitrogen can remove SO_3 from activated carbon up to 80% of the removal efficiency achievable by supercritical carbon dioxide. Pre-heating the carbon bed up to 65°C is necessary, as the SO_3 boiling point at atmospheric pressure is 44.5°C.

5.2 Recommendations

1. Reduce the interfacial velocity of $SCCO_2/SO_3$ phase to enhance the LAB sulfonation reaction. Carrying out LAB sulfonation in reactors with larger interface area would boost LAB/LAS conversion. The proposed reactor would be a Continuous Stirred Tank Reactor equipped with tubular gas sparger.

2. Evaluating thermodynamic pressure effect on LAB sulfonation reaction could shed light on low LAB/LAS conversion problem.

3. Investigate the affinity between supercritical CO_2 and SO_3 molecules, which could provide valuable insight into the causes of low mass transfer rate.

4. Nitrogen gas may be used for SO_3 removal from activated carbon. It is recommended to use nitrogen in lieu of supercritical carbon dioxide for this purpose in similar future research projects.

References

1. Cooper, C.D., Alley, F.C., *Air Pollution Control* ed. 3. Illinois: Waveland Press, 2002.

2. Panthaky, M.D., M.A.Sc. Thesis, Department of Chemical Engineering, University of Waterloo, 1998.

3. Wattanakasemtham, N., M.A.Sc. Thesis, Department of Chemical Engineering, University of Waterloo, 2003.

4. Yuan,Y., M.A.Sc.Thesis, Department of Chemical Engineering, University of Waterloo, 2007.

5. Weale, K.E. *Chemical reactions at high pressures*, London: E. & F.N. Spon, 1967.

6. Bradley, R.S. *High Pressure Physics and Chemistry* vol.2., New York: Academic Press, 1963.

7. Spain, I.L., Paaue, J. *High Pressure Technology* vol.2., New York: M.Dekker, 1977.

8. Taylor, L.T. *Supercritical Fluid Extraction*, New York : Wiley, 1996.

9. Kiran, E., Brennecke, J.F. *Supercritical Fluid Engineering Science, Fundamentals and Applications*, Washington : ACS, 1993.

10. Iwasaki, H., Takahashi, M. "Viscosity of carbon dioxide and ethane," *J.Chem.Phys.*, vol.74, no.3, p.p.1930-1943, 1981.

11. Zagrobelny, J., Betts, T.A., Bright, F.V "Steady-state and time-resolved fluorescence investigations of pyrene excimer formation in supercritical CO_2," J.*Am.Chem.Soc.* vol. 114, no.13, p.p.5249-5257, 1992.

12. Paulaitis, M.E, Alexander, G.C. "Reactions in supercritical fluids. A case study of the thermodynamic solvent effects on a Diels-Alder reaction in supercritical carbon dioxide," *J.Pure & Appl.Chem.* vol.59, no.1, p.p.61-68, 1987.

13. Brennecke, J.F., Tomasko, D.L., Eckert, C.A. " Naphthalene/triethylamine exciplex and pyrene excimer formation in supercritical fluid solutions," *J.Phys.Chem.*, vol.94, iss.19, p.p.7692-7700, 1990.

14. Kim, S., Johnston, K.P. "Clustering In supercritical fluid mixtures," *AICHE J.*, vol.33, no.10, p.p.1603-1611, 1987.

15. Johnston, K.P., Kim, S. " Molecular interactions in dilute supercritical fluid solutions," *Ind. Eng. Chem. Res*., vol.26, no.6, p.p.1206 - 1213, 1987.

16. Petsche, I.B., Debenedetti, P.G. " Solute-solvent interactions in infinitely dilute supercritical mixtures; a molecular dynamic investigation," *J.Chem.Phys*., vol.91, no.11, p.p. 7075-7084, 1989.

17. LAS information website, http://www. lasinfo.org

18. Detergents, soaps and maintenance products information website by A.I.S.E. and Cefic, http://uk.cleanright.eu/

19. Roberts, D.W. "Sulfonation technology for anionic surfactant manufacture," *J. Org.Proc.Res.Dev*. vol.2, no.3, p.p. 194 -202, 1998.

20. Roberts, D.W. "Optimization of the linear alkyl benzene sulfonation process for surfactant manufacture," *J. Org.Proc.Res.Dev*., vol.7, no.2, pp. 172-184, 2003.

21. Cross, J. *Anionic Surfactants-Analytical Chemistry* . New York: M.Dekker, 1998.

22. Schmitt, T.M. *Analysis of Surfactants*, New York: M. Dekker, 1992.

23. PraxAir Canada Inc. catalogue, 2008.

24. Teledyne Isco Company website, http://www.isco.com/

25. W.A. Hammond Drierite Company website, http://www.drierite.com

26. Calgon Carbon Corporation website, http://www.calgoncarbon.com,2009

Appendices

Appendix A   Experimental Data and Results

Table A.1 Data and results of experiments No.1 to 5

	Oct.19,09	Oct.23,09	Oct.27,09	Nov.01,09	Nov.04,09
Experiment No.	1	2	3	4	5
Activity/Modification	Evaluating Pressure Effects				Increasing LAB column diameter to 1 in.
Adsorption					
Activated carbon type	BPL4x6	BPL4x6	BPL4x6	BPL4x6	BPL4x6
Active carbon weight in column (g)	151	151	151	151	151
Activated carbon column height (cm)	100	100	100	100	100
SO_2 mass flow rate (mg/min)	250.8	250.8	250.8	250.8	250.8
Air mass flow rate (g/min)	9.3	9.3	9.3	9.3	9.3
N_2 mass flow rate (g/min)	30.1	30.1	30.1	30.1	30.1
Feed gas volumetric flow rate (lit / min)	33.5	33.5	33.5	33.5	33.5
Feed gas O_2 content (% volume)	4.6	4.6	4.6	4.6	4.6
Feed gas SO_2 concentration (ppm)	2800	2800	2800	2800	2800
Mass SO_2 adsorbed (g)	6.433	6.338	6.444	6.42	6.359
mmol SO_2 adsorbed	100.516	99.031	100.688	100.313	99.359
mmol SO_2/gr activated carbon	0.666	0.656	0.667	0.664	0.658
No. of desiccant in service	0	0	0	0	0
Ave. gas flow rate/desiccant (lit/min)	0	0	0	0	0
Desorption					
Active carbon column pressure (psig)	1300	1300	1300	1300	1300
Active carbon column temperature (ºC)	40	40	40	40	40
$SCCO_2$ recycle duration (min)	5	5x10 min	5x10 min	5x10 min	5x10 min
$SCCO_2$ recycle flow rate (ml/min)	20	20	20	20	20
Fresh CO_2 flush time (hrs)	0	0	30	37.5	19.5
Fresh CO_2 flush volume (ml)	0	0	300	340	350
Fresh CO_2 flush flow rate (ml/min.)	0	0	0.15	0.15	0.3
CO_2 release duration(hrs)	7.5	7.5	7.5	7	4
CO_2 release flow rate towards LAB columns (scfm)	53.3	61.2	61.2	27	27
N_2 flow after CO_2 release	No	No	No	No	No
N_2 pressure (psig)	0	0	0	0	0

Continued data of experiment No.	1	2	3	4	5
N_2 flow duration (hrs)	0	0	0	0	0
Sulfonation					
Column 1 LAB					
Pressure (psig)	850	500	300	1200	1200
Temperature (ºC)	35	35	22	35	35
Column diameter (in.)	1/2	1/2	1/2	1/2	1
LAB volume (ml)	47	0	0	40	100
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	60	60
Initial LAB height in column (cm)	60	0	0	60	60
Glass beads height in column (cm)	40	40	40	40	45
Glass beads size (mm)	3	3	3	3	3
Hyamine concentration (mol/lit)	0.004	0	0	0.004	0.004
Product LAB/LAS sample volume (ml)	10	0	0	10	10
Volume Hyamine used in titration (ml)	3	0	0	4	11.25
Product LAS molarity (mol/lit.)	0.0012	0	0	0.0016	0.0045
mmol SO_3 reacted to form LAS	0.0564	0	0	0.064	0.45
Percent SO_3 reacted to form LAS (%)	0.056	0.000	0.000	0.064	0.453
Column 2 LAB					
Pressure (psig)	700	400	220	1100	1100
Temperature (ºC)	35	35	22	35	35
Column diameter (in.)	1/2	1/2	1/2	1/2	1
LAB volume (ml)	40	40	40	40	100
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	60	60
Initial LAB height in column (cm)	60	60	60	60	60
Glass beads height in column (cm)	40	40	40	40	45
Glass beads size (mm)	3	3	3	3	3
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	3	5	5	4	9
Product LAS molarity (mol/lit)	0.0012	0.002	0.002	0.0016	0.0036
mmol SO_3 reacted to form LAS	0.048	0.08	0.08	0.064	0.36
Percent SO_3 reacted to form LAS (%)	0.048	0.081	0.079	0.064	0.362
Column 3 LAB					
Pressure (psig)	400	300	140	950	950

Continued data of experiment No.	1	2	3	4	5
Temperature (°C)	35	35	22	35	35
Column diameter (in.)	1/2	1/2	1/2	1/2	1/2
LAB volume (ml)	40	40	40	40	40
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	60	60
Initial LAB height in column (cm)	60	60	60	60	60
Glass beads height in column (cm)	40	40	40	40	40
Glass beads size (mm)	3	3	3	3	3
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	3	4	4	4	8
Product LAS molarity (mol/lit)	0.0012	0.0016	0.0016	0.0016	0.0032
mmol SO_3 reacted to form LAS	0.048	0.064	0.064	0.064	0.128
Percent SO_3 reacted to form LAS (%)	0.048	0.065	0.064	0.064	0.129
Collector Water Vessel					
Initial water volume (ml)	600	720	700	600	600
NaOH concentration (mol/lit.)	0.02	0.02	0.02	0.02	0.02
Water sample volume (ml)	25	30	25	30	30
Volume NaOH used in titration (ml)	42	66.6	55.2	78	76.2
Final H_2SO_4 molarity (mol/lit)	0.0168	0.0222	0.0221	0.026	0.0254
Captured SO_3 mmol as H_2SO_4	10.080	15.984	15.470	15.600	15.240
mmol SO_3 extracted by $SCCO_2$ (as LAS & H_2SO_4)	10.232	16.128	15.614	15.792	16.178
mmol SO_3 extracted by N_2	0	0	0	0	0
mmol SO_3 extracted by H_2O flush	0	0	0	0	0
Total SO_3 extracted (mmol)	10.232	16.128	15.614	15.792	16.178
SO_3 recovery efficieny (%)	10.18	16.29	15.51	15.74	16.28
No. of sulfonation columns in service	3	2	2	3	3
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment (%)	1.489	0.893	0.922	1.216	5.798
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment per sulfonation column (%)	0.496	0.446	0.461	0.405	1.933
Percent SO_3 reacted to form LAS / SO_3 adsorbed (%)	0.152	0.145	0.143	0.191	0.944

Continued data of experiment No.	1	2	3	4	5
Percent SO_3 captured in collector water throughout the experiment (%)	10.028	16.140	15.364	15.551	15.338
Percent SO_3 reacted to form LAS / SO_3 adsorbed per sulfonation column (%)	0.051	0.073	0.072	0.064	0.315

