LOW TEMPERATURE CONVERSION OF SO$_2$ to SO$_3$

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NOMENCLATURE

- **A**: Cross section of the reactor
- **D**: Diameter of the reactor
- **t**: time
- **Q**: Volumetric flow rate of the fluid
- **R**: Universal gas constant
- **D_{gas}**: Density of the gas
- **P**: Pressure of the gas
- **T**: Temperature of the gas
- **C_{p,mix}**: Specific heat of the mixture
- **C_{p,gas,l}**: Specific heat of the gas in the mixture
- **M_{f,gas}**: Mass flow rate of the gas in the mixture
- **T_{mix}**: Temperature of the gas mixture
- **M_{f,mix}**: Mass flow rate of the mixture
- **C_{p,mix}**: Specific heat of the mixture
- **[SO_{2}]**: Concentration of SO_{2}
- **[SO_{3}]_{peak}**: Concentration of SO_{3} at the peak of the graph
- **[SO_{3}]_{0\%methane}**: Concentration of SO_{3} at 0% Methane level
CHAPTER 1
INTRODUCTION

Coal has been the major source of power generation in the United States because of its availability and low cost. However, burning coal to produce electricity results in the emission of fly ash, metal fumes, sulfur oxides, unburned and partially burned hydrocarbons, \( \text{NO}_x \), carbon monoxide, and greenhouse gases like \( \text{N}_2\text{O} \), and \( \text{CO}_2 \). Exposure to fly ash is associated with increased mortality risk among the individuals with pre-existing diseases, such as chronic obstructive pulmonary disease, pneumonia, and chronic heart disease. The epidemiological studies also provide evidence for associations that ambient particulate matter exposure increases the risk of respiratory and cardiovascular morbidity effects (e.g., increased hospital admissions or emergency room visits for asthma or other respiratory problems, alterations in pulmonary function, etc) (Parker, 1997).

Coal has a relatively high ash (incombustible inorganic) content compared to other fuels. Coal ash consists of carbon, silica \( (\text{SiO}_2) \), alumina \( (\text{Al}_2\text{O}_3) \), iron oxide \( (\text{FeO} \quad \text{and} \quad \text{Fe}_2\text{O}_3) \), and some unburned carbon. The light ash that leaves the coal furnace with the exhaust gas is called fly ash. Fly ash may be hazardous to health, because inhalation of the particulate matter may damage lungs or other surfaces of the respiratory tract. Very fine ash less than 2.5 microns in size are a potential biological threat to humans. It penetrates into the lungs resulting in asthma and chronic obstructive pulmonary disease (Parker, 1997).
Numerous devices are available for particulate control, including settling chambers, cyclones, filters, scrubbers, and electrostatic precipitators. Electrostatic precipitators are widely used by the power industry to control particulate emission because of high particulate removal efficiency compared to that of other available devices. Electrostatic precipitators are expensive, however, they are rarely inflexible to changes in process operating conditions, such as switching from high to low sulfur coal. Electrical resistivity of the fly ash is of paramount importance to the performance and the size of the electrostatic precipitator. Most particles from power station are complex compounds of silica and allumina both having excellent insulation properties. The electrical resistivity can be modified by the presence of impurities in the ash or by conditioning the surface of the particles by conductive substances.

Prior to 1995, high sulfur coal was widely used in coal-fired boilers. The fly ash produced from this fuel is readily collectable in electrostatic precipitators. The combustion of high sulfur coals produces high concentrations of \( \text{SO}_3 \), typically 1-2\% of the \( \text{SO}_2 \) concentration. \( \text{SO}_3 \) and moisture combine to form sulfuric acid, which deposits on the fly ash surface creating a conductive film and lowering the electrical resistivity of the fly ash. Consequently, the ash surrenders its charge more easily, making the ash easier to collect compared to the high resistivity ash. High resistivity ash will coat the collecting electrodes, and because they are unable to surrender their charge they will repel similarly charged ash, thus reducing the collecting electrodes efficiency.

The 1990 Clean Air Act restricted the emission of sulfur oxides. In an attempt to comply with these new limitations, many coal-fired power-generating stations have
switched to lower sulfur coals. Unfortunately, low sulfur coals tend to generate more fly ash and flue gas per megawatt and because of the high resistivity of this ash, it is difficult to collect in existing precipitators. Consequently, electrostatic precipitators in these plants experience serious ash collection problems, including increased opacity and corresponding de-ratings.Opacity-related de-rating can result in significant financial losses.

One solution is to install more expensive precipitators with larger collection areas. This is usually dismissed under all but extreme circumstances. Instead, most plants install flue gas conditioning systems that inject SO$_3$ in the exhaust ducts before the precipitators. The SO$_3$ produced from the combustion of elemental sulfur forms SO$_2$, which is further oxidized to SO$_3$ (2-10ppm) (Nettleton et al., 1969) are then injected into the flue gas upstream of the precipitator.

Injection of SO$_3$ has its own set of problems. Flue gas conditioning produces bluish-colored plumes of sulfate particles and, in addition to this, creates acid rain precursors by adding sulfur to the flue gas. Often, injection of ammonia or steam is also needed for particle agglomeration in order to improve collection efficiency.

Further, SO$_3$ injection typically requires a catalyst to oxidize SO$_2$. This catalyst would be rapidly degraded in flue gas. Therefore, the injection process must take place mostly above the flue gas, thus requiring more space and equipment. External SO$_3$ injection could be replaced with a process entirely contained in the exhaust gas ducts.

Studies conducted by Khan (1999) have shown the formation of SO$_3$ at low free stream gas temperature. At low free stream gas temperatures, a flame front could
generate enough oxygen radicals to convert SO₂ to SO₃. Addition, the level of oxygen radicals downstream of the flame are reduced at lower temperatures, which leads to a decrease in decomposition of SO₃ back to SO₂. The decrease in decomposition of SO₃ could be very helpful for a fly ash conditioning process. When natural gas is burned, relatively large quantities of water are generated. For example, the combustion of one molecule of methane produces two molecules of water. The addition of water could assist in agglomeration of the fly ash and lead to easy collection at the electrostatic precipitator plates, which would then increase the collection efficiency (Bayless et al., 2000).

The main focus of this work was to examine the conversion of SO₂ to SO₃, due to the interaction of a perpendicularly introduced natural gas flame at average free stream gas temperatures of 450K and 1000K. Excess oxygen varied between 1, 4 and 10%. Initial SO₂ concentrations considered are 500ppm, 3500ppm, and 2000ppm to represent low and high sulfur coals. Experiments were performed with 1.25-inch and 4-inch diameter reactor tubes to study the effects of reaction volume on the conversion of SO₂ to SO₃. Results indicate that low temperature conversion occurs for an extended duration.

1.2 Thesis Organization

This work is organized into six chapters with each chapter providing information about a specific topic. Chapter 1 focuses on the introduction and the problem statement. Chapter 2 gives an in-depth description about the literature concerned with the work. Chapter 3 discusses the experimental setup used and the design of the setup. Chapter 4 focuses on the description of the procedure followed to conduct the experiments and methods adapted for analysis. Chapter 5 presents the results obtained from various
experiments conducted under different operating conditions, which are shown in the appendix. Chapter 6 concentrates on the summary of the work and recommendations for future work.
CHAPTER 2
LITERATURE REVIEW

2.1 Kinetics of Sulfur

The oxides of sulfur are commonly referred to as SOx. SO2 is the most common form of SOx, formed when sulfur or sulfur containing compounds are burned in O2 in the presence of a catalyst, such as vanadium, to produce sulfur dioxide (Andrew, W.F, 1936).

Sulfur dioxide is a gas of pungent odor, choking, and suffocating even when largely diluted with air. Sulfur trioxide (SO3) is formed when sulfur dioxide is oxidized. This process can be greatly accelerated under certain conditions by means of some catalyst, such as finely divided platinum, vanadium oxide, or chromium oxide (Andrew, W.S., 1936). SO3 combines readily with water to form sulfuric acid, which is very corrosive.

The oxidation of SO2 to SO3 has been studied by several researchers (Wendt et al., 1973, Whittingham, 1949, Hedley., 1967, Barrett et al., 1966, Merryman et al., 1979, Fenimore et al., 1965, Nettleton et al., 1969). In a study of the effects of SO2 on flame stability of CO-H2 flame, Bawn and Garner have found that SO3 was found and destroyed by

\[ \text{SO}_2 + \text{O} \rightarrow \text{SO}_3 \] \hspace{1cm} (2.1)

\[ \text{SO}_3 + \text{H} \rightarrow \text{SO}_2 + \text{OH} \] \hspace{1cm} (2.2)

Studies conducted by Dooley and Whittingham (1949) on the formation of sulfur trioxide in bunsen and diffusion flames containing added sulfur compounds have shown
that sulfur trioxide is produced by the reaction of sulfur dioxide with atomic oxygen that is, by reaction

\[ \text{O} + \text{SO}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M} \] (2.3)

Sulfur trioxide is produced when sulfur compound is introduced into a hydrogen, carbon monoxide, or hydrocarbon flame burning with excess oxygen (Cullis et al., 1972). Flames with pure sulfur compounds, such as hydrogen sulfphide and carbonyl sulfphide, also produce sulfur trioxide. Such flames, when burning with excess oxygen at atmospheric pressure, convert approximately the same fraction of sulfur to sulfur trioxide as do flames containing sulfur in small proportions as an additive (Cullis et al., 1972). This points to the existence of pseudo-equilibrium between the dioxide and the trioxide in the flame gases. Sulfur trioxide is also formed from SO\textsubscript{2} exposure to a hydrocarbon flame (Bayless et al., 1998). Excess oxygen in a hydrocarbon flame forms oxygen radicals,

\[ \text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}, \] (2.4)

which combine with SO\textsubscript{2} to form SO\textsubscript{3},

\[ \text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}. \] (2.5)

Once sulfur gas has passed through the flame, SO\textsubscript{3} concentration decreases as it reacts with oxygen and hydrogen radicals (to a much lesser extent),

\[ \text{SO}_3 + \text{O} \rightarrow \text{SO}_2 + \text{O}_2, \] (2.6)

\[ \text{SO}_3 + \text{H} \rightarrow \text{SO}_2 + \text{OH}, \] (2.7)

\[ \text{SO}_3 + \text{M} \rightarrow \text{SO}_2 + \text{O} + \text{M}. \] (2.8)

SO\textsubscript{3} concentrations remain at super equilibrium levels for a few hundred milliseconds after the sulfur gas passes through a flame (Bayless et al., 1998).
The transient super equilibrium of SO₃ that forms when excess oxygen and SO₂ pass through a reacting flame was studied extensively (Wendt et al., 1973, Whittingham., 1949, Hedley., 1967, Barrett et al., 1966, Merryman et al., 1979, Fenimore et al., 1965, Nettleton et al., 1969) and reviewed by Cullis and Mulcally (1972). The motivating factor for many of these efforts was boiler corrosion. These previous studies indicated that the primary mechanism for flame-based formation of SO₃ was the interaction of SO₂ with O in the presence of a third body (M) given by

$$\text{SO}_3 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M} \quad (2.9)$$

Third bodies (M) can be virtually any non-reacting species. Earlier work focused on Ar, O₂, and N₂, with recent work investigating CO₂ and H₂O (Cullis et al., 1972).