Table A.2 Data and results of experiments No.6 to 10

	Nov.07,09	Nov.09,09	Nov.11,09	Nov.27,09	Dec.01,09
Experiment No.	**6**	**7**	**8**	**9**	**10**
Activity/Modification	Increasing LAB Column Diameter to 1" Reducing glass beads size			Using BPR with Cv=0.004 Reducing glass beads size	
Adsorption					
Activated carbon type	BPL4x6	BPL4x6	BPL4x6	BPL4x6	BPL4x6
Active carbon weight in column (g)	151	151	151	151	151
Activated carbon column height (cm)	100	100	100	100	100
SO_2 mass flow rate (mg/min)	240	240	240	250.8	250.8
Air mass flow rate (g/min)	30.1	30.1	30.1	9.3	9.3
N_2 mass flow rate (g/min)	8.9	8.9	8.9	30.1	30.1
Feed gas volumetric flow rate (lit / min)	32.6	32.6	32.6	33.5	33.5
Feed gas O_2 content (% volume)	15.3	15.3	15.3	4.6	4.6
Feed gas SO_2 concentration (ppm)	2760	2760	2760	2800	2800
Mass SO_2 adsorbed (g)	6.435	6.399	6.362	6.334	6.372
mmol SO_2 adsorbed	100.547	99.984	99.406	98.969	99.563
mmol SO_2/g activated carbon	0.666	0.662	0.658	0.655	0.659
No. of desiccant in service	0	0	0	0	0
Ave. gas flow rate/desiccant (lit./min)	0	0	0	0	0
Desorption					
Active carbon column pressure (psig)	1300	1350	1300	1350	1350
Active carbon column temperature (ºC)	37	37	37	37	37
$SCCO_2$ recycle duration (min.)	5x10 min	5x10 min	5x10 min	5x10 min	5x10 min
$SCCO_2$ recycle flow rate (ml/min.)	20	20	20	20	20
Fresh CO_2 flush time (hrs.)	18.5	18.5	18.5	18.5	18.5
Fresh CO_2 flush volume (ml)	340	340	340	340	340
Fresh CO_2 flush flow rate (ml/min.)	0.3	0.3	0.3	0.3	0.3
CO_2 release duration (hrs)	5	5	5	7	7
CO_2 release flow rate towards LAB columns (scfm)	30.7	63.5	27	9.3	11
N_2 flow after CO_2 release	No	No	No	No	No
N_2 pressure (psig)	0	0	0	0	0

Continued data of experiment No.	6	7	8	9	10
N$_2$ flow duration (hrs)	0	0	0	0	0
Sulfonation					
Column 1 LAB					
Pressure (psig)	1170	300	1200	1280	1250
Temperature (ºC)	35	35	35	35	40
Column diameter (in.)	1	1	1	1	1
LAB volume (ml)	140	140	140	135	120
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	60	60
Initial LAB height in column (cm)	80	80	80	100	80
Glass beads height in column (cm)	80	80	80	100	100
Glass beads size (mm)	2	2	2	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	8	6	8	10.5	10.5
Product LAS molarity (mol/lit.)	0.0032	0.0024	0.0032	0.004	0.0042
mmol SO$_3$ reacted to form LAS	0.448	0.336	0.448	0.54	0.504
Percent SO$_3$ reacted to form LAS (%)	0.446	0.336	0.451	0.546	0.506
Column 2 LAB					
Pressure (psig)	1040	15	1100	1200	1200
Temperature (ºC)	35	35	35	35	40
Column diameter (in.)	1	1	1	1	1
LAB volume (ml)	140	130	120	130	115
Gas diffuser diameter (in.)	1/2"	1"	1"	1"	1"
Gas diffuser media grade (micron)	60	60	60	60	60
Initial LAB height in column (cm)	80	75	70	90	
Glass beads height in column (cm)	80	80	80	100	100
Glass beads size (mm)	2	2	2	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	8	6	6	10.5	10.5
Product LAS molarity (mol/lit)	0.0032	0.0024	0.0024	0.0042	0.0042
mmol SO$_3$ reacted to form LAS	0.448	0.312	0.288	0.546	0.483
Percent SO$_3$ reacted to form LAS (%)	0.446	0.312	0.290	0.552	0.485
Column 3 LAB					

Continued data of experiment No.	6	7	8	9	10
Pressure (psig)	880	15	900	960	1000
Temperature (ºC)	35	35	35	35	40
Column diameter (in.)	1/2"	1	1	1	1
LAB volume (ml)	40	40	40	100	100
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	60	60
Initial LAB height in column (cm)	60	60	60	80	80
Glass beads height in column (cm)	40	40	40	100	100
Glass beads size (mm)	2	2	2	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	4	4	6	7	10.5
Product LAS molarity (mol/lit)	0.0016	0.0016	0.0024	0.0028	0.0042
mmol SO_3 reacted to form LAS	0.064	0.064	0.096	0.28	0.42
Percent SO_3 reacted to form LAS (%)	0.064	0.064	0.097	0.283	0.422
Collector Water Vessel					
Water volume (ml)	600	800	600	600	600
NaOH concentration (mol/lit.)	0.02	0.02	0.02	0.02	0.02
Water sample volume (ml)	30	30	25	30	30
Volume NaOH used in titration (ml)	78.3	59.7	63.7	79.2	77.7
Final H_2SO_4 molarity (mol/lit)	0.0261	0.0199	0.0255	0.0264	0.0259
Captured SO_3 mmol	15.6600	15.9200	15.3000	15.8400	15.5400
mmol SO_3 extracted by $SCCO_2$ (as LAS & H_2SO_4)	16.620	16.632	16.132	17.206	16.947
mmol SO_3 extracted by N_2	0	0	0	0	0
mmol SO_3 extracted by H_2O flush	0	0	0	0	0
Total SO_3 extracted (mmol)	16.620	16.632	16.132	17.206	16.947
SO_3 recovery efficieny (%)	16.53	16.63	16.23	17.39	17.02
No. of sulfonation columns in service	3	3	3	3	3
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment (%)	5.776	4.281	5.157	7.939	8.302
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment per sulfonation column (%)	1.925	1.427	1.719	2.646	2.767
Percent SO_3 reacted to form LAS / SO_3 adsorbed (%)	0.955	0.712	0.837	1.380	1.413

Continued data of experiment No.	6	7	8	9	10
Percent SO$_3$ captured in collector water throughout the experiment(%)	15.575	15.922	15.391	16.005	15.608
Percent SO$_3$ reacted to form LAS / SO$_3$ adsorbed per sulfonation column (%)	0.318	0.237	0.279	0.460	0.471

Table A.3 Data and results of experiments No.11 to 15

	Dec.03,09	Dec.05,09	Dec.08,09	Dec.11,09	Dec.12,09
Experiment No.	**11**	**12**	**13**	**14**	**15**
Activity/Modification	Evaluating Pressure Effect			Using N_2 as Desorbing agent	
Adsorption					
Activated carbon type	BPL4x6	BPL4x6	BPL4x6	BPL4x6	BPL4x6
Activated carbon weight in column (g)	151	151	151	151	151
Activated carbon column height (cm)	100	100	100	100	100
SO_2 mass flow rate (mg/min)	250.8	250.8	250.8	250.8	250.8
Air mass flow rate (g/min)	9.3	30.1	9.3	9.3	9.3
N_2 mass flow rate (g/min)	30.1	8.9	30.1	30.1	30.1
Feed gas volumetric flow rate (lit / min)	33.5	32.5	33.5	33.5	33.5
Feed gas O_2 content (% volume)	4.6	15.3	4.6	4.6	4.6
Feed gas SO_2 concentration (ppm)	2800	2760	2800	2800	2800
Mass SO_2 adsorbed (g)	6.387	6.166	5.999	5.945	6.062
mmol SO_2 adsorbed	99.797	96.344	93.734	92.891	94.719
mmol SO_2/g activated carbon	0.661	0.638	0.621	0.615	0.627
No. of desiccant in service	0	0	0	0	0
Ave. gas flow rate/desiccant (lit./min)	0	0	0	0	0
Desorption					
Active carbon column pressure (psig)	1350	1350	1350	15	15
Active carbon column temperature (ºC)	40	40	40	65	65
$SCCO_2$ recycle duration (min)	5x10 min	5x10 min	5x10 min	0	0
$SCCO_2$ recycle flow rate (ml/min)	20	20	20	0	0
Fresh CO_2 flush time (hrs)	22.5	19	19.5	0	0
Fresh CO_2 flush volume (ml)	340	340	350	0	0
Fresh CO_2 flush flow rate (ml/min.)	0.25	0.3	0.3	0	0
CO_2 release duration (hrs)	7	7	7	0	0
CO_2 release flow rate towards LAB columns (scfm)	25.4	25.4	25.4		0
N_2 flow after CO_2 release	No	No	Yes	Yes	Yes
Nitrogen pressure (psig)	0	0	50	40	20

Continued data of experiment No.	11	12	13	14	15
N_2 flow duration (hrs)	0	0	1	6.5	14.5
Absorption					
Column 1 LAB					
Pressure (Psig)	520	500	15	15	15
Temperature (ºC)	40	40	40	40	40
Column diameter (in.)	1	1	1	1	1
LAB volume (ml)	115	115	120	120	120
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	2	2
Initial LAB height in column (cm)	75	75	75	75	75
Glass beads height in column (cm)	75	75	75	75	75
Glass beads size (mm)	1	1	1	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume(ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	8	8	6	8	9
Product LAS molarity (mol/lit.)	0.0032	0.0032	0.0024	0.0032	0.0036
mmol SO_3 reacted to form LAS	0.368	0.368	0.288	0.384	0.432
Percent SO_3 reacted to form LAS (%)	0.369	0.382	0.307	0.413	0.456
Column 2 LAB					
Pressure (Psig)	480	460	15	15	15
Temperature(ºC)	40	40	40	40	40
Column diameter (in.)	1	1	1	1	1
LAB volume (ml)	115	115	115	115	120
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	7	7
Initial LAB height in column (cm)	75	75	75	75	75
Glass beads height in column (cm)	75	75	75	75	75
Glass beads size (mm)	1	1	1	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	7	9	8	9	8
Product LAS molarity (mol/lit)	0.0028	0.0036	0.0032	0.0036	0.0032
mmol SO_3 reacted to form LAS	0.322	0.414	0.368	0.414	0.384
Percent SO_3 reacted to form LAS (%)	0.323	0.430	0.393	0.446	0.405
Column 3 LAB					
Pressure (Psig)	440	440	15	15	15

Continued data of experiment No.	11	12	13	14	15
Temperature (ºC)	40	40	40	40	40
Column diameter (in.)	1	1	1	1	1
LAB volume (ml)	115	115	120	120	120
Gas diffuser diameter (in.)	1/2"	1/2"	1/2"	1/2"	1/2"
Gas diffuser media grade (micron)	60	60	60	15	15
Initial LAB height in column (cm)	75	75	75	75	75
Glass beads height in column (cm)	75	75	75	75	75
Glass beads size (mm)	1	1	1	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	7	7	8	9	9
Product LAS molarity (mol/lit)	0.0028	0.0028	0.0032	0.0036	0.0036
mmol SO_3 reacted to form LAS	0.322	0.322	0.384	0.432	0.432
Percent SO_3 reacted to form LAS (%)	0.323	0.334	0.410	0.465	0.456
Collector Water Vessel					
Water volume (ml)	600	600	600	600	600
NaOH concentration (mol/lit.)	0.02	0.02	0.02	0.02	0.02
Water sample volume (ml)	30	22	30	25	30
Volume NaOH used in titration (ml)	76.2	58.5	79.8	37.3	54.3
Final H_2SO_4 molarity (mol/lit)	0.0254	0.0266	0.0266	0.0149	0.0181
Captured SO_3 mmol	15.2400	15.9600	15.9600	8.9400	10.8600
mmol SO_3 extracted by $SCCO_2$	16.2520	17.0640	17.0000	0.0000	0.000
mmol SO_3 extracted by N_2	0	0	1.685	10.1700	12.1080
mmol SO_3 extracted by H_2O flush	0	0	0	0	0
Total SO_3 extracted (mmol)	16.252	17.064	18.685	10.170	12.108
SO_3 recovery efficieny (%)	16.29	17.71	19.93	10.95	12.783
No. of sulfonation columns in service	3	3	3	3	3
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment (%)	6.227	6.470	5.566	12.094	10.307
Percent SO_3 reacted to form LAS / Total SO3 desorbed in the experiment per sulfonation column (%)	2.076	2.157	1.855	4.031	3.436
Percent SO_3 reacted to form LAS / SO_3 adsorbed (%)	1.014	1.146	1.110	1.324	1.318

Continued data of experiment No.	11	12	13	14	15
Percent SO_3 captured in collector water throughout the experiment (%)	15.271	16.566	18.824	9.624	11.466
Percent SO_3 reacted to form LAS / SO_3 adsorbed per sulfonation column (%)	0.338	0.382	0.370	0.441	0.439

Table A.4 Data and results of experiments No.16 to 20

	Dec.14,09	Dec.22,09	Jan.19,10	Jan.26,10	Feb.02,10
Experiment No.	**16**	**17**	**18**	**19**	**20**
Activity/Modification	Using N_2 as desorption agent	Reducing gas diffuser media grade	Gad diffuser 1 inch & 2 micron installed at LAB1 inlet	1/8 inch Needle valve installed at LAB1 inlet	Reducing AC column height to 45cm
Adsorption					
Activated carbon type	BPL4x6	BPL4x6	BPL4x6	BPL4x6	BPL 6x16
Active carbon Weight in column (g)	151	151	151	151	65.1
Activated carbon column height (cm)	100	100	100	100	45
SO_2 mass flow rate (mg/min)	250.8	250.8	250.8	250.8	85
Air mass flow rate (g/min)	9.3	9.3	9.3	9.3	3.7
N_2 mass flow rate (g/min)	30.1	30.1	30.1	30.1	9.4
Feed gas volumetric flow rate (lit/min)	33.5	33.5	33.5	33.5	11.18
Feed gas O_2 content (% volume)	4.6	4.6	4.6	4.6	5.5
Feed gas SO_2 concentration (ppm)	2800	2800	2800	2800	2845
Mass SO_2 adsorbed (g)	5.928	5.841	5.841	5.82	2.891
mmol SO_2 adsorbed	92.625	91.266	91.266	90.938	45.172
mmol SO_2/g activated carbon	0.613	0.604	0.604	0.602	0.694
No. of desiccant in service	0	0	0	0	0
Ave.gas flow rate/desiccant (lit./min)	0	0	0	0	0
Desorption					
Active carbon column pressure (psig)	15	1350	1200	1350	1350
Active carbon column temperature (°C)	65	40	40	40	40
$SCCO_2$ recycle duration (min)	0	5x10 min	5x 10 min	5x 10 min	5x 10 min
$SCCO_2$ recycle flow rate (ml/min)	0	20	20	20	20
Fresh CO_2 flush time (hrs)	0	19	19	14	17
Fresh CO_2 flush volume (ml)	0	340	340	340	345
Fresh CO_2 flush flow rate (ml/min)	0	0.3	0.3	0.4	0.35
CO_2 release duration (hrs)	0	7	26	7	7
CO_2 release flow rate towards LAB columns (scfm)	0	25.4	22.6	12.7	9.8

Continued data of experiment No.	16	17	18	19	20
N_2 flow after CO_2 release	Yes	No	No	No	No
N_2 pressure (psig)	20	0	0	0	0
N_2 flow duration (hrs)	14	0	0	0	0
Sulfonation					
Column 1 LAB					
Pressure (psig)	15	15	15	15	1000
Temperature(ºC)	40	40	40	22	40
Column diameter (in.)	1	1	1	1	1
LAB volume (ml)	120	120	120	120	120
Gas diffuser diameter (in.)	1/2"	1/2"	1"	1"	1"
Gas diffuser media grade (micron)	2	2	2	2	2
Initial LAB height in column (cm)	75	75	75	75	75
Glass beads height in column (cm)	75	75	75	75	75
Glass beads size (mm)	1	1	1	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume (ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	9	7	11	12	7
Product LAS molarity (mol/lit.)	0.0036	0.0028	0.0044	0.0048	0.0028
mmol SO_3 reacted to form LAS	0.432	0.336	0.528	0.576	0.336
Percent SO_3 reacted to form LAS (%)	0.466	0.368	0.579	0.633	0.744
Column 2 LAB					
Pressure (psig)	15	15			
Temperature(ºC)	40	40	Not	Not	Not
Column diameter (in.)	1	1	In	In	In
LAB volume (ml)	115	115	Service	Service	Service
Gas diffuser diameter (in)	1/2"	1/2"			
Gas diffuser media grade (micron)	7	7			
Initial LAB height in column (cm)	75	75			
Glass beads height in column (cm)	75	75			
Glass beads size (mm)	1	1			
Hyamine concentration (mol/lit)	0.004	0.004			
Product LAB/LAS sample volume (ml)	10	10			
Volume Hyamine used in titration (ml)	9	8			
Product LAS molarity (mol/lit)	0.0036	0.0032			
mmol SO_3 reacted to form LAS	0.414	0.368			
Percent SO_3 reacted to form LAS (%)	0.447	0.403	0.000	0.000	0.000

Continued data of experiment No.	16	17	18	19	20
Column 3 LAB					
Pressure (psig)	15	15			
Temperature(ºC)	40	40	Not	Not	Not
Column diameter (in.)	1	1	In	In	In
LAB Volume (ml)	120	120	Service	Service	Service
Gas diffuser diameter (in)	1/2"	1/2"			
Gas diffuser media grade (micron)	15	15			
Initial LAB height in column (cm)	75	75			
Glass beads height in column (cm)	75	75			
Glass beads size (mm)		1			
Hyamine concentration (mol/lit)	0.004	0.004			
Product LAB/LAS sample volume (ml)	10	10			
Volume Hyamine used in titration (ml)	9	7			
Product LAS molarity (mol/lit)	0.0036	0.0028			
mmol SO3 reacted to form LAS	0.432	0.336			
Percentage SO reacted to form LAS(%)	0.466	0.368	0.000	0.000	0.000
Collector Water Vessel					
Water volume (ml)	600	600	600	600	600
NaOH concentration (mol/lit.)	0.02	0.02	0.02	0.02	0.02
Water sample volume (ml)	30	30	30	30	30
Volume NaOH used in titration (ml)	58.5	77.7	78.3	77.4	46.5
Final H_2SO_4 molarity (mol/lit)	0.0195	0.0259	0.0261	0.0258	0.0155
Captured SO_3 mmol	11.7000	15.5400	15.6600	15.4800	9.3000
mmol SO_3 extracted by $SCCO_2$	0.000	16.5800	16.1880	16.0560	9.636
mmol SO_3 extracted by N_2	12.9780	0	0	0	0
mmol SO_3 extracted by H_2O flush	0	0	0	0	0
Total SO_3 extracted (mmol)	12.978	16.580	16.188	16.056	9.636
SO_3 recovery efficieny (%)	14.011	18.17	17.737	17.656	21.332
No. of sulfonation columns in service	3	3	1	1	1
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment (%)	9.847	6.273	3.262	3.587	3.487
Percent SO_3 reacted to form LAS / Total SO3 desorbed in the experiment per sulfonation column (%)	3.282	2.091	3.262	3.587	3.487

Continued data of experiment No.	16	17	18	19	20
Percent SO_3 reacted to form LAS / SO_3 adsorbed (%)	1.380	1.140	0.579	0.633	0.744
Percent SO_3 captured in collector water throughout the experiment (%)	12.632	17.027	17.159	17.023	20.588
Percent SO_3 reacted to form LAS / SO_3 adsorbed per sulfonation column (%)	0.460	0.380	0.579	0.633	0.744

Table A.5 Data and results of experiments No. 21 to 25

	Feb.08,10	Feb.17,10	Feb.27,10	Mar.06,10	Mar.12,10
Experiment No.	**21**	**22**	**23**	**24**	**25**
Activity/Modification	1/8 inch Metering valve installed at LAB1 inlet	2 desiccants In service in Adsorption stage	Reducing Feed gas flow rate & N2 in desorption	3 desiccants In service in Adsorption stage	Reducing Feed gas flow rate
Adsorption					
Activated carbon type	BPL6x16	BPL6x16	BPL6x16	BPL6x16	BPL6x16
Active carbon weight in column (g)	46.7	46.7	46.7	46.7	46.7
Activated carbon column height (cm)	45	45	45	45	45
SO_2 mass flow rate (mg/min)	85.0	85.0	50.4	50.4	50.4
Air mass flow rate (g/min)	3.7	3.7	7.6	7.6	7.6
N_2 mass flow rate (g/min)	9.4	9.4	0	0	0
Feed gas volumetric flow rate (lit/min)	11.18	11.18	6.300	6.300	6.300
Feed gas O_2 content (% volume)	5.5	5.5	20	20	20
Feed gas SO_2 concentration (ppm)	2845	2845	3000	3000	3000
Mass SO_2 adsorbed (g)	1.998	1.98	1.9845	1.9712	1.9607
mmol SO_2 adsorbed	31.219	30.938	31.008	30.800	30.636
mmol SO_2/g activated carbon	0.668	0.662	0.664	0.660	0.656
No. of desiccant in service	0	2	2	3	3
Ave. gas flow rate/desiccant(lit/min)	0	5.588	3.15	2.100	2.100
Desorption					
Active carbon column pressure (psig)	**1300**	**1350**	**15**	**1350**	**1350**
Active carbon column temperature (ºC)	40	40	65	40	40
$SCCO_2$ recycle duration (min)	10x10 min	29x10min	0	10x10min	13 x10 min
SCCO2 recycle flow rate (ml/min)	40	40	0	40	40
Fresh CO_2 flush time (hrs)	14	17	0	15	19
Fresh CO_2 flush volume (ml)	230	230	0	230	290
Fresh CO_2 flush flow rate (ml/min.)	0.28	0.22	0	0.25	0.25
CO_2 release duration (hrs)	7	7	0	7	7
CO_2 release flow rate towards LAB columns (scfm)	1.8	1.1	0	1.1	1.1
N_2 flow after CO_2 release	No	No	Yes	Yes	Yes

Continued data of experiment No.	21	22	23	24	25
N$_2$ pressure (psig)	0	0	20	50	50
N$_2$ flow duration (hrs)	0	0	103	2	11
Sulfonation					
Column 1 LAB					
Pressure (psig)	**1000**	**1250**	**15**	**1250**	**1250**
Temperature(ºC)	40	40	40	40	40
Column diameter (in)	1	1	1	1	1
LAB Volume (ml)	120	120	120	120	120
Gas diffuser diameter (in)	1"	1"	1"	1"	1"
Gas diffuser media grade (micron)	2	2	2	2	2
Initial LAB height in column (cm)	75	75	75	75	75
Glass beads height in column (cm)	75	75	75	75	75
Glass beads size (mm)	1	1	1	1	1
Hyamine concentration (mol/lit)	0.004	0.004	0.004	0.004	0.004
Product LAB/LAS sample volume(ml)	10	10	10	10	10
Volume Hyamine used in titration (ml)	9.5	9	16.2	21.8	23
Product LAS molarity (mol/lit.)	0.0038	0.0036	0.0065	0.0087	0.0092
mmol SO$_3$ reacted to form LAS	0.456	0.432	0.78	1.044	1.104
Percent SO$_3$ reacted to form LAS (%)	1.461	1.396	2.515	3.390	3.604
Column 2 LAB					
Pressure (psig)					
Temperature (ºC)	Not	Not	Not	Not	Not
Column diameter (in.)	In	In	In	In	In
LAB volume (ml)	Service	Service	Service	Service	Service
Gas diffuser diameter (in.)					
Gas diffuser media grade (micron)					
Initial LAB height in column (cm)					
Glass beads height in column (cm)					
Glass beads size (mm)					
Hyamine concentration (mol/lit)					
Product LAB/LAS sample volume(ml)					
Volume Hyamine used in titration (ml)					
Product LAS molarity (ml/lit)					
mmol SO$_3$ reacted to form LAS	0.000	0.000	0.000	0.000	0.000
Percent SO$_3$ reacted to form LAS (%)					
Column 3 LAB					