Rate constant value of $2.5 \times 10^{-10} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$ have been reported for temperature ranges as wide as 1250-2150 (Fenimore et al., 1965, Nettleton et al., 1969), with activation energies ranging from 2500-6000 cal mol⁻¹ (Wendt et al., 1973, Whittingham., 1949, Hedley., 1967, Barrett et al., 1966, Merryman et al., 1979, Fenimore et al., 1965, Nettleton et al., 1969). This work uses the kinetic expression of Troe (Bayless et al., 2000), which establishes $k_1$ as

$$K_1 = 4 \times 10^{28} \text{ Exp} \left[ \frac{-5250}{RT} \right] \text{ cm}^6 \text{mol}^{-2} \text{sec}^{-1} \quad (2.10)$$

In systems with flames, the primary source of O atoms in reaction 2.9 is the oxidation of CO described as (Fenimore et al., 1965),

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad (2.11)$$
\[ CO + OH \rightarrow H, \quad (2.12) \]

which is crucial if significant dissociation of \( O_2 \) is not necessary to promote \( SO_3 \) formation. Thus, low bulk gas temperatures should not drastically inhibit \( SO_3 \) formation if a flame can generate sufficient \( O \) atoms (Verhoff et al., 1974).

Once formed, \( SO_3 \) reacts with oxygen and hydrogen atoms to form \( SO_2 \) (Hedley, 1967), as given by

\[
\begin{align*}
SO_2 + O & \rightarrow SO_2 + O_2, \quad (2.13) \\
SO_3 + H & \rightarrow SO_2 + OH. \quad (2.14)
\end{align*}
\]

Rate constants for Reaction 2.13 \((k_3)\) vary with the assumed activation energy of Reaction 2.9. Smith et al. found \( k_3 \) to be

\[
K_3 = 6.1 \times 10^{14} \exp \left[ \frac{-14750}{RT} \right] \text{cm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad (2.15)
\]

Estimates for rate constants for Reaction 2.14 are nebulous, at best. Because the concentration of \( H \) atoms is far less than \( O \) atoms in lean flames, Cullis and Mulcahy (1972) conducted that the role of Reaction 2.14 in controlling \( SO_3 \) decomposition is doubtful (Nettleton et al., 1969). However Merryman and Levy (1979), using \( H_2S \) flames, found evidence that the activation energy for Reaction 2.14 was less than that of Reaction 2.13. Fenimore and Jones (1965) found evidence that suggests the magnitude of \( k_4 \) approximately \( 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \) at 1740K.

\( SO_3 \) also can dissociate through third body collision to \( SO_2 \) and \( O \) as given by the equation
SO₃ + M → SO₂ + O + M. \hspace{1cm} (2.16)

The kinetic parameters of thermal decomposition are not well understood at lower temperatures although they have been quantified at temperatures above 1700K (Cullis et al., 1972). In their work, Astholz et al. (1972) determined a kinetic expression for \( k_9 \) (where M was Argon) given by

\[
K_9 = 10^{15.5 \pm 0.2} \exp \left( \frac{-63000}{RT} \right) \text{cm}^3 \text{mol}^{-1} \text{sec}^{-1}
\] \hspace{1cm} (2.17)

2.2 Equilibrium

The equilibrium level of SO₃ in fuel-lean combustion products is determined by the overall reaction (Flagan and Sienfeld, 1988)

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{SO}_3,
\] \hspace{1cm} (2.18)

the equilibrium constant \( K_p \) is given by

\[
K_p = 1.53 \times 10^{-5} e^{11.760/T} \text{atm}^{-1/2}.
\] \hspace{1cm} (2.19)

The equilibrium yield of SO₃ increases with decreasing temperature. In combustion products below about 900K, SO₃ would be the dominant species at chemical equilibrium.

2.3 Electrostatic Precipitator

An electrostatic precipitator (ESP) is an apparatus that utilizes electric forces to separate suspended particles from gases (Parker, 1997). An ESP primarily consists of electrodes and collecting plates. In an electrostatic precipitator, gas-born particles are passed through a corona (direct current) or charging field, usually negative in polarization, which may have an electrical potential of 50kV or more. The charged particles then move across the gas stream from the negative electrode to be deposited on
the collecting electrode, which is electrically grounded. From the collectors, the particles are removed into receiving hoppers or troughs, either by mechanical shock impulse rapping in a dry application or by water washing in the case of wet precipitators.

Electrostatic precipitators have been used for almost a century in the collection of dust, fume, and mist particles from all types of processes (Levy and Merryman, 1964). The initial applications from mainly chemical/metallurgical-based applications were both for reducing air pollution and for the recovery of valuable by-products (Cullis and Mulcahy, 1972); for example, the cleaning of combustible gases or material losses from metal smelting processes. More recently, the major application has been in controlling air pollution to meet specific legislative emissions and consequently, design efficiencies can now exceed 99.9%.

2.4 Fly Ash Resistivity

Particles carried in suspension when pulverized coal is burned are called fly ash. Fly ash is inorganic residue of the coal and may contain unburned carbon particles. Electrostatic precipitators are widely used to collect fly ash.

The electrical resistivity of the particles is very important to performance and size of the precipitator (Parker, 1997). Most particles from power stations are complex compounds of silica and alumina both having the excellent insulating properties one would anticipate resistivities in the $10^{14}$ ohm-cm and higher range as a bulk resistivity (Cullis et al., 1972). The electrical resistivity of the particles can be modified by the presence of impurities in the ash or where the surface of the particle is naturally
conditioned by components present or added in the entraining gases, such as Na₂O or H₂SO₄.

The electrical resistivity is determined by two mechanisms: the bulk volume conductivity, a function of the particle matrix constituents, and surface conduction. The latter is governed by the adsorbed surface layer, which is related to the surface reactivity and gas components. For particles such as fly ash, which are mostly silica, the bulk volume conductivity tends to be extremely low, making conduction a surface phenomena (Parker, 1997).

Moisture is present in the flue gas, either from the converted hydrogen in the coal or from atmospheric moisture. SO₃ can react with this moisture to produce condensed phase sulfuric acid. This then uses the surface of the particles as condensation nuclei, reducing their resistivity, so electrical conduction can proceed through the layer of acid. Due to the strict regulations on the emission of sulfur dioxide many power generating plants switched to low sulfur coals. As a result, natural SO₃ levels were reduced, in some cases, to a point where not enough SO₃ was formed to produce H₂SO₄, thus increasing the resistivity of the fly ash.

Ash particles with high resistivity slowly lose their charge once they reach the collector surface in an electrostatic precipitator, and a voltage, according to Ohm's law begins to develop across the dust layer. Depending on the resistivity and the layer thickness voltage, for resistivities in the 10¹³ ohm-cm range, positive ions can be emitted from the surface of the dust. These positive ions cross the inter-electrode space. They collide with, and neutralize negative ions and charged particles, which significantly
reduces precipitator performance. This condition is termed as reverse ionization or back corona that reduces the average voltage while increasing the overall current. As a result, ash from low sulfur coal used in an ESP sized for high sulfur coal, will resist collection and create unacceptable emissions (Parker, 1997).

2.5 Flue Gas Conditioning

The use of additives to ESP inlet gas streams to enhance the performance of electrostatic precipitators is well known and has been applied to commercial installations since the early part of this century (Parker, 1997). Commercial conditioning of fly ash usually involves the injection of a chemical reagent into the flue gas stream to control the electrical resistivity of the dust and thus improve its collection. The most common conditioning agent used for modifying high fly ash resistivity is sulfur trioxide. Controlled injection of small quantities of sulfur trioxide into the flue gas stream reduces the resistivity of the fly ash and permits its collection in the existing precipitator. Flue gas conditioning of fly ash relies on one or more of the following effects:

a) Modifying the surface electrical conductivity of the dust,

b) Increasing the inter-electrode space charge, and

c) Increasing dust cohesivity to reduce losses during rapping

When the temperature of the flue gas drops down to around 300°C (about 572 F) a significant portion of the sulfur trioxide gas reacts with water vapour to produce sulfuric acid vapor [Parker, 1997]. This process is complete at a temperature of around 200°C, where electrostatic precipitators normally operate. The sulfuric acid vapor is adsorbed or condensed on an otherwise poorly conducting fly ash surface and directly participates in
the electrical conduction process. The acid may, however, react with basic constituents of the ash and thus undergo conversion to a poorly conducting layer of sulfate salts. Calcium oxide a fairly common component of coals may cause acid neutralization and thus reduce its conducting capability. Thus two coals similar in sulfur content may produce similar concentrations of sulfur trioxide, but the one containing more alkaline ash is likely to have a substantially higher resistivity.