Continued data of experiment No.	21	22	23	24	25
Pressure (psig)					
Temperature(°C)	Not	Not	Not	Not	Not
Column diameter (in)	In	In	In	In	In
LAB volume (ml)	Service	Service	Service	Service	Service
Gas diffuser diameter (in)					
Gas diffuser media grade (micron)					
Initial LAB height in column (cm)					
Glass beads height in column (cm)					
Hyamine concentration (mol/lit)					
Product LAB/LAS sample volume(ml)					
Volume Hyamine used in titration (ml)					
Product LAS molarity (mol/lit)					
mmol SO_3 reacted to form LAS	0.000	0.000	0.000	0.000	0.000
Percent SO_3 reacted to form LAS (%)					
Collector Water Vessel					
Water volume (ml)	600	575	600	600	600
NaOH concentration (mol/lit.)	0.02	0.02	0.02	0.02	0.02
Water sample volume (ml)	30	30	30	30	30
Volume NaOH used in titration (ml)	46.5	50.1	46.2	85.2	93.6
Final H_2SO_4 molarity (mol/lit)	0.0155	0.0167	0.0154	0.0284	0.0312
Captured SO_3 mmol	9.3000	9.6025	9.2400	17.0400	18.7200
mmol SO_3 extracted by $SCCO_2$	9.756	10.035	0.000	18.084	19.824
mmol SO_3 extracted by N_2	0	0	10.016	2.011	3.66
mmol SO_3 extracted by H_2O flush	0	0	0	0	2.99
Total SO_3 extracted (mmol)	9.756	10.035	10.016	20.095	26.474
SO_3 recovery efficieny (%)	31.250	32.435	32.302	65.244	86.415
No. of sulfonatino columns in service	1	1	1	1	1
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment (%)	4.674	4.305	7.788	5.195	4.701
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment per sulfonation column (%)	4.674	4.305	7.788	5.195	4.701

Continued data of experiment No.	21	22	23	24	25
Percent SO_3 reacted to form LAS / SO_3 adsorbed (%)	1.461	1.396	2.515	3.390	3.604
Percent SO_3 captured in water collector throughout the experiment	29.790	31.038	29.786	61.854	82.811
Percent SO_3 reacted to form LAS /SO_3 adsorbed per sulfonation column (%)	1.461	1.396	2.515	3.390	3.604

Appendix B   Sample Calculation

Table B.1 Data and results of experiment No.17

	Dec.22,09
Experiment No.	17
Activity/Modification	Reducing gas diffused Media grade at LAB 1 , 2, &3 to 2 , 7 &15 microns
Adsorption	
Activated carbon type	BPL4x6
Activated carbon weight in column (g)	151
Activated carbon column height (cm)	100
SO_2 mass flow rate (mg/min)	250.8
Air mass flow rate (g/min)	9.3
N_2 mass flow rate (g/min)	30.1
Feed gas volumetric flow rate (lit/min)	33.5
Feed gas O_2 content (% volume)	4.6
Feed gas SO_2 concentration (ppm)	2800
Mass SO_2 adsorbed (g)	5.841
mmol SO_2 adsorbed	91.266
mmol SO_2/g activated carbon	0.604
No. of desiccant in service	0
Ave.gas flow rate/desiccant (lit./min)	0
Desorption	
Active carbon column pressure (psig)	1350
Active carbon column temperature (°C)	40
$SCCO_2$ recycle duration (min)	5x10 min
$SCCO_2$ recycle flow rate (ml/min)	20
Fresh CO_2 flush time (hrs)	19
Fresh CO_2 flush volume (ml)	340
Fresh CO_2 flush flow rate (ml/min)	0.3
CO_2 release duration (hrs)	7
CO_2 release flow rate towards LAB columns (scfm)	25.4
N_2 flow after CO_2 release	No
N_2 pressure (psig)	0

	Table B.1 Continued
N$_2$ flow duration (hrs)	0
Sulfonation	
Column 1 LAB	
Pressure (psig)	15
Temperature(ºC)	40
Column diameter(in.)	1
LAB volume (ml)	120
Gas diffuser diameter (in.)	1/2"
Gas diffuser media grade (micron)	2
Initial LAB height in column (cm)	75
Glass beads height in column (cm)	75
Glass beads size (mm)	1
Hyamine concentration (mol/lit)	0.004
Product LAB/LAS sample volume (ml)	10
Volume Hyamine used in titration	7
Product LAS molarity (mol/lit.)	0.0028
mmol SO$_3$ reacted to form LAS	0.336
Percent SO$_3$ reacted to form LAS (%)	0.368
Column 2 LAB	
Pressure (psig)	15
Temperature(ºC)	40
Column diameter (in.)	1
LAB volume (ml)	115
Gas diffuser diameter (in.)	1/2"
Gas diffuser media grade (micron)	7
Initial LAB height in column (cm)	75
Glass beads height in column (cm)	75
Glass beads size (mm)	1
Hyamine concentration (mol/lit)	0.004
Product LAB/LAS sample volume (ml)	10
Volume Hyamine used in titration (ml)	8
Product LAS molarity (mol/lit)	0.0032
mmol SO$_3$ reacted to form LAS	0.368
Percent SO$_3$ reacted to form LAS (%)	0.403
Column 3 LAB	
Pressure (psig)	15

	Table B.1 Continued
Temperature ($^{\circ}$ C)	40
Column diameter (in.)	1
LAB volume (ml)	120
Gas diffuser diameter (in.)	1/2"
Gas diffuser media grade (micron)	15
Initial LAB height in column (cm)	75
Glass beads height in column (cm)	75
Glass beads size (mm)	1
Hyamine concentration (mol/lit)	0.004
Product LAB/LAS sample volume (ml)	10
Volume Hyamine used in titration (ml)	7
Product LAS molarity (mol/lit)	0.0028
mmol SO_3 reacted to form LAS	0.336
Percent SO_3 reacted to form LAS (%)	0.368
Collector Water Vessel	
Water volume (ml)	600
NaOH concentration (mol/lit)	0.02
Water sample volume (ml)	30
Volume NaOH used in titration (ml)	77.7
Final H_2SO_4 molarity (mol/lit)	0.0259
Captured SO_3 mmol	15.5400
mmol SO_3 extracted by $SCCO_2$	16.5800
mmol SO_3 extracted by N_2	0
mmol SO_3 extracted by H_2O flush	0
Total SO_3 extracted (mmol)	16.580
SO_3 recovery efficieny (%)	18.17
No. of sulfonation columns in service	3
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment (%)	6.273
Percent SO_3 reacted to form LAS / Total SO_3 desorbed in the experiment per sulfontion column (%)	2.091
Percent SO_3 reacted to form LAS / SO_3 adsorbed (%)	1.140

	Table B.1 Continued
Percent SO_3 captured in collector water throughout the experiment (%)	17.027
Percent SO_3 reacted to form LAS / SO_3 adsorbed per sulfonation column (%)	0.380

B1. Adsorption

The adsorption break-through curve obtained was shown in figure B1. The feed gas SO_2 concentration was 2680 ppm. Feed gas Oxygen content was 5% volume, balanced with nitrogen. In order to shorten the operation and reduce gas consumption, adsorption run was stopped when the outlet SO_2 concentration of the bed exceeded 2500 ppm. The outlet SO_2 concentration was recorded versus time.
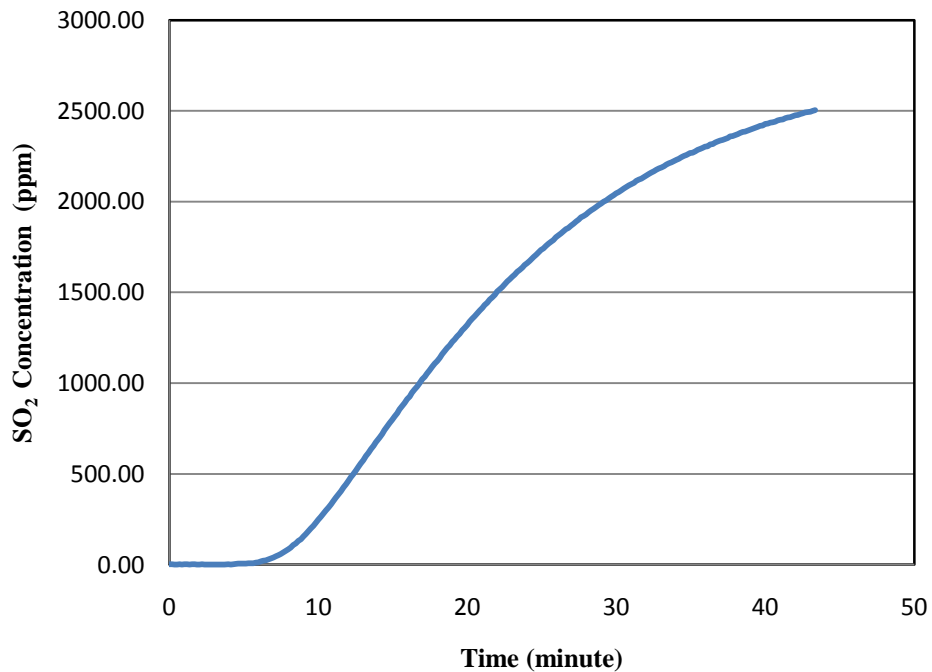

Figure B.1 Adsorption break-through curve obtained in experiment No. 17

The area under the curve was measured to calculate the mass of SO_2 escaped from the bed during adsorption run. Integration was done by using 'PolyMath" software.

The following data was used;

Adsorption run duration: 43.36   min
SO_2 density: 0.00266 g/ml
SO_2 mass flow rate :   250.8   mg/min
Air mass flow rate   :   9.3   g/min
Nitrogen mass flow rate   30.1   g/min

Calculated Parameters;

Total feed gas flow rate (at 15 psig & 25 °C) =   33.538   lit/min
Area under the curve: 56420   ppm.min

Total mass of SO_2 fed   = (SO_2 mass flow rate $\times$ Adsorption run time) =   10.875   g

Mass of SO_2 left the AC bed =
(SO_2 density $\times$ area under the curve $\times$ total feed gas volumetric flow rate) =
(0.00266 g/ml) (56420 ppm.min.) (33.538 lit/min) (1 lit/ 1×10^6 ppm) (1000 ml / 1 lit) =
5.033 g

Mass of SO_2 adsorbed on activated carbon = 10.875 $-$ 5.033 = 5.841 g

Weight of activated carbon in column = 151   g

Mass of SO_2 adsorbed = 5.841 g   =   91.266 mmol   = 0.604 mmol / g AC

B2. Sulfonation

LAB/LAS Sample Titration:

The titration was carried out according to the following equation;

LAS Concentration in sample (mol/lit) =

$$\frac{(Titrant\ Concentration, \frac{mol}{lit})\ (Titrant\ Volume,\ ml)}{Sample\ Volume,\ ml}$$

Titrant : Hyamine1622

Titrant Concentration= 0.004 mol/lit

LAB/LAS sample volume =10 ml

Column LAB 1:

LAB/LAS volume in the column = 120 ml

Volume Hyamine used in titration = 7 ml

LAS concentration in the sample = 0.0028 mol/lit

Mass LAS formed in the column =

(120 ml) × (0.0028 mol/lit) × (1lit /1000 ml) × (1000 mmol/1mol) = 0.336 mmol

Percentage of SO_3 reacted to form LAS =

(mmol SO_3 reacted to form LAS)× 100 / (mmol SO_2/SO_3 adsorbed) = 0.336 × 100 / 91.266 = 0.368 %

Column LAB 2:

LAB/LAS volume in the column = 115   ml

Volume Hyamine used in titration = 8 ml

LAS concentration in the sample =   0.0032 mol/lit

Mass LAS formed in the column =

(115 ml) × (0.0032 mol/lit) × (1lit /1000 ml) × (1000 mmol/1mol) = 0.368 mmol

Percentage of SO_3 reacted to form LAS =

(mmol SO_3 reacted to form LAS)× 100 / (mmol SO_2/SO_3 adsorbed – mmol SO_3 reacted in column LAB1) = 0.368 × 100 / (91.266 – 0.336) = 0.405 %

Column LAB 3:

LAB/LAS volume in the column = 120   ml

Volume Hyamine used in titration = 7 ml

LAS concentration in the sample =   0.0028   mol/lit

Mass LAS formed in the column =

$(120$ ml$) \times (0.0028$ mol/lit $) \times (1$lit $/1000$ ml $) \times (1000$ mmol/1mol $) =$ 0.336 mmol

Percentage of SO_3 reacted to form LAS =

(mmol SO_3 reacted to form LAS) $\times 100 /$ (mmol SO_2/SO_3 adsorbed $-$ mmol SO3

reacted in column LAB1 $-$ mmol SO_3 reacted in column LAB 2 $) = 0.336 \times 100 /$

$(91.266 - 0.336$-$0.368) =$ 0.371 %

H_2O/H_2SO_4 Titration:

A collector water vessel was located downstream of column LAB3 to capture any un-reacted SO_3.

H_2SO_4 Concentration in sample (mol/lit) $=$
$$\frac{(Titrant\ Concentration, \frac{mol}{lit}) (Titrant\ Volume,\ ml)}{2 \times Sample\ Volume,\ ml}$$

Titrant : NaOH solution

Titrant concentration = 0.02 Normal

Water volume in the vessel = 600 ml

Sample volume = 30 ml
Volume NaOH used in titration = 77.7 ml

H_2SO_4 concentration in sample (mol/lit) = (0.02 mol/lit) $\times$ (77.7 ml) / 2/(30 ml) = 0.0259 mol/lit

Total mass SO_3 reacted to form H_2SO_4 in water collector =

(600 ml) $\times$ (0.0259 mol/lit) $\times$ (1lit /1000 ml) $\times$ (1000 mmol/1mol) = 15.54 mmol

Total mass SO_3 extracted in the experiment =

mass SO_3 reacted to form LAS in columns LAB1, LAB2 and LAB3 + mass SO_3 reacted in water collector to form H_2SO_4 = 0.336 + 0.368 + 0.336 + 15.54 = 16.58 mmol

SO_3 recovery efficiency =

Total mass SO_3 extracted in the experiment $\times$ 100 / Total mass SO_2/SO_3 adsorbed = (16.58 mmol) $\times$100 / (91.266 mmol) = 18.17 %

Percentage SO_3 reacted to form LAS / SO_3 Adsorbed =

(mass SO_3 reacted to form LAS in columns LAB1, LAB2 and LAB3) $\times$ 100 / (mass SO_2/SO_3 adsorbed) =   (0.336 + 0.368 + 0.336) $\times$ 100 / 91.266 = 1.14 %

Percentage SO_3 captured in collector water throughout the experiment =

(SO_3 recovery efficiency) – (Percentage SO_3 reacted to form LAS / SO_3 Adsorbed) = 18.17 – 1.14 = 17.0 3%

B.3 Feed gas moisture content calculation for Experiment No.17

Feed gas temperature = 25℃ = 298 K

Feed gas pressure (downstream of mass flow controllers) = 15 psig

SO_2 mass flow rate = 250.8   mg/min

SO_2 source moisture content = 100 ppm

Air mass flow rate = 9.3 g/min

Air source moisture content = 1 ppm

Nitrogen mass flow rate = 30.1 g/min

Nitrogen source moisture content = 1 ppm

Adsorption run time= 43.36 min

SO_2 volumetric flow rate = [(250.8 × 10^{-3} g/min)×(8.314 N. m/mol. K)×(298 K)] /

[(64 g/mol)× (103393 N/m^2)] = 9.4 × 10^{-5} m^3/min =

9.4 × 10^{-2} lit/min

Air volumetric flow rate = [(9.3 g/min)×(8.314 N. m/mol. K)×(298 K)] / [(29 g/mol)×

(103393 N/m^2)] = 7.96 × 10^{-3} m^3/min = 7.96 lit/min

N_2 volumetric flow rate = [(30.1 g/min)×(8.314 N. m/mol. K)×(298 K)] / [(28 g/mol)×

(103393 N/m^2)] = 2.57 × 10^{-2} m^3/min = 25.7 lit/min

H_2O flow rate (carried by SO_3 stream) = SO_2 volumetric flow rate × SO_2 cylinder H_2O

Content = (9.4 ×10^{-2} lit/min)×(1×10^{-6} ppm/lit)

= 9.4 × 10^{-8} lit/min = 9.4 ×10^{-5} ml/min

H_2O flow rate (carried by Air stream) = Air volumetric flow rate × Air source H_2O

Content = (7.96 lit/min)×(1×10^{-6} ppm/lit)

= 7.96 × 10^{-6} lit/min = 7.96 × 10^{-3} ml/min

H_2O flow rate (carried by N_2 stream) = N_2 volumetric flow rate × Air source H_2O

Content = (25.7 lit/min)×(1×10^{-6} ppm/lit)

= 2.57 × 10^{-5} lit/min = 2.57 × 10^{-2} ml/min

Total H_2O flow rate carried by feed gas = (9.4 ×10^{-5} ml/min) + (7.96 × 10^{-3} ml/min) +

$$(2.57 \times 10^{-2} \text{ ml/min}) = 3.37 \times 10^{-2} \text{ ml/min}$$

Total H_2O volume transferred to activated carbon bed by feed gas during adsorption run=

Total H_2O flow rate carried by feed gas $\times$ Adsorption run time

$= (3.37 \times 10^{-2} \text{ ml/min}) \times (43.36 \text{ min}) = 1.46 \text{ ml} = 81.18 \text{ mmol } H_2O$

Appendix C   Analytical Procedure

The analytical procedure to prepare indicators, sample aliquots and to perform titration was adopted from references 20 and 21.

Mixed Indicator Method

Titrant : Hyamine 1622 - 0.004 M solution

Indicator Preparation:

<u>Stock Solution</u>

0.50 g   Dimidium Bromide   dissolve in 30 ml hot 10% ethanol solution

0.25 g   Disulfine Blue   dissolve in 30 ml hot 10% ethanol solution

transfer the above solutions to a 250 ml volumetric flask and dilute to volume.

<u>working indicator</u>

20 ml stock solution

20 ml H_2SO_4 (2.5M)

transfer to a 500 ml volumetric flask and dilute with de-ionized water up to volume

Sample Aliquot

weight out 4 meq of anionic active material and dissolve in water

neutralize to phenolphthalein

make up to 1 liter in standard volumetric flask

mix thoroughly

Titration Mixture

20 or 25 ml sample aliquot

10 ml water

10 ml indicator

10 ml chloroform

At the beginning of the titration Chloroform layer would have a magenta color that would turn into neutral grey at the end point. If excess amount of titrant is added chloroform layer it turns blue.

This modification is covered by the standard methods ISO 6121:1988 and BS 6829.

Laboratory Practice:

Due to uncertainties about the yield of sulfonation reaction and the amount of LAS in the samples, proposed indicator concentrations reduced to half. The following procedure was practiced to prepare Indicator and titration mixture;

Stock solution

Prepared – same as above

working indicator

10 ml stock solution

1000 ml water

10 ml H_2SO_4 (2.5 N)

Sample Aliquot

This part has been eliminated.

Titration Mixture

10 sample

10 ml water

10 ml Mixed Indicator

20 ml chloroform

Appendix D   Supplementary Tables

Reaction			$\Delta V^{\ddagger}_{(1)b}$ (cm³/mole)	$\Delta V^{\ddagger}_{(1)f}$ (cm³/mole)
N_2O	$\rightarrow$	N_2+O	2.2	-4.8
$H+CH_4$	$\rightarrow$	CH_4+H	1.1	-10
H_3C+H_2	$\rightarrow$	CH_4+H	0.5	-4.2
$H+CH_4$	$\rightarrow$	CH_3+H_2	0.9	-9.7
$Cl+H_2$	$\rightarrow$	$HCl+H$	1.8	-2.7
$Br+H_2$	$\rightarrow$	$HBr+H$	2.1	-2.5
H_2+I_2	$\rightarrow$	2 HI	0.6	-3.7

$\Delta V^{\ddagger}_{(1)b}$ Change in the volume of reactants as they form transition state, associated with bond breakage, $\Delta V^{\ddagger}_{(1)f}$ Change in the volume of reactants as they form transition state, associated with bond formation.

Table D.1 Contribution to reactants volume change ($\Delta V^{\ddagger}_{(1)}$) as they form transition state. [6]

Functional Group	Type	wt%
Surfactants	Anionic Surfactants	5-15
	Nonionic Surfactants	1-15
Alkalinity sources	Carbonate, silicate	15-30
Bleach Precursors	Bleach Activators	1-5
	Polycarboxylates	1-5
	Soap	1-5
Builders	Zeolite	1-15
	Amylase	
	Cellulase	
	Lipase	
	Mannanase	
	Other enzymes	
Enzymes	Protease	0.2-0.5
Fragrances		0.2-0.5
Optical Brighteners	Optical Brighteners	0.2-0.5
Oxidising Agents	Oxygen-based bleaching agents	5-15
Processing Agent	Sodium Sulphate	Balance to 100
Sequestrants	Phosphonates	0.2-0.5

Table D.2 Typical ingredients of heavy duty laundry detergent-powder regular. [18]

Gas	N_2	Air	CO_2	SO_2
Grade	Vehicle Emission Zero	Vehicle Emission Zero	Supercritical Fluid Chromatography	3.8 Liquid Phase
PraxAir Catalogue No.	NI 4.8 VE	AI 0.0VE	CD 4.8 SC	SD 3.8
Composition				
Purity	99.998%		99.998%	99.98%
O_2	< 0.5 ppm	20.0 + - 1%	< 5 ppm	
H_2O	< 1 ppm	< 1 ppm	< 1 ppm	< 100 ppm
CO_2	< 1 ppm	< 1 ppm		
CO	< 0.5 ppm	< 0.5 ppm	< 0.1 ppm	
THC	< 0.1 ppm	< 0.1 ppm	< 2 ppm	
No_x	< 0.1 ppm	< 0.1 ppm		
H_2				
N_2			< 10 ppm	
Total extractable Hydrocarbon			< 50 ppb	
Residue (as H_2SO_4)				< 75 ppm/w
Acid (as H_2SO_4)				< 25 ppm/w

Table D.3 Specifications of gases used in experiments. [23]

Table D.4 Specifications of High Pressure Pump Model 260 D. [24]