The most commonly used method for generating sulfur trioxide is catalytic conversion from sulfur dioxide. This method can use liquid sulfur dioxide as a feedstock, but the majority of installations burn elemental sulfur to produce gaseous sulfur dioxide, which is then catalytically converted to sulfur trioxide. Heated ambient air is normally used as a carrier gas in the injection systems, with the sulfur trioxide a small percentage of the carrier volume. The sulfur trioxide flow is modulated to match boiler load changes, fuel variations, or other variables. Injection into the flue gas stream may be either upstream or downstream of the air heater, depending on convenience and accessibility.

Homogeneous conversion of SO₂ to SO₃ was found to be possible even at temperatures as low as 450K (Khan, 1999), which is the temperature generally found in industrial electrostatic precipitators. The presence of SO₃ in the flue gas stream could lead to the reduction of resistivity of the fly ash and thus enhancing the performance of the electrostatic precipitator.
CHAPTER 3
EXPERIMENTAL FACILITY

3.1 Overview

The primary objective of these experiments was to study the conversion of SO$_2$ to SO$_3$ under perpendicularly introduced natural flame, at an average free stream gas temperature of 450K. The goals of the experiments were to determine if sulfur reactivity could be increased at low temperatures and to quantify the effect of excess air in the process of conversion of SO$_2$ to SO$_3$. Experiments were performed to quantify the level of SO$_3$ conversion for the temperature of 450K as the function of time, downstream of the flame, and as the function of O$_2$ concentration using the Environmental Protection Agency's Method 8.

3.2 Sulfur Reactivity Experimental Facility (SREF)

The Sulfur Reactivity Experimental Facility used for the study of the SO$_3$ conversion is shown in Figure 3.1. The following are the major components of SREF.

- Primary and secondary reactor
- Water cooling system
- Natural gas injection probe

The reactor facility allowed the user to collect the samples under controlled conditions of flow, temperature, and composition. The conditions simulating the typical exhaust gas stream in a power plant were achieved by using the characteristics, which are described in Table 3.1.
Table 3.1 Operating Characteristics of the Furnace Setup

<table>
<thead>
<tr>
<th>Operating Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Temperatures</td>
<td>450K-1000K</td>
</tr>
<tr>
<td>Excess Oxygen</td>
<td>1 to 4%</td>
</tr>
<tr>
<td>Percentage of CH₄</td>
<td>2% and 4%</td>
</tr>
<tr>
<td>SO₂ Concentration</td>
<td>500 – 3500ppm</td>
</tr>
<tr>
<td>Gas Velocity</td>
<td>0.667 to 2.032 m/s</td>
</tr>
</tbody>
</table>

The first stage of the two-stage electrical resistance-heated reactor preheats the sulfur bearing gas stream to the approximate temperature of the secondary furnace. This limits quenching effects. A 1.25-inch reactor tube made of stainless steel was used in both the primary and secondary furnace to minimize the catalyzation of SO₂ to SO₃ (Khan, 1999).

In the secondary furnace a pre-mixed natural flame, which was controlled by varying the percentage of natural gas and oxygen, was introduced perpendicular to the direction of the axis of the reactor tube.

Gas was sampled from the secondary furnace using a 0.25-inch diameter stainless steel probe, which could be positioned at any point along the axis of the reaction tube of the secondary furnace. The gas stream collected was passed via a heated connection to the Method 8-setup train with the aid of a vacuum pump, for the purpose of collecting the sample and analysis of SO₃ content.
Figure 3.1 Sulfur Reactivity Experimental Facility
3.2.1 Primary Reactor

The main purpose of the primary reactor was to pre-heat the gas mixture, basically to prevent the thermal shock of the gas stream. Temperatures up to 1200 °C could be generated in the primary reactor. A schematic representation of the primary reactor is shown in Figure 3.2. The gases SO_2 and N_2 are brought through a three-way connector into the reactor tube of the primary reactor. The temperature inside the primary reactor was set to 450K by the use of the Lindbergh Controller (Khan, 1999). As the gases pass through the primary reactor, they attain the desired temperature of 450K and are then passed into the secondary reactor. (For a more detailed description of the primary reactor, refer to Khan, 1999).
Figure 3.2 Schematic representation of the primary reactor
3.2.2 Secondary Reactor

The preheated gas stream entered the secondary furnace, then reacted with the natural gas flame introduced perpendicularly to the direction of the axis of the reaction tube in the secondary furnace, as shown in Figure 3.3.

The secondary reactor was able to generate temperatures up to 1700 °C with the aid of the U-shaped MoSi$_2$ heating elements. With the aid of the variable transformer, the temperature inside the reactor is maintained at an average value of 450K for all the experiments performed. (For more details on the design of the secondary reactor, refer to Khan, 1999).

The natural gas injection probe as shown in Figure 3.4 (Khan, 1999) has been used for certain sets of experiments. The natural gas injection probe as shown in Figure 3.4 was basically designed to inject pre-mixed natural gas and air at the desired rate. The probe was cooled by a water-cooling system to reduce the flame mixture reactant temperature.
3.3 Gas Sampling Train

Gas samples were extracted from the gas mixture with the aid of a sampling probe, which consisted of a 0.25-inch tube with variable axial position control. A schematic diagram for the gas sampling train specified by EPA Method 8 (EMTIC) is shown in Figure 3.5. The sulfuric acid mist sampling train was employed to separate sulfuric acid mist (including SO$_3$ in the absence of other particulate matter) and SO$_2$
emissions from the furnace. Tests performed by the EPA show that the minimum detectable limits of the method are 0.05 mg/m³ for SO₃ and 1.2 mg/m³ for SO₂.

The sulfuric acid mist (including SO₃) and the SO₂ are separated using a midget bubbler and impinges in the sampling train. The concentration of H₂SO₄ (including SO₃) and SO₂ were measured. The impinges used in the set were placed in the ice bath. (For a more detailed description of the sampling train, refer to EPMTS NSPS Test Method 8, 1998).

Figure 3.4 Natural gas injection probe
3.4 Experiments With 4-inch reactor tube furnace

The primary objective of using a 4-inch diameter reactor tube as opposed to a 1.25-inch diameter tube in the existing reactor was to study the effect of reaction volume on the process of conversion of SO$_2$ to SO$_3$.
3.4.1 Design of the 4-inch Diameter Tube Furnace

The 4-inch diameter reactor tube furnace looks similar in design to the furnace shown in Figure 3.3. The thickness of insulation was increased twofold, compared to the secondary furnace shown in Figure 3.3, in order to allow high temperature operation of the secondary furnace. The increase in thickness was achieved by placing 1 inch thick allumina board and 2 inch thick allumina mat on each side of the rectangular walls surrounding the reactor tube, as shown in Figure 3.7. The diameter of the secondary reactor tube was stepped down to 1.12 inches at the top, to establish a slip fit with the primary reactor tube. The size of the natural gas injection port was changed to a 0.8-inch (diameter), to fit with the size of the designed burner.

The material of the insulation, cover plates, and the top and base plates was the same as that of the design shown in Figure 3.3. The dimensional changes involved in the new furnace are represented in top and side sectional views as shown in Figures 3.6 and 3.7, respectively.
A: 4-inch stainless steel reactor tube  
B: 0.25-inch U-shaped molybdenum heating elements  
C: Alumina Mat and Alumina Board Insulation  
D: Aluminum sheet to provide outer cover to the furnace  
E: Aluminum plate to hold the reactor tube and the heating elements

Figure 3.6 Top view of the 4-inch furnace
Figure 3.7 Side sectional view of the 4-inch reactor tube furnace

3.4.2 Burner Design

The burner used for the experiments is shown in Figure 3.8. Natural gas was injected through a 0.25-inch diameter stainless steel tube and air was injected through the inlet indicated in Figure 3.8. A stainless steel cone made by drilling steps in a hollow 0.45-inch diameter tube was attached to the end of the 0.25 inch stainless steel tube. The
primary purpose of the cone was to generate a pilot flame to keep the temperature high, to avoid the quenching of the main flame by the incoming cool air and to keep the root of the flame stable.

The pilot flame was generated inside the cone by establishing natural gas flow in the 0.25-inch stainless steel tube and igniting it. After the pilot flame was established, airflow was introduced through a 0.5 inch tube, as indicated in Figure 3.8. A small amount of natural gas flow was established through the section upstream of the airflow to pre mix natural gas and air before the mixture enters the conical section. In the conical section, the pilot flame ignites the natural gas and air mixture to generate a more stable flame, which is shown in Figure 3.8.

Figure 3.8 Schematic representation of the burner used for 4-inch reactor tube furnace
CHAPTER 4
TEST PROCEDURE AND SAMPLE COLLECTION

4.1 Overview

Experiments were conducted to study the effects of average free stream gas temperature, natural gas concentration, O$_2$ concentration and residence time on the gas phase homogeneous conversion of SO$_2$ to SO$_3$. The parameters considered for experimentation are shown in Table 4.1.

Table 4.1 Experimental Parameters

<table>
<thead>
<tr>
<th>Controlled Parameters</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>450K and 1000K</td>
</tr>
<tr>
<td>Excess Oxygen Percentage</td>
<td>1%, 2%, 3%, 4% and 10%</td>
</tr>
<tr>
<td>Initial Concentration of SO$_2$</td>
<td>500ppm, 2000ppm and 3500ppm</td>
</tr>
<tr>
<td>Reaction Volume (Tube Size)</td>
<td>1.25 inch and 4 inch</td>
</tr>
<tr>
<td>Methane Percentage</td>
<td>2% and 4%</td>
</tr>
</tbody>
</table>

Single parameter testing was performed on the conversion of SO$_2$ and SO$_3$ with the expectation that the change in the individual parameter would not subsequently affect other key parameters in the experimental matrix. This expectation was based on the relative effects of these parameters on each other in the context of their known interactions. For instance, when temperature was varied (with all other parameters constant), there is shift in SO$_2$ and O$_2$ levels with temperature, described by an equilibrium shift. However, these changes in equilibrium are very slow with respect to the rate of the reactions describing the formation of SO$_3$. Similarly, when SO$_2$ and O$_2$
levels were changed, there were corresponding equilibrium shifts, but they were much slower than the rates of participating reactions of interest. Finally, CH₄ levels had no effect on SO₂ or SO₃ (until ignition) because CH₄ was a non-participating species.

In the operation of the sulfur reactivity experiment, the following general procedures were used in the performance of each test.

4.2 Furnace Operation

4.2.1 Temperature

4.2.1.1 Primary Reactor

Primary reactor temperature was set by using the scroll button on the panel of the display unit of the controller, as shown in Figure 4.1, attached to the primary reactor and was set to adequately preheat the gas before it entered the secondary reactor. The parameter settings were performed according to the instructions provided by the Eurotherm manual (Khan, 1999). A detailed description of the primary controller adjustment can also be found in there.

4.2.1.2 Secondary Reactor

After setting the temperature in the primary reactor, the secondary controller assembly, as shown in Figure 4.2, was energized by turning the power switch to ‘on’ (Khan, 1999). The dial indicator of the variac (variable AC transformer) attached to the secondary furnace transformer was always maintained at a zero position before the transformer was switched. The required voltage of the heating element, controlled by the variac, was incremented by 5V at a 10-12 minute interval to prevent a sudden increase in voltage that could have caused, a thermal shock to the heating elements. The resistance
of heating elements varies with temperature. A sudden increase in voltage will increase the current flow in the heating elements, which in turn would result in an abrupt change in the temperature, which could cause the heating element to become brittle.

![Schematic representation of the Lindbergh controller](image)

**Figure 4.1 Schematic representation of the Lindbergh controller**

The voltage, current, and temperature were measured using Amprobe Multimeter and Type K thermocouple at both the input and output end of the transformer (Khan, 1999). The thermocouple and Amprobe Multimeter are as shown in Figure 4.2. Tests conducted by Khan (1999) on the temperature characteristics and the Variac reading showed that a variac dial setting of 25-28 gives a mean temperature of 450K inside the secondary reactor without the natural flame, and a setting of 15-18 will provide the
required temperature with the flame. Although this rule of thumb was used, the temperature inside the secondary reactor was routinely confirmed after the gas flow was initiated.

The temperature inside the reactor tube of the secondary furnace was taken by inserting a Type K thermocouple from the bottom of the reactor tube at different axial locations starting from 3cm downstream of the position where the flame could be introduced. The spatial temperature profiles for the 450K setting and the 1000K setting are as shown in Figures 4.4 and 4.5.

4.2.2 Flow

After the temperatures in the primary and the secondary furnace were set, the flow of SO₂, O₂, and natural gas was established using Omega rotameters, according to the matrix as shown in Appendix-I prepared for different operational conditions. The flow established not only the corresponding concentrations, but were used to assure correct residence time.
Figure 4.2 Schematic of the secondary controller assembly

Figure 4.3 Type K thermocouple and amprobe meter assembly
Figure 4.4 Temperature profile for 450K
Figure 4.5 Temperature profile for 1000K
4.3 Sampling

The primary goal of gaseous sampling was to investigate the quantity of conversion of \( \text{SO}_2 \) to \( \text{SO}_3 \). To this end, gas was sampled at various axial locations downstream of the flame, starting from the position of the flame, with and without natural gas flame. The different conditions considered for experimentation are shown in Appendix-I. The experimental procedure is as described in the following sections.

4.3.1 Sampling Procedure Without Natural Gas Flame

The samples were collected using a 0.25-inch probe with the aid of a vacuum pump at different axial positions inside the secondary reactor tube. The adjustable 0.25-inch stainless steel tube had a length of 40 cm, which would traverse the entire reaction tube. The other end of this tube was connected to a 0.25-inch copper tube wrapped with a thermal tape to avoid the condensation of the gas mixture. The open end of the copper tube was connected to the sulfuric acid mist train setup.

Crushed ice was placed inside the bath of the sampling train, 30 ml of 80% isopropanol was taken in the bubbler and 30 ml of 3% hydrogen peroxide in both the second and third impingers was placed at the beginning of the preparation. About 200-g of silica gel was placed in the fourth impinger. All the impingers and tubes, together with the copper tube, were connected as shown in Figure 3.2.

The initial readings of the wet test flow meter, rotameter, and dial thermometer were recorded. The vacuum pump was turned on after the adjustment of the flows, and the temperature settings and initial time were noted for further calculations. The gaseous sample from the exit of the gas meter was sent into the atmosphere using an exhaust pipe.
connection. After running the sample for about 10 to 20 minutes, the pump was turned off and the rotameter readings were set to zero.

The contents of the first impinger were transferred to a 250ml-graduated cylinder. The probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder were rinsed with 80% isopropanol. The level of the liquid on the container was marked and the sample container was identified as container #1.

The solution from the second and the third impingers was transferred to a graduated cylinder. The impingers and all connecting glassware between the filter and silica gel impinger were rinsed with the distilled water. The solution was then transferred to a storage container and the level of the liquid on the container was marked, and the sample was identified as container #2.

The analyses for containers #1 and #2 were performed separately according to EMTIC NSPS Test Method 8 (1998), and the calculation for concentration of \(\text{SO}_2\) and \(\text{H}_2\text{SO}_4\) (Khan, 1999).

4.3.2 With Flame Sampling Procedure

The sampling procedure with methane flame was similar to that of the non-flame sampling procedure, except for the injection of premixed gas into the secondary furnace reactor tube, which was introduced perpendicularly to the axis of the reactor tube. Then the mixture was ignited using the propane torch. Once the mixture had ignited, the sampling procedure was as previously described for the non-flame case.
4.4 Analysis

Before analyzing the samples, container #1 was shaken properly. A 30-ml aliquot of this solution was poured into a 250-ml Erlenmeyer flask and 2 to 4 drops of thorin indicator were added. Titration was performed for the solution until it reached a pink end-point using a 0.01000 N barium perchlorate. The titration was repeated with a second aliquot of sample and the average values for titration were taken into account.

In the case of container #2, the solution was mixed thoroughly in the container by holding the contents of the second and the third impingers. A 10-ml aliquot of sample was poured into a 250-ml Erlenmeyer flask and 40-ml of isopropanol, together with 2 to 4 drops of thorin indicator, were added. Titration for the solution to a pink endpoint was done using 0.01000 N barium perchlorate. The titration was repeated with a second aliquot of sample and the average titration values were taken into account. The blanks were also prepared by adding 2 to 4 drops of thorin indicator to 100-ml of 80 percent isopropanol. Titration for the blanks was performed in the same manner as the samples.

4.5 Experimental Uncertainty

On the advice of researchers at Consol Coal Company, an error analysis was performed and an unacceptable error (approximately 4ppm of SO$_3$) was determined. As a result, the sampling and titration method were modified following Consol’s Controlled Condensation technique. Using these modifications, the estimated uncertainty dropped to 2ppm for measurements less than 100ppm and 3ppm for measurements exceeding 100ppm SO$_3$. 
CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Overview

The purpose of this chapter is to present the experimental results examining the effects of reaction volume (tube size), temperature, excess O₂, and initial SO₂ concentration, particularly to emulate the condition in an actual pulverized coal fired furnace.

5.2 Effect of Temperature on the Conversion of SO₂ to SO₃

Comparing several graphed results shows the effect of temperature. Figures 5.1 and 5.2 display the concentration of SO₃ as a function of time (after the position of the flame holder) determined from data taken under similar conditions (1% excess O₂, 2000 ppm initial SO₂ concentration, 1.25 inch tube reactor), with the average free stream gas temperature at 1000K for the data in Figure 5.1 and 450K for Figure 5.2. In both cases concentration of SO₃ exhibited similar trends. The peak SO₃ concentration occurred around 100 milliseconds downstream of the flame, which is consistent with results documented in the literature (Hedley, 1967). Similar trends are observed when comparing results shown in Figure 5.3 and Figure 5.4 (2% Excess O₂), Figure 5.5 and Figure 5.6 (3% Excess O₂), Figure 5.7 and Figure 5.8 (4% Excess O₂).

However, there are significant differences between the different temperature results. This is evident in the comparison shown in Figure 5.9, in which the percentage conversion of SO₂ to SO₃ at low and high free stream gas temperature regimes were plotted as a function of time. The level of excess oxygen was chosen to represent the
average level found in pulverized coals. The maximum percentage of conversion of SO\textsubscript{2} to SO\textsubscript{3} as defined by Eqn. 5.1 below, at 100 milliseconds after the flame was higher for 1000K compared to the 450K case.

\[
\%\text{conversion} = \frac{([SO_3]_{\text{peak}} - [SO_3]_{\text{0\%\text{methane}}})}{[SO_2]} \tag{5.1}
\]

In Figure 5.9, the results indicate that peak conversion percentage is greater at 1000K. The decrease in the peak conversion percentage at 450K may be due to the decreased oxygen radicals near the flame at lower temperatures. Lower free-stream gas temperatures reduce the flame temperature and the rate of oxygen radical formation.

One other significant temperature effect is shown in Figures 5.4, 5.6, and 5.8 (450K). At 400 milliseconds, the level of SO\textsubscript{3} is significantly (5-10ppm) higher than the level without a flame, while in Figures 5.3, 5.5, and 5.7 (1000K), the SO\textsubscript{3} concentration has returned to the non-flame levels at 400 milliseconds. Further in Figure 5.9, the conversion percentage remains higher following the peak for the 450K case, which is consistent with these other results. This is likely due to a lower concentration of oxygen radicals at 450K to attack SO\textsubscript{3} in the region outside the flame. In addition, there is virtually no thermal decomposition of SO\textsubscript{3} at lower free stream gas temperatures (450K).