POWER REQUIREMENTS1	100 ± 10 Vac, 1.5 A maximum
(Mains voltage line cord is a	117 ± 12 Vac, 1.5 A maximum
"Disconnect Device")	234 ± 23 Vac, 0.75 A maximum
LINE FREQUENCY	50 or 60 Hz
LINE VOLTAGE NOISE TOLERANCE	$1.7 \times$ nominal rms line voltage, 10 μsecond pulses, any phase angle, random or repetitive
DIMENSIONS PUMP CONTROLLER	PUMP CONTROLLER
	Width: 27.18 cm 27.18 cm
	Depth: 46.74 cm 30.48 cm
	Height: 101.09 cm 13.59 cm
WEIGHT	PUMP CONTROLLER
	32.8 kg 2.96 kg
FLOW RATE RANGE	See Figure D9 Appendix D
FLOW RATE ACCURACY2	± 0.5% (maximum 0.50 μl/min seal leakage)
FLOW RATE DISPLAY RESOLUTION	1.0 μl/min
ANALOG OUTPUT ACCURACY3	± 1% of selected range
DISPLACEMENT RESOLUTION	16.63 nl
REFILL TIME	2.5 minutes
REFILL OR DEPRESSURIZATION RATE	1.0 μl/min to 107 ml/min at any pressure from 0 to 517.1 bar
PRESSURE RANGE	0.6895 to 517.1 bar
PRESSURE ACCURACY	± 0.5% of full scale at constant temperature
PRESSURE REPEATABILITY	± 0.5% of full scale within 48 hours at constant temperature
ZERO PRESSURE DRIFT	± 0.25% of full scale within 48 hours at constant temperature
PRESSURE DISPLAY RESOLUTION	6.895 kPa
AMBIENT TEMPERATURE RANGE	5 to 40°C
TEMPERATURE DRIFT	± 0.015% of full scale/°C within −1 to 70°C
HUMIDITY	95% maximum
CYLINDER CAPACITY	266.05 ml
DEAD (HEADSPACE) VOLUME	2.10 ± 0.020 ml

Table D.5 Specifications of Activated Carbon BPL 4x6. [26]

Iodine Number	1000	mg/g
Butane Activity	23.3	% (min.)
Hardness Number	95	(min.)
Apparent Density	0.43	g/cc
Mean Particle Diameter	3.7	mm (min.)
Screen Size US Sieve Series		
On Mesh 4	15.00	%(max)
Through Mesh 7	8	% (max.)

Table D.6 Specifications of Activated Carbon BPL 6x16. [26]

Iodine Number	1050	mg/g (min)
Butane Activity by Weight	23.3	% (min.)
Hardness Number	90	(min.)
Apparent Density	0.44	g/cc (min.)
Mean Particle Diameter	2.5	mm (min.)
Screen Size US Sieve Series		
On 6 Mesh	6	% (max)
Through Mesh 7	5	% (max.)

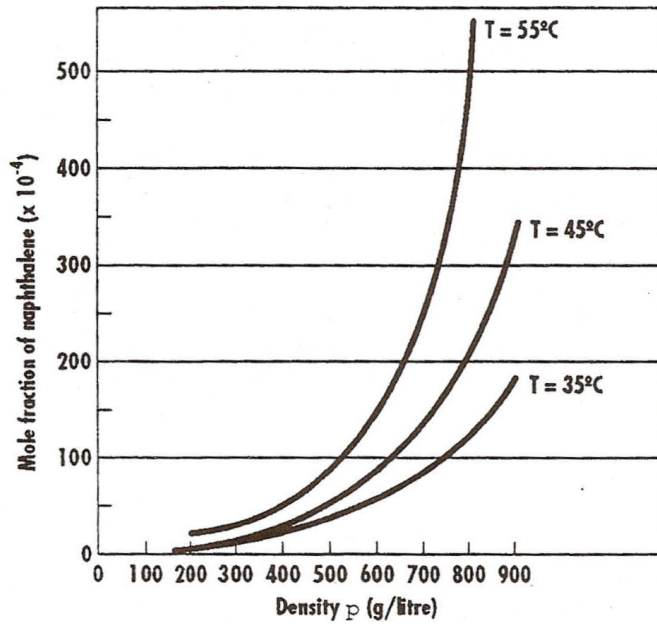# Appendix E   Supplementary Figures

Figure E.1 **S**olubility (mole fraction) of Naphthalene in CO_2 as a function of density at various temperatures. [8]
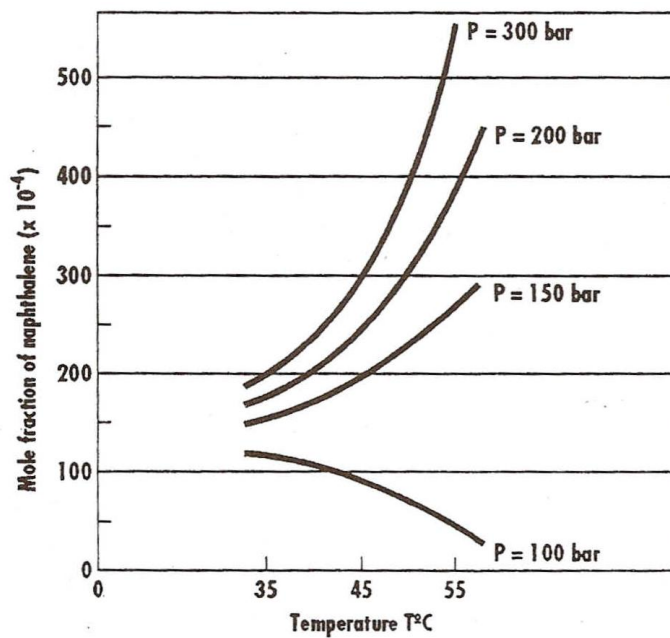

Figure E.2 **S**olubility (mole fraction) of Naphthalene in CO_2 as a function of temperature at various pressures. [8]

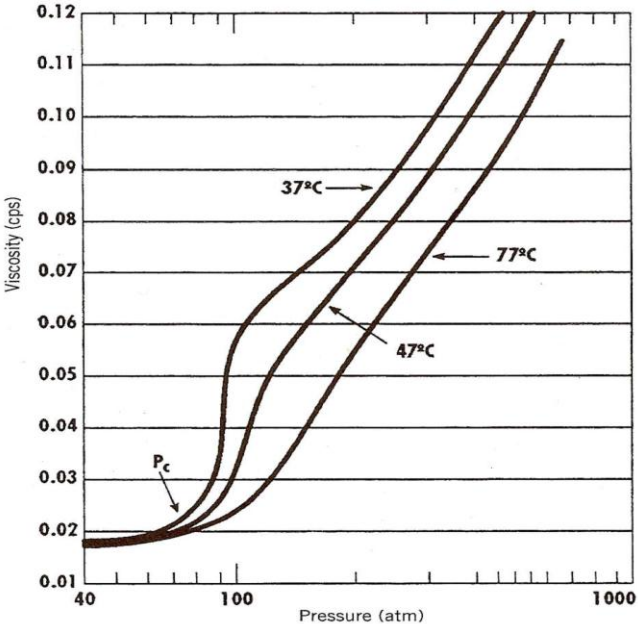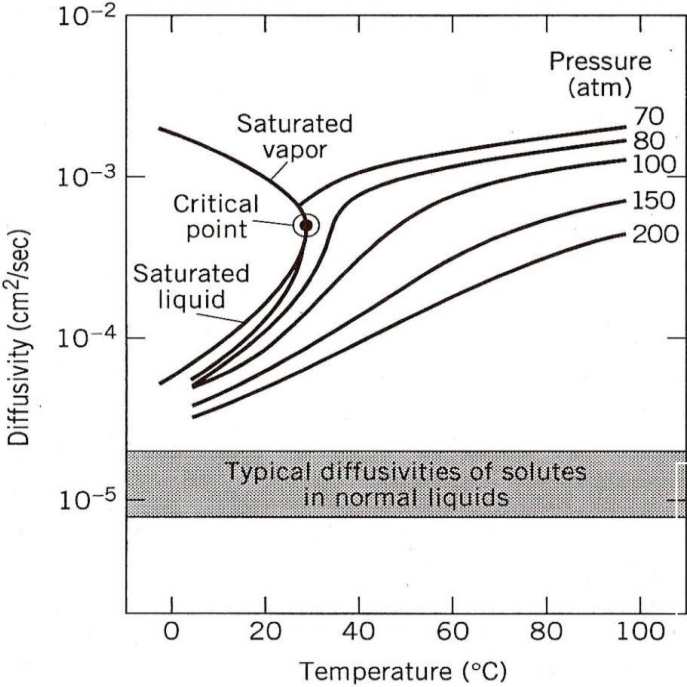**Figure E.3** Viscosity behavior of CO_2 at various temperatures and pressures. [8]

Figure E.4 Diffusivity of CO_2 versus temperature at various pressures. [8]
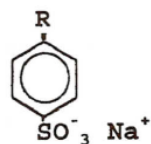
A. Alkylbenzene Sulfonate
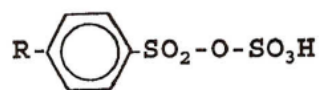
B. Pyrosulfonic acid(intermediate)
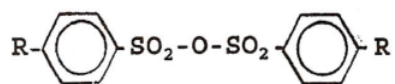
C. Sulfonic acid anhydride(intermediate)
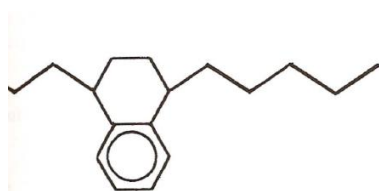
D. dialkyltetralin structure
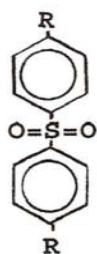
E. dialkyldiarylsulfone(by-product)

Figure E.5 ByProducts of LAB sulfonation reaction. [20]

A . cetylpyridinium chloride

B. cetyltrimethylammonium
chloride(bromide)

C. alkyl dimethylbenzylammonium chloride
also known as benzalkonium chloride

D. p-tert-octylphenoxy ethyl dimethyl benzyl
ammonium chloride monohydrate, also known
as benzethonium chloride and Hyamine 1622

E. 1-(ethoxy-carbonyl)pentadecyl trimethyl
ammonium chloride also known as Septonex

F. 1,3-didecyl-2-methylimidazolinium chloride also
known as TEGOtrant

Figure E.6 Quaternary ammonium salts used for the titration of anionic surfactants. [20]
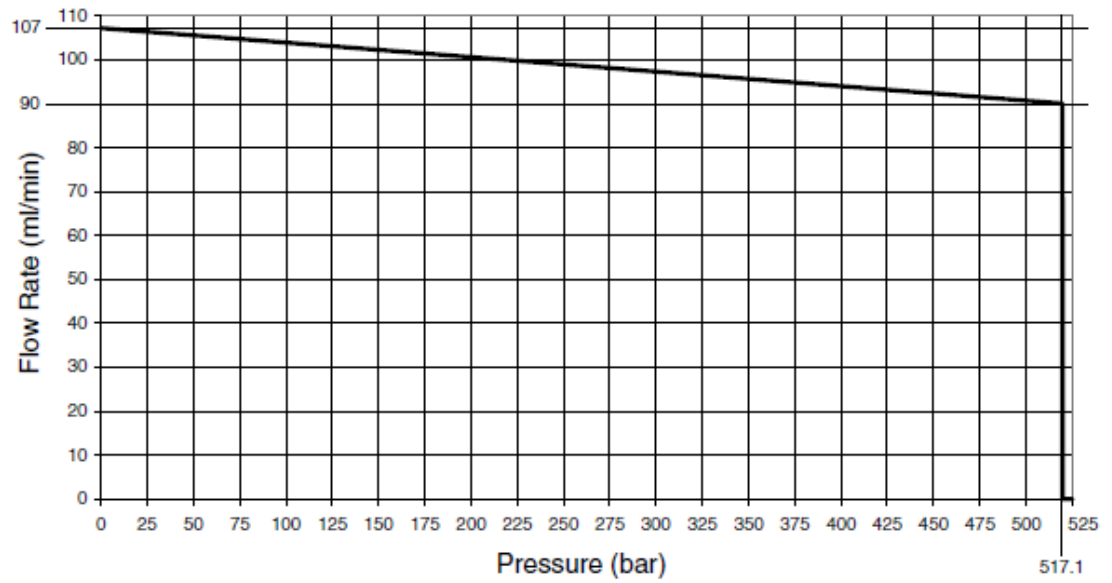
Figure E.7 Flow characteristic of high pressure pump model ISCO 260 D. [24]

Figure E.8 Specifications of Linear Aklylbenzene

PETRESA CANADA

CERTIFICATE OF ANALYSIS

Product : PETRELAB P 550-Q   Customer :   Certificate number :   3472
Our ref. : 266821   Origin :   455-SN-7   Sampling date :   2009-03-31
Code :   Purchase order :   CAS :
Note: Release number:

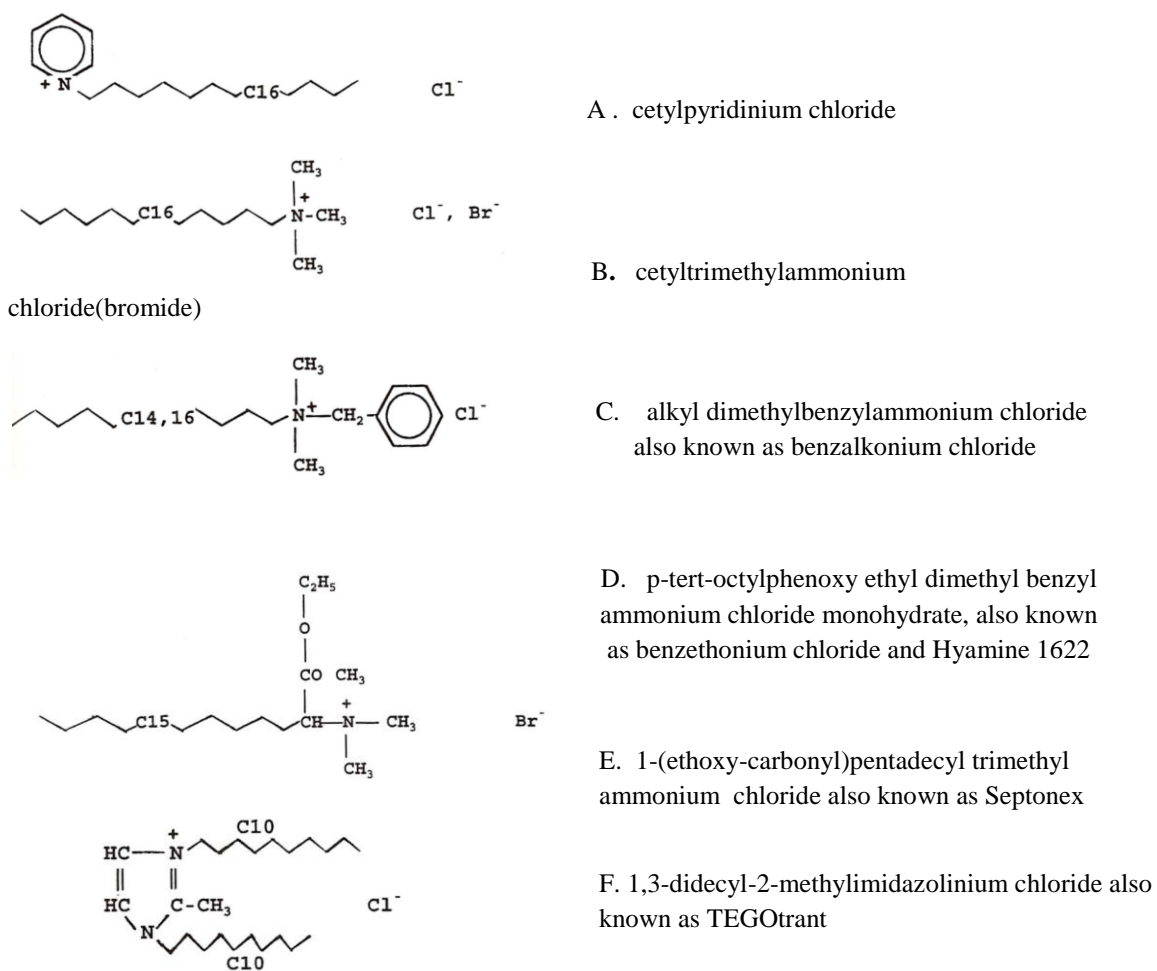| TEST	Method	Results	Specification
			Rev. 12, February 2007
DENSITY (15°C, g/ml)	ASTM D-4052	0.8598	0.858 - 0.868
WATER, PPM	UOP 481	9	100 max.
BROMINE INDEX	ASTM D-2710	1	10 max.
AVERAGE MOLECULAR WEIGHT	UOP 673	240.2	239 to 243
2 PHENYL LAB	UOP 673	27.1	25 to 30 %
SAYBOLT COLOR *	ASTM D-156	30	+ 29 min.
TETRALINE/INDANE *	ECOSOL HPLC	0.1	0.5 max.
PARAFFIN C14	PCI PR-671	0.08	
< PHENYL C10	UOP 673	0.9	1.0 max.
PHENYL C10	UOP 673	15.3	16.0 max.
PHENYL C11	UOP 673	30.4	
PHENYL C12	UOP 673	28.3	
PHENYL C13	UOP 673	24.6	
PHENYL C14	UOP 673	0.5	3 max.
> PHENYL C14	UOP 673	0.0	0.5 max.
PHENYL C10 + C11	UOP 673	45.7	35 - 55
PHENYL C13 + C14	UOP 673	25.1	29 max.
ACID WASH TEST *	PETRESA LC 414.1	90.9	15 min.

96

Appendix F   Mass Flow Controller Calibration data

Figure F.1 Calibration data of SO_2 Mass Flow Controller

Bronkhorst®
HIGH-TECH

CALIBRATION CERTIFICATE

We herewith certify that the instrument mentioned below has been calibrated in accordance with the stated values and conditions. The calibration standards used are traceable to national standards of the Dutch Weights & Measures (NMi).

Identifications

	Calibrated Instrument	Calibration Standard
Type :	Flow controller (D)	Piston Prover
Serial number :	M9203017D	INM0205301B
Model number :	F-201DV-AAD-11-E	FPP T-016-TD
Certificate no. :	BHTG34/744793	BHTG09/418235A

Conditions

	Customer			Calibration
Fluid :	SO2	Fluid :	AiR	
Pressure :	30 psi (g)	Pressure :	3.0 bar (a)	
Temperature :	20 °C	Temperature :	23.5 °C	
Flow :	467 mg/min	Room temperature :	23.5 °C	
Output range :	0 - 100 %	Atm. pressure :	1022 hPa	

Results

Nominal Flow Setting		Calibrated Output Signal		Customer Flow		Deviation	
0.0	%	0.006000	%	0.0000	mg/min	0.0	%FS
25.0	%	24.99	%	116.7	mg/min	0.0	%FS
50.0	%	49.99	%	233.6	mg/min	0.0	%FS
75.0	%	74.99	%	350.2	mg/min	0.0	%FS
100.0	%	99.99	%	467.5	mg/min	-0.1	%FS

Notes

*   The calibrated flow is converted to customer flow using Bronkhorst High-Tech FLUIDAT® software.

Figure F.2 Calibration data of Air Mass Flow Controller

Copy
Printed by T.A.
Page : 1-1

Bronkhorst®
HIGH-TECH

CUSTOMER CALIBRATION CERTIFICATE

We herewith certify that the instrument mentioned below meets its specified accuracy and has been calibrated in accordance with the stated values and conditions. The calibration standards used are traceable to national standards of the Dutch Weights & Measures (NMi).

Identifications

	Calibrated Instrument	Calibration Standard
Type :	Flow controller (D)	Rotor meter
Serial number :	M9203017F	M0205926G
Model number :	F-202AV-M10-AAD-55-V	FRM R-025-TD
Certificate no. :	BHTC69/CL9/746092	NMi/G1S10117

Conditions

	Customer			Calibration	
Fluid :	AiR		Fluid :	AiR	
Pressure :	40	psi (g)	Pressure :	5.0	bar (a)
Temperature :	20	°C	Temperature :	23.5	°C
Flow :	133	g/min			
Output range :	0 - 100	%	Atm. pressure :	1021	hPa

Results

Calibration Results		Conversion Results	Calculation Results	
Calibrated Sensor Signal	Calibrated Flow AiR	Customer Flow(*) AiR	Customer Output Signal	Customer Output Signal
0.0000 [%]	0.000E+00 [ln/min]	0.0000 [g/min]	0.0000 [%]	0.0000 [V]
3.814 [%]	8.009E+00 [ln/min]	10.37 [g/min]	7.799 [%]	0.3900 [V]
7.032 [%]	1.482E+01 [ln/min]	19.19 [g/min]	14.43 [%]	0.7214 [V]
10.26 [%]	2.159E+01 [ln/min]	27.95 [g/min]	21.02 [%]	1.051 [V]
13.50 [%]	2.838E+01 [ln/min]	36.76 [g/min]	27.64 [%]	1.382 [V]
16.74 [%]	3.520E+01 [ln/min]	45.58 [g/min]	34.27 [%]	1.714 [V]
19.98 [%]	4.202E+01 [ln/min]	54.41 [g/min]	40.91 [%]	2.046 [V]
26.37 [%]	5.558E+01 [ln/min]	71.98 [g/min]	54.12 [%]	2.706 [V]
32.64 [%]	6.917E+01 [ln/min]	89.56 [g/min]	67.34 [%]	3.367 [V]
38.73 [%]	8.279E+01 [ln/min]	107.2 [g/min]	80.59 [%]	4.029 [V]
44.56 [%]	9.635E+01 [ln/min]	124.8 [g/min]	93.82 [%]	4.691 [V]
50.21 [%]	1.099E+02 [ln/min]	142.4 [g/min]	107.0 [%]	#N/A

Notes

* The calibrated flow is converted to customer flow using Bronkhorst High-Tech FLUIDAT® software.

* Related Primary Certificate: BHTG60/JST/744910

Figure F.3 Calibration data of Nitrogen Mass Flow Controller

Copy
Printed by T.A.
Page : 1 - 1

Bronkhorst®
HIGH-TECH

CUSTOMER CALIBRATION CERTIFICATE

We herewith certify that the instrument mentioned below meets its specified accuracy and has been calibrated in accordance with the stated values and conditions. The calibration standards used are traceable to national standards of the Dutch Weights & Measures (NMi).

Identifications

	Calibrated Instrument	Calibration Standard
Type :	Flow controller (D)	Rotor meter
Serial number :	M9203017E	M0205926G
Model number :	F-202AV-M10-AAD-55-V	FRM R-025-TD
Certificate no. :	BHTC69/CL9/746091	NMi/G1S10117

Conditions

	Customer			Calibration	
Fluid :	N2		Fluid :	AiR	
Pressure :	40	psi (g)	Pressure :	5.0	bar (a)
Temperature :	20	°C	Temperature :	22.9	°C
Flow :	133	g/min			
Output range :	0 - 100	%	Atm. pressure :	1023	hPa

Results

Calibration Results		**Conversion Results**		**Calculation Results**	
Calibrated Sensor Signal	Calibrated Flow AiR	Customer Flow(*) N2		Customer Output Signal	Customer Output Signal
0.0000 [%]	0.000E+00 [ln/min]	0.0000 [g/min]		0.0000 [%]	0.0000 [V]
3.380 [%]	7.322E+00 [ln/min]	9.166 [g/min]		6.892 [%]	0.3446 [V]
6.510 [%]	1.412E+01 [ln/min]	17.67 [g/min]		13.29 [%]	0.6644 [V]
9.639 [%]	2.088E+01 [ln/min]	26.13 [g/min]		19.64 [%]	0.9822 [V]
12.78 [%]	2.766E+01 [ln/min]	34.62 [g/min]		26.03 [%]	1.302 [V]
15.92 [%]	3.446E+01 [ln/min]	43.13 [g/min]		32.43 [%]	1.621 [V]
19.06 [%]	4.125E+01 [ln/min]	51.62 [g/min]		38.82 [%]	1.941 [V]
25.25 [%]	5.479E+01 [ln/min]	68.58 [g/min]		51.56 [%]	2.578 [V]
31.35 [%]	6.831E+01 [ln/min]	85.50 [g/min]		64.29 [%]	3.214 [V]
37.27 [%]	8.186E+01 [ln/min]	102.4 [g/min]		77.03 [%]	3.851 [V]
42.94 [%]	9.530E+01 [ln/min]	119.2 [g/min]		89.66 [%]	4.483 [V]
48.45 [%]	1.088E+02 [ln/min]	136.2 [g/min]		102.4 [%]	5.119 [V]

Notes

* The calibrated flow is converted to customer flow using Bronkhorst High-Tech FLUIDAT® software.