To study the duration period of SO\textsubscript{3} levels, conversion of SO\textsubscript{2} to SO\textsubscript{3} was tested for 800 milliseconds in the secondary furnace. The duration period of SO\textsubscript{3} level is important for potential applications, such as fly ash conditioning in an electrostatic precipitator. If the duration is too short, there will not be enough time for coating of the fly ash by the resulting sulfuric acid. On the other hand, if the duration of increased SO\textsubscript{3}
is too long, then it would lead to the formation of sulfate particles (blue plumes) outside the stack or the corrosion of metal in the duct work.

The results of this test are shown in Figure 5.10, where the SO$_2$ level was maintained at 2000ppm, average free stream gas temperature was maintained at 450K, and the inlet gas velocity was maintained at 1.032 m/s. The results indicate that the SO$_3$ level above the base case (0% methane) with the flame at 800 milliseconds is around 5-10 ppm, which is ideal for fly ash conditioning. The results also indicate that the higher concentration of SO$_3$ occurs for an extended period, compared to Hedley (1967).

**5.3 Effect of Excess O$_2$ on the Conversion of SO$_2$ to SO$_3$**

The effect of excess oxygen is shown by comparing the data plotted in Figures 5.2, 5.4, 5.6, 5.8, and 5.10, where excess oxygen was varied from 1, 2, 3, 4, and 10%. These levels of excess oxygen percentages were chosen to reflect the different levels found in pulverized coal fired furnaces. The other conditions considered for the experiments were the temperature of 450K, initial SO$_2$ concentration of 2000ppm, and 1.25-inch diameter reactor tube.

From Figure 5.2 (1% excess O$_2$), the peak conversion percentage of SO$_2$ to SO$_3$ was calculated to be 0.75% using Eqn. 5.1. Note that the SO$_3$ level with flame returned to approximately the same value without the flame at 400 milliseconds downstream of the flame holder. In Figure 5.4 (2% excess O$_2$), the peak conversion percentage of SO$_2$ to SO$_3$ was calculated at 2.0%. But in this case, it can be observed that the SO$_3$ level with flame remained significantly higher (5-10ppm) than the level found without flame at 400 milliseconds downstream of the flame holder.
In Figure 5.6 (3% excess O₂), the peak conversion percentage of SO₂ to SO₃ was calculated to be 2.5%, whereas the peak conversion percentage of SO₂ to SO₃ at 4% excess O₂ from Figure 5.8 was calculated to be 2.75%. Also, it can be noted from Figures 5.6 and 5.8 that the level of SO₃ found with flame is 5-10 ppm higher than that found without flame at 400 milliseconds downstream of the flame similar to Figure 5.4. In Figure 5.10 (10% excess O₂), the peak conversion percentage of SO₂ to SO₃ was calculated to be 4.75%.

The effect of variation of excess oxygen on the conversion of SO₂ to SO₃ is summarized in Figure 5.11 and Figure 5.12, which compare the percentage conversions at 2% excess O₂, 4% excess O₂, 10% excess O₂ at 450K, 500ppm initial SO₂ concentration. Lower initial concentration was considered to represent low sulfur coals and low free stream gas temperature was considered to represent typical temperature found in electrostatic precipitators. The results indicate an increase in SO₃ conversion percentage with an increase in excess oxygen. A similar trend was observed with a higher initial concentration of SO₂ (2000ppm) as shown in Figure 5.12. An increase in excess oxygen might have generated enough oxygen radicals to promote a considerable conversion of SO₂ to SO₃, thus increasing peak conversion percentage even at low temperature.

It can also be observed from Figure 5.10 that the level of SO₃ concentration with the flame remains above that found without the flame even at 800 milliseconds downstream of the flame holder. From the results discussed above, it can be concluded
that there is a significant increase in the conversion of SO₂ to SO₃ with increasing excess oxygen levels.

Figure 5.1 Measured SO₃ concentration at 1000 K, 1% excess O₂
Figure 5.2 Measured SO$_3$ concentration at 450 K, 1% excess O$_2$
Figure 5.3 Measured SO$_3$ concentration at 1000 K, 2% excess O$_2$
Figure 5.4 Measured SO$_3$ concentration at 450 K, 2% excess O$_2$
Figure 5.5 Measured SO₃ concentration at 1000 K, 3% excess O₂
Figure 5.6 Measured $\text{SO}_3$ concentration at 450 K, 3% excess $\text{O}_2$
Figure 5.7 Measured SO$_3$ concentration at 1000 K, 4% excess O$_2$
Figure 5.8 Measured $\text{SO}_3$ concentration at 450 K, 4% excess $\text{O}_2$
Figure 5.9 Percentage conversion of SO$_2$ to SO$_3$ at 4% excess O$_2$, 2000ppm, 450K and 1000K
Figure 5.10 Extended measurement of $\text{SO}_3$ concentration at 450K, 10% excess $\text{O}_2$
Figure 5.11 Percentage conversion of SO$_2$ to SO$_3$ at 450K, 500ppm initial SO$_2$ concentration, 2%, 4%, 10% excess O$_2$
Figure 5.12 Percentage conversion of SO\textsubscript{2} to SO\textsubscript{3} at 450K, 2000ppm, 2\%, 4\% and 10\% excess O\textsubscript{2}
5.4 Effect of Initial Concentration of SO$_2$ on the Conversion of SO$_2$ to SO$_3$

The effect of initial SO$_2$ concentration is shown by comparing the results shown in Figures 5.13 and 5.14. The experimental conditions are the same for the data shown in these figures, except that for the results in Figure 5.13, 500 ppm was used at the inlet, and in Figure 5.14, 3500 ppm was used. These levels of initial SO$_2$ concentration were chosen to reflect low and very high sulfur coals.

In Figure 5.13 (500 ppm), the peak conversion of SO$_2$ to SO$_3$ was calculated to be 7% using Eqn.5.1, whereas in Figure 5.14 (3500 ppm), the peak conversion of SO$_2$ to SO$_3$ was calculated to be 2.85%. The effect of initial SO$_2$ concentration on the conversion of SO$_2$ to SO$_3$ is summarized in Figure 5.15. In Figure 5.15, percentage conversion at 500ppm and 3500ppm initial SO$_2$ concentrations was plotted as a function of time. The free stream gas temperature of 450K was considered to represent the typical temperatures found in electrostatic precipitators. The levels of initial SO$_2$ concentration was chosen to reflect low and high sulfur coals. The results indicate an increase in SO$_3$ conversion percentage with a decrease in initial SO$_2$ concentration.

The increase in percentage of conversion at lower initial concentrations of SO$_2$ may be due to increased consumption of oxygen radicals. SO$_2$ reacts with oxygen radicals to form SO$_3$, as defined by Eqn. 5.2.

$$SO_2 + O + M \rightarrow SO_3 + M$$  \hspace{1cm} (5.2)

As the initial concentration of SO$_2$ decreases, the percentage of available oxygen radicals to react with the SO$_2$ for further conversion of SO$_2$ to SO$_3$ increases, thus leading to an increase in the percentage of conversion at lower initial concentrations of SO$_2$. 
Figure 5.13 Measured SO₃ concentration at 450 K, 500ppm, 10% excess O₂
Figure 5.14 Measured SO$_3$ concentration at 450K, 3500ppm, 10% excess O$_2$. 
Figure 5.15 Percentage conversion of SO$_2$ to SO$_3$ at 10% excess O$_2$, 450K, 500ppm and 3500ppm initial SO$_2$ concentration.
5.5 Effect of Natural Gas on the Conversion of SO\textsubscript{2} to SO\textsubscript{3}

The effect of natural gas concentration is shown in Figures 5.16 and 5.17. The experimental conditions are the same for both Figure 5.16 and Figure 5.17 (450K, 2000ppm initial SO\textsubscript{2} concentration, 10% excess O\textsubscript{2}, 4-inch diameter reactor tube), except for the percentage of natural gas for Figure 5.16 was 2%, and for Figure 5.17, the percentage of is 4%. Both figures exhibit similar trends: the peak concentration of SO\textsubscript{3} was observed to occur at around 50 milliseconds downstream of the flame. In Figure 5.18 (4% CH\textsubscript{4}), the peak conversion of SO\textsubscript{2} to SO\textsubscript{3} was calculated to be 3% using Eqn. 5.1, whereas with 2% natural gas case, the peak concentration was observed to be 2.15%.

Figure 5.18 summarizes the effect of variation of natural gas percentage on the conversion process. In Figure 5.18, the percentage conversion of SO\textsubscript{2} to SO\textsubscript{3} at 2% and 4% natural gas concentration was plotted as a function of time. The results indicate a decrease in percentage conversion with the decrease in natural gas concentration.

The decrease in the percentage of peak SO\textsubscript{3} concentration in Figure 5.16 may be attributed to the fact that a decrease in natural gas concentration would reduce the oxygen radical concentration by decreasing CO oxidation steps and, would in turn effect the conversion of SO\textsubscript{2} to SO\textsubscript{3}. Such a decrease may also be due to the fact that lower natural gas concentration would result in cooler flame, which would then reduce the percentage of oxygen radicals present near the flame and hence effect the conversion of SO\textsubscript{2} to SO\textsubscript{3}. 
Figure 5.16 Measured SO$_3$ concentration for 450K, 2% methane, 2000ppm, 10% excess O$_2$.
Figure 5.17 Measured SO₃ concentration at 450K, 2000ppm, 4% methane 10% excess O₂
Figure 5.18 Percentage Conversion of SO₂ to SO₃ at 10% excess O₂, 450K, 2000ppm initial SO₂ concentration, 2% and 4% methane
5.6 Effect of Reaction Volume (Tube Size) on the Conversion of SO₂ to SO₃

The drop tube furnace used to obtain the set of results presented in Figures 5.1 to 5.10 does not simulate the actual flow characteristics of a practical flue cleaning system. As per the recommendation proposed by Khan (1999), the experiments were conducted with a larger diameter tube to take into account the flow rate and volume involved in practical systems.

Gaseous sampling experiments were performed under flame and no-flame conditions at an average free stream gas temperature of 450K. The excess oxygen percentages considered were 2%, 4%, and 10%. The initial SO₂ concentrations considered were 500 ppm and 2000 ppm. The gas was sampled at 20, 50, 100, 200, 300, 400 and 800 milliseconds downstream of the flame starting from the position of the flame and the inlet gas velocity was maintained at 0.667 m/s.

The results presented in Figures 5.19 to 5.21 that were all gathered using the 4-inch reaction tube, indicate that the peak concentration of SO₃ occurs at around 50 milliseconds. The percentage conversion at peak SO₃ concentrations with an inlet SO₂ concentration of 2000 ppm and an inlet free stream gas temperature of 450K at different percentages of excess air with increased reaction volume, (4-inch tube size), are summarized in Table 5.1, which indicates that no significant change in the peak conversion percentage of SO₃ with the increased reaction volume.

Similarly, in Figures 5.13 (1.25 inch reactor tube) and 5.21 (4-inch reactor tube), the peak conversion percentage of SO₃ is 7% with both the 4-inch reactor tube and 1.25-inch reactor tube. This indicates that there is no significant effect of change in inlet SO₂
concentration on the conversion of SO$_2$ to SO$_3$ with increased reaction volume (4-inch reactor tube).

**Table 5.1 Comparison of Effect of Excess O$_2$ Percentage on the Conversion of SO$_2$ to SO$_3$ for 4-inch with Drop Tube Furnace**

<table>
<thead>
<tr>
<th>Percentage of Excess O$_2$</th>
<th>Peak Percentage of SO$_3$ conversion with 4-inch reactor tube</th>
<th>Peak percentage of SO$_3$ conversion with 1.25 inch reactor tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>2.5%</td>
<td>2.0%</td>
</tr>
<tr>
<td>4%</td>
<td>2.9%</td>
<td>2.75%</td>
</tr>
<tr>
<td>10%</td>
<td>3%</td>
<td>3%</td>
</tr>
</tbody>
</table>
Figure 5.19 Measured SO$_3$ concentration at 450K, 500ppm, 4% excess O$_2$ using the 4-inch reaction tube
Figure 5.20 Measured SO$_3$ concentration at 450K, 2000ppm, 2% excess O$_2$ using the 4-inch reaction tube.
Figure 5.21 Measured SO$_3$ concentration at 450K, 500ppm, 10% excess O$_2$ using the 4-inch reaction tube
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The primary concern of this work was to investigate a potential method for SO$_3$ generation to replace external sulfur burning, for fly ash conditioning in ESPs. Homogeneous conversion of SO$_2$ to SO$_3$ using natural gas combustion for ash conditioning eliminates the need to inject additional sulfur into the flue gas stream and adds moisture to the flue gas to increase ash agglomeration. Both effects improve particle collection in typical ESPs. This work involved examination of the effects of excess oxygen percentage, lower free stream gas temperature, residence-time, and reaction volume (tube size) on the homogeneous conversion of SO$_2$ to SO$_3$ via a natural gas combustion process. Experiments were performed in a non-catalytic stainless steel combustor, simulating conditions of a cooled exhaust gas stream from a coal-fired power plant.

6.1 Conclusions

Results indicated that the presence of an energetic hydrocarbon flame generated enough O radicals to convert sufficient SO$_2$ to SO$_3$ for conditioning the fly ash 2-10 ppm SO$_3$ at 800 milliseconds after the flame, even under the most adverse conditions to SO$_3$ formation and without the use of a heterogeneous catalyst. This is significant, as these results indicate that this technique might provide a viable alternative to replace external sulfur burning for SO$_3$ generation in the conditioning of highly resistive fly ash that is often needed when high sulfur coal is replaced with low sulfur coal.
The peak percentage of SO\textsubscript{2} to SO\textsubscript{3} conversion was observed to be less for lower temperatures (450K) when compared to that of higher (1000K) temperatures. The decrease in conversion at a lower free stream gas temperature is primarily due to the reduction in formation of O radicals. At 450K virtually no dissociation of O\textsubscript{2} (O\textsubscript{2} \leftrightarrow 2O) occurs. Therefore, the only significant source of oxygen radicals was from the combustion of natural gas, particularly from the oxidation of CO to CO\textsubscript{2}. But, at lower free stream gas temperatures, however, the rate of CO oxidation was reduced and, thus, the rate of O radicals formation was lower.

In addition, the rate at which SO\textsubscript{3} decomposes to SO\textsubscript{2} apparently decreased at lower temperatures. In fact, SO\textsubscript{3} levels at 450K remained above those found without a flame for up to 800 milliseconds. Extended duration of increased concentration of SO\textsubscript{3} at low temperatures may be due to the presence of a smaller percentage of excess oxygen radicals to attack SO\textsubscript{3} and convert it back to SO\textsubscript{2}. Also, the thermal decomposition of SO\textsubscript{3} by a third body attack, as defined by Equation 6.1, might be reduced at lower free-stream gas temperatures (450K), thus extending the super-equilibrium effect.

\[ \text{SO}_3 + M \leftrightarrow \text{SO}_2 + O + M \]  

(6.1)

The duration of enhanced SO\textsubscript{3} levels is extremely important to potential applications. If the duration is short, on the order of 100 milliseconds, there would not be enough residence time for the coating and significant capture of fly ash. On the other hand, if the duration is too long, then SO\textsubscript{3} could lead to increased corrosion due to the formation of sulfuric acid or sulfate particles ("blue flume") outside the stack. The duration of the SO\textsubscript{3} level was tested at 800 milliseconds and it was observed that the
levels of SO\textsubscript{3} found were significantly (2-10ppm) above background (non-flame) levels, sufficient to condition fly ash for electrostatic precipitator collection.

Free-stream excess oxygen levels also influenced the homogeneous conversion of SO\textsubscript{2} to SO\textsubscript{3}. As the percentage of excess O\textsubscript{2} increased, the conversion of SO\textsubscript{2} to SO\textsubscript{3} also increased. It is speculated that as excess oxygen levels decreased, the resulting decrease in oxygen radicals may also limit CO oxidation steps, further reducing the supply of O atoms.

Results also indicated that at lower initial concentrations of SO\textsubscript{2}, the percentage of conversion of SO\textsubscript{2} to SO\textsubscript{3} was higher when compared to that at higher initial concentrations of SO\textsubscript{2}. This increase in percentage at lower concentrations might have been due to the higher percentage of available oxygen radicals to convert SO\textsubscript{2} to SO\textsubscript{3}. SO\textsubscript{2} reacts with molecular oxygen at lower temperatures where equilibrium is more in favor of SO\textsubscript{3}, as shown in Eqn. 6.1:

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3
\]

The presence of a lower percentage of SO\textsubscript{2} to react with oxygen to form SO\textsubscript{3} would leave a higher percentage of oxygen radicals to react further with SO\textsubscript{2} to form SO\textsubscript{3} and thus results in a higher percentage of conversion of SO\textsubscript{2} to SO\textsubscript{3} at lower initial concentrations of SO\textsubscript{2}.

It was also observed that there was no significant increase in the percentage conversion of SO\textsubscript{2} to SO\textsubscript{3} with increased reaction volume. This indicates that the results presented with base scale could scale up.
6.2 Recommendations

This research can be further extended to examine the effects of high temperatures on the conversion of SO$_2$ to SO$_3$ using natural gas re-burning process for NO$_x$ control. Experiments can be conducted to study the catalytic effects of fly ash.

This system can be implemented with an actual electrostatic precipitator to investigate the effects of conversion of SO$_2$ to SO$_3$ on the collection of the fly ash. Modeling work could be extended to high temperature conversion processes to estimate the reaction rate constants.
REFERENCES


EMTIC NSPS Test Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources, 1998.


### APPENDIX A

**Matrix for Data Collection**

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Qnet[3000rpm]: Qnet at 3000 rpm.
Qnet 1rpm: Qnet at 1 rpm.
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<td>88716.63024</td>
<td>44.3901512</td>
<td>2217.915756</td>
<td>3548.66521</td>
<td>729.27025</td>
<td>48891.00002</td>
<td>34480.95865</td>
</tr>
<tr>
<td>Velocity (ms)</td>
<td>Qcut @ room T</td>
<td>Qcut [500 ppm]</td>
<td>Qcut finank</td>
<td>Q for 4% CH4</td>
<td>Q for 2% CH4</td>
<td>Q for 4% CO</td>
<td>Q for 2% O2</td>
</tr>
<tr>
<td>2.02</td>
<td>26620.95345</td>
<td>133.1404672</td>
<td>6657.023602</td>
<td>5325.6869</td>
<td>1064.26213</td>
<td>72724.4045</td>
<td>51713.8873</td>
</tr>
<tr>
<td>1.016</td>
<td>133.410.472</td>
<td>66.5702362</td>
<td>3328.511681</td>
<td>5325.6869</td>
<td>1064.26213</td>
<td>72724.4045</td>
<td>51713.8873</td>
</tr>
<tr>
<td>0.677</td>
<td>88716.63024</td>
<td>44.3901512</td>
<td>2217.915756</td>
<td>3548.66521</td>
<td>729.27025</td>
<td>48891.00002</td>
<td>34480.95865</td>
</tr>
</tbody>
</table>
APPENDIX B

Program to Calculate Mixture Temperature

B.1 Overview

This software module simulates the flow in the furnace reactor tube for the calculation the temperature of the resulting mixture in the secondary furnace, which is shown in Figure 3.3. This module is built on the basis of two assumptions:

1. All the gases obey Ideal gas law.
2. Natural gas and air undergo stochiometric reaction.

B.2 Description of the Model

![Flow representation in secondary furnace reactor tube](image)