* Related Primary Certificate: BHTG60/JST/742874

Appendix G   BET Results

```
        File Name: C:/DOCUME~1/ADMIN/DESKTOP/CARBON~1/C28.MGD
        Sample ID: Carbon Black 30.6
      Setup Group: Carbon Black setup

          Started: 3/25/3810 10:59:41AM        Sat. Pressure: 748.96 mmHg
        Completed: 3/25/3810 1:06:22PM      Meas. Freespace: 0.2184 cm³
      Report Time: 3/25/2010 2:07:09PM        Sample Weight: 0.1063 g
        Evac. Rate: 500.0 mmHg/min               Evac. Time: 6.000000 minutes
    Analysis Mode: Equilibration            Equil. Interval: 5 secs
```

Analysis Log

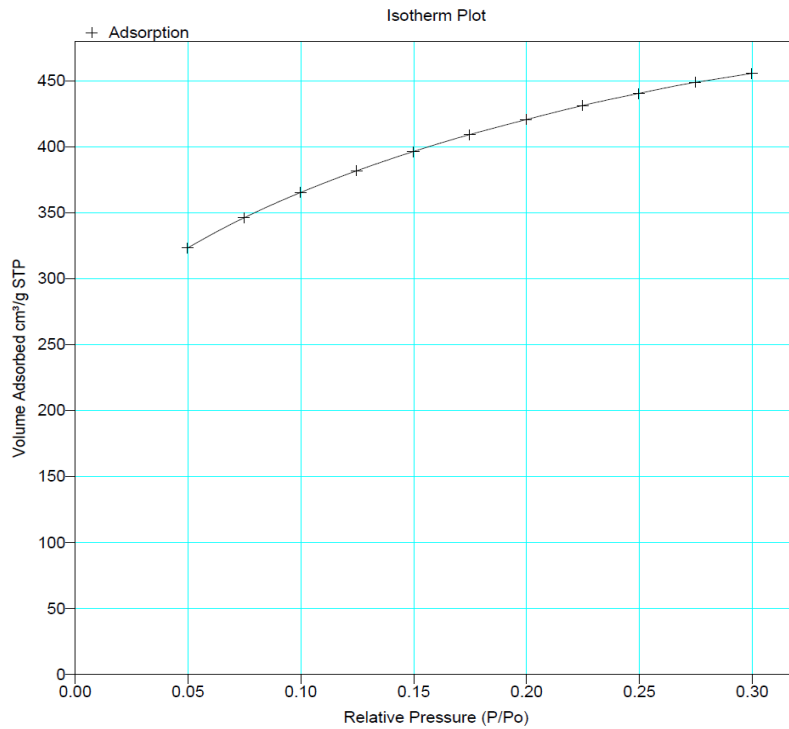| Relative Pressure	Pressure (mmHg)	Vol Adsorbed (cm³/g STP)	Elapsed Time (HR:MN)	Saturation Press.(mmHg)
				748.96002
0.049802390	37.30000	323.3538	00:42	
0.074803728	56.02500	346.2549	00:52	
0.099805060	74.75000	365.3891	01:02	
0.124766339	93.44500	381.9053	01:11	
0.149801053	112.19500	396.4499	01:20	
0.174755649	130.88499	409.3129	01:29	
0.199770336	149.62000	420.6701	01:37	
0.224785023	168.35500	431.3649	01:45	
0.249732947	187.03999	440.5540	01:53	
0.274774343	205.79500	448.8995	02:00	
0.299735632	224.49001	455.7134	02:05	

100

File Name: C:/DOCUME~1/ADMIN/DESKTOP/CARBON~1/C28.MGD
Sample ID: Carbon Black 30.6
Setup Group: Carbon Black setup

Started: 3/25/3810 10:59:41AM   Sat. Pressure: 748.96 mmHg
Completed: 3/25/3810 1:06:22PM   Meas. Freespace: 0.2184 cm³
Report Time: 3/25/2010 2:07:09PM   Sample Weight: 0.1063 g
Evac. Rate: 500.0 mmHg/min   Evac. Time: 6.000000 minutes
Analysis Mode: Equilibration   Equil. Interval: 5 secs

Isotherm Plot

+ Adsorption

File Name: C:/DOCUME~1/ADMIN/DESKTOP/CARBON~1/C28.MGD
Sample ID: Carbon Black 30.6
Setup Group: Carbon Black setup

Started: 3/25/3810 10:59:41AM   Sat. Pressure: 748.96 mmHg
Completed: 3/25/3810 1:06:22PM   Meas. Freespace: 0.2184 cm³
Report Time: 3/25/2010 2:07:09PM   Sample Weight: 0.1063 g
Evac. Rate: 500.0 mmHg/min   Evac. Time: 6.000000 minutes
Analysis Mode: Equilibration   Equil. Interval: 5 secs

_____

BET Surface Area Report

BET Surface Area: 1421.9581   ±   24.3707 m²/g
Slope: 0.003067 ±   0.000052
Y-Intercept: -0.000005 ±   0.000010
C: -589.847129
VM: 326.646709   cm³/g STP
Correlation Coefficient: 9.987318e-01

Molecular Cross-section: 0.1620   nm²

Relative Pressure	Vol Adsorbed (cm³/g STP)	1/ [VA*(Po/P - 1)]
0.049802390	323.3538	0.000162
0.074803728	346.2549	0.000234
0.099805060	365.3891	0.000303
0.124766339	381.9053	0.000373
0.149801053	396.4499	0.000444
0.174755649	409.3129	0.000517
0.199770336	420.6701	0.000593
0.224785023	431.3649	0.000672
0.249732947	440.5540	0.000756
0.274774343	448.8995	0.000844
0.299735632	455.7134	0.000939

File Name: C:/DOCUME~1/ADMIN/DESKTOP/CARBON~1/C28.MGD
Sample ID: Carbon Black 30.6
Setup Group: Carbon Black setup

         Started: 3/25/3810 10:59:41AM   Sat. Pressure: 748.96 mmHg
       Completed: 3/25/3810 1:06:22PM   Meas. Freespace: 0.2184 cm³
     Report Time: 3/25/2010 2:07:09PM   Sample Weight: 0.1063 g
       Evac. Rate: 500.0 mmHg/min   Evac. Time: 6.000000 minutes
   Analysis Mode: Equilibration   Equil. Interval: 5 secs

BET Surface Area Plot
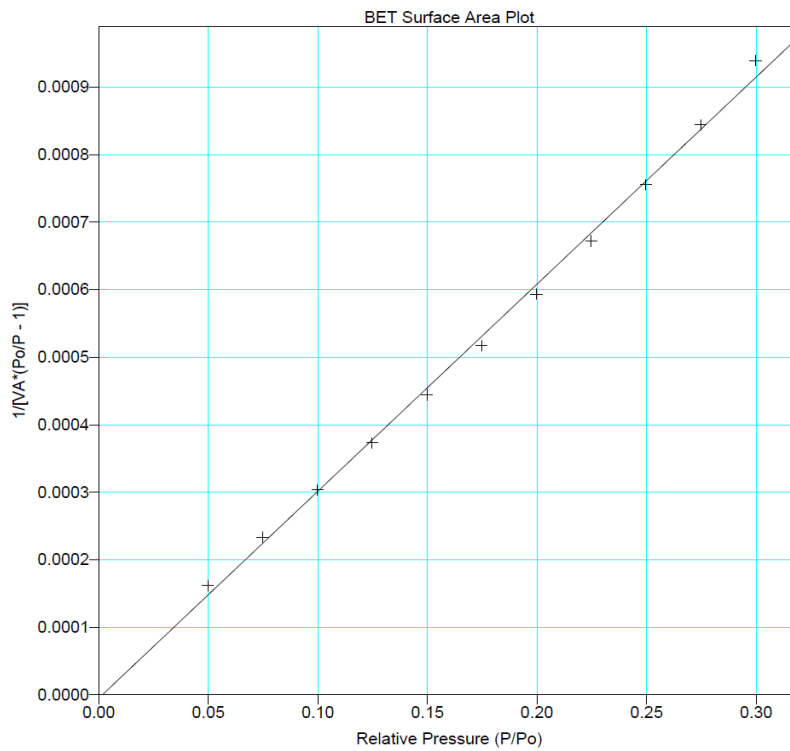
File Name: C:/DOCUME~1/ADMIN/DESKTOP/CARBON~1/C28.MGD
Sample ID: Carbon Black 30.6
Setup Group: Carbon Black setup

      Started: 3/25/3810 10:59:41AM   Sat. Pressure: 748.96 mmHg
    Completed: 3/25/3810 1:06:22PM   Meas. Freespace: 0.2184 cm³
  Report Time: 3/25/2010 2:07:09PM   Sample Weight: 0.1063 g
   Evac. Rate: 500.0 mmHg/min   Evac. Time: 6.000000 minutes
Analysis Mode: Equilibration   Equil. Interval: 5 secs
_____

Langmuir Surface Area Report

Langmuir Surface Area: 2188.0847 ±   35.9554 m²/g
Slope: 0.001990 ±   0.000033
Y-Intercept: 0.000071 ±   0.000006
b: 0.035756
VM: 502.638336   cm³/g STP
Correlation Coefficient: 9.987871e-01

Molecular Cross-section: 0.1620   nm²

Relative Pressure	Vol Adsorbed (cm³/g STP)	1/ [VA*(Po/P)]
0.049802390	323.3538	0.000154
0.074803728	346.2549	0.000216
0.099805060	365.3891	0.000273
0.124766339	381.9053	0.000327
0.149801053	396.4499	0.000378
0.174755649	409.3129	0.000427
0.199770336	420.6701	0.000475
0.224785023	431.3649	0.000521
0.249732947	440.5540	0.000567
0.274774343	448.8995	0.000612
0.299735632	455.7134	0.000658

            File Name: C:/DOCUME~1/ADMIN/DESKTOP/CARBON~1/C28.MGD
            Sample ID: Carbon Black 30.6
          Setup Group: Carbon Black setup

              Started: 3/25/3810 10:59:41AM   Sat. Pressure: 748.96 mmHg
            Completed: 3/25/3810 1:06:22PM   Meas. Freespace: 0.2184 cm³
          Report Time: 3/25/2010 2:07:09PM   Sample Weight: 0.1063 g
            Evac. Rate: 500.0 mmHg/min   Evac. Time: 6.000000 minutes
        Analysis Mode: Equilibration   Equil. Interval: 5 secs

                              Summary Report

                                  Area

Single Point Surface Area at P/Po 0.29973563 :   1389.1923   m²/g

BET Surface Area: 1421.9581   m²/g

Langmuir Surface Area: 2188.0847   m²/g