Figure B.1 Flow representation in secondary furnace reactor tube

As indicated in Figure B.1, the gases SO₂, N₂, which compose Stream-1, gets pre-heated in the primary furnace and enter into the secondary furnace, whereas the methane
and air mixture, which is treated as Stream-2, is introduced perpendicular to the axis of the reactor tube. Methane and air undergo stociometric reaction as indicated by Equation 1:

\[
\text{CH}_4 + 3.76(\text{O}_2 + \text{N}_2) \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{N}_2
\]  

(B.1)

The temperature of the Stream-1 is the temperature to which the stream is preheated in the primary furnace, and the temperature of the Stream-2 is the adiabatic flame temperature of Equation B.1. Adiabatic flame temperature is calculated by using Engineering Equation Solver, which is presented, in section B.4

The various formulae used in the model are described as below.

\[
D_{\text{gas}} = \frac{P \times R}{T}
\]

(B.2)

Where,

\[D_{\text{GAS}} - \text{density of the gas}\]
\[P - \text{pressure of the gas}\]
\[R - \text{gas constant}\]
\[T - \text{temperature of the gas}\]

\[
C_{P_{\text{mix}}} = C_{P_{\text{gas1}}} \times M_{f_{\text{gas1}}} + \cdots + C_{P_{\text{gasn}}} \times M_{f_{\text{gasn}}}
\]

(B.3)

Where,

\[C_{P_{\text{mix}}} - \text{specific heat of the mixture}\]
\[C_{P_{\text{gas1}} - \text{specific heat of the gas in the mixture}}\]
\[M_{f_{\text{gas1}}} - \text{mass flow rate of the gas in the mixture}\]
Mixture temperature is calculated from the energy balance equation, which is defined in Equation 4.

\[ \text{Energy of stream1} + \text{Energy of stream2} = \text{Energy of the mixture} \]  
\[ \text{(B.4)} \]

Energy of stream1 composed of gases \( \text{SO}_2 \) and \( \text{N}_2 \) and stream2 composed of air and natural gas mixture is calculated from the generalized equation shown below

\[ \text{Energy of stream} = Mf_{\text{gas1}} \cdot \text{Cp}_{\text{gas1}} \cdot (T - 298) + \ldots + Mf_{\text{gasn}} \cdot \text{Cp}_{\text{gasn}} \cdot (T - 298) \]  
\[ \text{(B.5)} \]

where,

- \( Mf_{\text{gas1}} \) - mass flow rate of the gas in the stream
- \( \text{Cp}_{\text{gas}} \) - specific heat of the gas in the stream
- \( T \) - absolute temperature of the gas stream.

and the energy of the mixture is calculated from the equation of as shown below

\[ \text{Energy of the mixture} = Mf_{\text{mix}} \cdot \text{Cp}_{\text{mix}} \cdot (T_{\text{mix}} - 298) \]  
\[ \text{(B.6)} \]

where,

- \( Mf_{\text{mix}} \) - mass flow rate of the mixture
- \( \text{Cp}_{\text{mix}} \) - specific heat of the mixture
- \( T_{\text{mix}} \) - Temperature of the mixture

From the Equations B.4, B.5 and B.6 mixture temperature is calculated by the equation as defined below

\[ T_{\text{mix}} = \frac{(\text{Energy of stream1} + \text{Energy of stream2})}{Mf_{\text{mix}} \cdot \text{Cp}_{\text{mix}}} \]  
\[ \text{(B.7)} \]
B.3 Program to Calculate Mixture Temperature

```c
#include<stdio.h>
#include<math.h>
#include<ctype.h>

/* Function prototypes */
float cpso2function(float);
float cpn2function(float);
float cpo2function(float);
float cpco2function(float);
float cph2ofunction(float);

main()
{
    /* Declaration of the variables */
    float cpso2, cpn2, cpo2, cpco2, cph20, cpstr1, cpstr2,
         cpmix, temp, fso2, fn2, fo2, fco2, fh2o, fstr1, fstr2, totalf;
    float cpo22, cpn22, fo22;
    float xso2, xo2, xn2, xco2, xh2o, xn22, fn22, fstr, fch4, fair;
    float dso2, do2, dn2, dco2, dh2o, dmix, temp2, ltmix, dn22, ddso2;
    float yco2, yh2o, dmi1x1, vpwo1d, min, t1, t2;
    float mso2, mo2, mn2, mso2, mfo2, mfn2, mtotal, mco2, mn22, mh20;
    float mfstr1, mfstr2, mmixt, mo22, mch4, mtotalp, mfo22, mfn22;
    float mfh20, mfco2, do22;
    float mstr1, mstr2, t11, t22, mstr, tmix1, t3;
    float en2, eo2, eso2, eco2, eh2o, en22, eo22, e1, e2, mixt;
    float Eso2, Eo2, En2, Eco2, Eh20, E2, mixt;
    float mso2, mo2, mn2, mso2, mfo2, mfso2, mfn2, mtotal, mco2, mn2, mh20;
    float mfstr1, mfstr2, mmixt, mo22, mch4, mtotalp, mfo22, mfn22;
    float mfco2, do22;
    float mstr1, mstr2, t11, t22, mstr, tmix1, t3;
    float En2, eo2, eso2, eco2, eh2o, en22, eo22, e1, e2, mixt;
    float Eso2, Eo2, En2, Eo2, En22, Eo22, Eh2o, E1, E2, mixt;

    printf("This Program is to calculate the mixture Properties");
    printf(" and the mixture temperature");
    printf("n");
    printf("n Please enter the temperature of stream1: -> ");
    scanf("%f", &temp);
    printf("n Please Enter the temperature at rotameter inlet: ");
    scanf("%f", &t3);

    cpso2 = cpso2function(temp);
    printf("n The Cp of SO2 is %f", cpso2);

    cpn2 = cpn2function(temp);
    printf("n The Cp of N2 is %f", cpn2);
```
printf("\n Please enter the temperature of the Stream 2: -> ");
scanf("%f", &temp2);
printf("\n ");

cph2o = cph2ofunction(temp2);
printf("\n \n The Cp of H20 is %f", cph2o);

cph2o = cph2ofunction(temp2);
printf("\n \n The Cp of H2O is %f", cph2o);
cpo22=cpo2function(temp2);
printf("\n \n The Cp of O2 in stream 2 is %f", cpo22);
cpn22=cpn2function(temp2);
printf("\n \n The Cp of N2 in stream 2 is %f", cpn22);
printf("\n \n ");

printf("\n Enter the flow rate for SO2 in stream 1: ");
scanf("%f", &fso2);

printf("\n Enter the flow rate for N2 in stream 1: ");
scanf("%f", &fn2);

printf("\n Enter the flow rate for CH4 in stream 2: ");
scanf("%f", &fch4);

printf("\n Enter the flow rate for AIR in stream 2: ");
scanf("%f", &fair);


dso2=density of sulfur dioxide
dn2=density of nitrogen in stream 1 */

dso2=779.985/t3;
dn2=341.73/t3;

/* Mass Flow Rates
--------------
ms02- mass flow rate of so2 in (kg/min)
mmn2- mass flow rate of n2 in (kg/min)
mtn2-Total mass flow rate of stream1 (kg/min)
mftso2-mass fraction of so2
mfn2-mass fraction of n2*/
mso2=fso2*dso2/1000000.00;
mn2=fn2*dn2/1000000.00;
mtotal=mso2+mn2;
mfso2=mso2/mtotal;
mfn2=mn2/mtotal;

/*
cpstrl - specific heat of stream1
---------------------------------------------*/

cpstrl = mfso2*cpso2 + mfn2*cpn2;
printf("\n the cp of stream 1 is: \%f", cpstrl);
printf("\n");

/*
dco2 - Density of co2 (kg/m^3)
do22 - Density of oxygen in stream 2 (kg/m^3)
dn22 - Density of nitrogen in stream 2 (kg/m^3)
dh2o - Density of water in stream 2 (kg/m^3)*/

dco2=536.2/(t3);
dn22=341.2436/(t3);
dh2o=219.3709/(t3);
do22=389.992/(t3);
printf("\n");

/*
Flow rates are in --------> m^3/min
---------------------------------------------

fco2- flow rate of co2 in stream 2
fo22- flow rate of oxygen in stream2
fn22- flow rate of nitrogen in stream2
fh2o- flow rate of water in stream2
fch4- flow rate of methane in stream2
fair- flow rate of air in stream 2 */

fco2=fch4*0.000001;
fh2o=2*fch4*0.000001;
fo22=((fair*0.000001/4.76)-(2*fch4*0.000001));
fair2=(fair*0.000001*3.76/4.76);
/*
  mco2- mass flow rate in kg/ min of co2 in stream 2
  mh2o- mass flow rate in kg/ min of h2o in stream 2
  mo22- mass flow rate in kg/ min of oxygen in stream 2
  mn22- mass flow rate in kg/ min of nitrogen in stream 2
  mtotalp- total mass flow rate of all the products
  mfco2- mass fraction of co2
  mfn22- mass fraction of nitrogen
  mfo22- mass fraction of oxygen
  mfh2o- mass fraction of water  */

mco2=dc02*fco2;
mh2o=dh2o*fh2o;
mo22=do22*fo22;
mn22=dn22*fn22;
mtotalp=mco2+mh2o+mo22+mn22;
mfco2=mco2/mtotalp;
mfh2o=mh2o/mtotalp;
mfo22=mo22/mtotalp;
mfn22=mn22/mtotalp;

/* cpstr2- specific heat of the products in stream 2 */

cpstr2 = mfco2*cpco2 +mfh2o*cph2o +mfn22*cpn22+mfo22*cpo22;
printf("\n The cp of steam 2 is : %f",cpstr2);

/*  The units of mass flow rate is ------ > kg/ min
-----------------------------------------------

mstr2- total mass flow rate of stream 2
mstr1- total mass flow rate of stream 1
mstr- massflowrate of stream1 + mass flow rate of stream2
mfstr1-  mass fraction of the gases in stream1
mfstr2-  mass fraction of the gases in stream2  */

mstr2=mco2+mo22+mh2o+mn22;
mstr1=mso2+mn2;
mstr=mstr1+mstr2;
mfstr1=(mso2+mn2)/mstr;
mfstr2=(mco2+mn22+mh2o+mo22)/mstr;

/*
cpmix - mixture specific heat */
cpmix =mfstr1*cpstr1 + mfstr2*cpstr2;

/*
The units for energy term is (kJ/min)
----------------------------------------
en2--->Energy associated with nitrogen in stream 1
eso2--->Energy associated with SO2 in stream 1
eco2--->Energy associated with CO2 in stream 2
eo22--->Energy associated with Oxygen in stream2
en22--->Energy associated with nitrogen in stream2 */

en2=mn2*cpn2*(temp-298);
eco2=mco2*cpco2*(temp2-298);
eso2=mso2*cpso2*(temp-298);
eh2o=mh2o*cph2o*(temp2-298);
eo22=mo22*cpo22*(temp2-298);
en22=mn22*cpn22*(temp2-298);

/*
e1- sum of the energies of gasses in stream1
e2- sum of the energies of gases in stream2
dmix- is the density of the mixture
mixt is the mixture temperature
tmix1- is also the mixture temperature */

e1=eso2+en2;
e2=en22+eo22+eh2o+eco2;
dmix=dso2+dn2+dh2o+dn22+do22+dco2;
mixt=((e1+e2)/(cpmix*mstr))+298;
printf("\n The CP of the mixture is %f ",cpmix);
printf("\n");

t11=(mstr1/mstr)*(cpstr1/cpmix)*(temp-298);
t22=(mstr2/mstr)*(cpstr2/cpmix)*(temp2-298);
tmix1=t11+t22+298;

printf("\n Mixture Specific Heat(Cpmix) = \%f\n",cpmix);
printf("\n Temperature of the mixture = \%f\n",mixt);
printf("\n");

float cpso2function(float temp)
{
    float a = 38.91, b = 0.039040, c = -0.00003104, d = 0.000000008606;
    return ((a + b * temp + c * temp * temp + d * temp * temp * temp)/64);
}

float cpn2function(float temp)
{
    float a = 29.00, b = 0.002199, c = 0.000005723, d = -0.000000002871;
    return ((a + b * temp + c * temp * temp + d * temp * temp * temp)/28);
}

float cpo2function(float temp)
{
    float a = 29.10, b = 0.01158, c = -0.000006076, d = 0.00000001311;
    return ((a + b * temp + c * temp * temp + d * temp * temp * temp)/32.0);
}

float cpco2function(float temp)
{
    float a = 36.11, b = 0.04233, c = -0.00002887, d = 0.00000007464;
    return ((a + b * temp + c * temp * temp + d * temp * temp * temp)/44.0);
}

float cph2ofunction(float temp)
{
    float a = 33.46, b = 0.006880, c = 0.000007604, d = 0.00000003593;
    return ((a + b * temp + c * temp * temp + d * temp * temp * temp)/18.0);
}
APPENDIX C

C.1 Sample SO₃ Readings for 1.25-inch Reactor Tube

Temperature=450K  2%Excess O₂  SO₂=500ppm

<table>
<thead>
<tr>
<th>Gas Meter Reading</th>
<th>Initial</th>
<th>Final</th>
<th>Distance(cm)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>697</td>
<td>700</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>703</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>703</td>
<td>706</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>707</td>
<td>709</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>709</td>
<td>712</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

Temperature=450K  4%Excess O₂  SO₂=500ppm

<table>
<thead>
<tr>
<th>Gas Meter Reading</th>
<th>Initial</th>
<th>Final</th>
<th>Distance(cm)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>744.2</td>
<td>747</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>741</td>
<td>743.7</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>737</td>
<td>740.2</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>733</td>
<td>736.4</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>730</td>
<td>733</td>
<td>40</td>
<td>15</td>
</tr>
</tbody>
</table>

Temperature=450K  2%Excess O₂  SO₂=500ppm

<table>
<thead>
<tr>
<th>Gas Meter Reading</th>
<th>Initial</th>
<th>Final</th>
<th>Distance(cm)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>765</td>
<td>769</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>769.4</td>
<td>771.9</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>772</td>
<td>774</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>774</td>
<td>776.7</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>777</td>
<td>779.7</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

Temperature=450K  2%Excess O₂  SO₂=500ppm

<table>
<thead>
<tr>
<th>Gas Meter Reading</th>
<th>Initial</th>
<th>Final</th>
<th>Distance(cm)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>797.7</td>
<td>800.6</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>800.7</td>
<td>803.6</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>803.7</td>
<td>807.3</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>
C.2 Sample SO$_3$ Readings for 4-inch Reactor Tube

<table>
<thead>
<tr>
<th>Temperature=450K</th>
<th>2%Excess O$_2$</th>
<th>SO$_2$=500ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Meter Reading</td>
<td></td>
<td>Distance(cm)</td>
</tr>
<tr>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>631.5</td>
<td>6344.4</td>
<td>40</td>
</tr>
<tr>
<td>634.6</td>
<td>637.5</td>
<td>20</td>
</tr>
<tr>
<td>637.5</td>
<td>640.3</td>
<td>15</td>
</tr>
<tr>
<td>640.3</td>
<td>642.9</td>
<td>10</td>
</tr>
<tr>
<td>642.9</td>
<td>645</td>
<td>5</td>
</tr>
<tr>
<td>645.2</td>
<td>647.6</td>
<td>2.5</td>
</tr>
<tr>
<td>647.6</td>
<td>649.4</td>
<td>1</td>
</tr>
<tr>
<td>649.4</td>
<td>652</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature=450K</th>
<th>10%Excess O$_2$</th>
<th>SO$_2$=2000ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Meter Reading</td>
<td></td>
<td>Distance(cm)</td>
</tr>
<tr>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>723</td>
<td>725.4</td>
<td>40</td>
</tr>
<tr>
<td>725.4</td>
<td>727.6</td>
<td>20</td>
</tr>
<tr>
<td>727.6</td>
<td>729.4</td>
<td>10</td>
</tr>
<tr>
<td>729.4</td>
<td>731</td>
<td>15</td>
</tr>
<tr>
<td>731</td>
<td>733</td>
<td>5</td>
</tr>
<tr>
<td>733</td>
<td>735.1</td>
<td>2.5</td>
</tr>
<tr>
<td>735.1</td>
<td>737.7</td>
<td>1</td>
</tr>
<tr>
<td>737.7</td>
<td>739.6</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature=450K</th>
<th>2%Excess O$_2$</th>
<th>SO$_2$=2000ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Meter Reading</td>
<td></td>
<td>Distance(cm)</td>
</tr>
<tr>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>757</td>
<td>759.9</td>
<td>40</td>
</tr>
<tr>
<td>759.9</td>
<td>761.7</td>
<td>20</td>
</tr>
<tr>
<td>761.7</td>
<td>763.8</td>
<td>15</td>
</tr>
<tr>
<td>763.9</td>
<td>766.3</td>
<td>10</td>
</tr>
<tr>
<td>766.3</td>
<td>768.5</td>
<td>5</td>
</tr>
<tr>
<td>768.5</td>
<td>770.3</td>
<td>2.5</td>
</tr>
<tr>
<td>770.3</td>
<td>772.5</td>
<td>1</td>
</tr>
<tr>
<td>772.5</td>
<td>774.3</td>
<td>0</td>
</tr>
</tbody>
</table>
C.3 Sample Measured SO₃ Concentration for 1.25-inch Reactor Tube

<table>
<thead>
<tr>
<th>Temperature = 450K</th>
<th>10% excess O₂</th>
<th>SO₂ = 500 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence (msec)</td>
<td>0% methane</td>
<td>4% methane</td>
</tr>
<tr>
<td>0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>100</td>
<td>5.0</td>
<td>40.0</td>
</tr>
<tr>
<td>200</td>
<td>10.0</td>
<td>25.0</td>
</tr>
<tr>
<td>300</td>
<td>10.0</td>
<td>15.0</td>
</tr>
<tr>
<td>400</td>
<td>5.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature = 450K</th>
<th>10% excess O₂</th>
<th>SO₂ = 3500 ppm</th>
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</thead>
<tbody>
<tr>
<td>Residence (msec)</td>
<td>0% methane</td>
<td>4% methane</td>
</tr>
<tr>
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<td>55.0</td>
</tr>
<tr>
<td>100</td>
<td>50.0</td>
<td>150.0</td>
</tr>
<tr>
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<td>45.0</td>
<td>95.0</td>
</tr>
<tr>
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2.857142857

<table>
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<th>Temperature = 1000K</th>
<th>4% excess O₂</th>
<th>SO₂ = 2000 ppm</th>
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<td>20.0</td>
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### C.4 Sample Measured SO$_3$ Concentration for 4-inch Reactor Tube

#### Temperature = 450K

<table>
<thead>
<tr>
<th>Residence (msec)</th>
<th>SO2 = 500 ppm</th>
<th>10% Excess air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% methane</td>
<td>4% methane</td>
</tr>
<tr>
<td>0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
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<tr>
<td>800</td>
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<td>15</td>
</tr>
</tbody>
</table>

#### Temperature = 450K, SO2 = 500ppm, 2% Excess air

<table>
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<td>10.0</td>
<td>40.0</td>
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<td>20.0</td>
</tr>
<tr>
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<td>14.0</td>
</tr>
<tr>
<td>800</td>
<td>12</td>
<td>14</td>
</tr>
</tbody>
</table>

#### Temperature = 450K, SO2 = 2000 ppm, 10% Excess air

<table>
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<th>4% methane</th>
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<tr>
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<td>52.0</td>
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