

EXPERIMENTAL STUDIES OF THE HOMOGENEOUS CONVERSION OF SULFUR DI-OXIDE TO SULFUR TRI-OXIDE VIA NATURAL GAS REBURNING

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ABSTRACT

Experiments involving pre-mixed natural gas combustion were conducted using a non-catalytic stainless steel reaction tube in a drop tube furnace to examine the homogeneous conversion of SO_2 to SO_3 . Homogeneous superequilibrium of SO_3 has been observed to form when SO_2 passes through a flame in the presence of excess oxygen. However, previous studies of this phenomenon were conducted at temperatures representative of those found in coal-fired combustors (1700K). The research presented in this work focuses on kinetics and mechanisms of the homogeneous conversion of SO_2 to SO_3 at free-stream gas temperatures ranging from 450K-1000K. The potential application for this work include reducing fly ash resistivity in electrostatic precipitators and enhancing the capture of sulfur gases in dry sorbent injection systems due to the fact that SO_3 is more reactive than SO_2 .

Experimental work focuses on two areas of investigation. First, to analyze the increased level of sulfur capture resulting from the conversion, a dry sorbent was injected in a flue gas stream with and without a natural gas flame. Second, the concentration of SO₃ as a function of residence time was measured using EPA test Method 8. The level of sulfur in the dry sorbents indicated that the presence of a natural gas flame greatly increased the percentage of sulfur capture. The measured SO₃ concentrations indicated that the flame produced a spike in SO₃ concentrations 100 milliseconds after the flame and that the duration of the increased concentration increases with decreasing free stream gas temperature.

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NOMENCLATURE

$C_{H_2SO_4}$	Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).	
C_{so_2}	Sulfur dioxide concentration, g/dscm (lb/dscf).	
ρ	Density of fluid.	
θ	Total sampling time, min.	
C _D	Drag co-efficient.	
d	Float diameter of the rotameter.	
F _D	Drag force.	
N	Normality of barium perchlorate titrant, g-equivalents/liter.	
$\dot{\mathcal{Q}}$	Volumetric flow rate of fluid.	
R _e	Reynolds number.	
u	Flow velocity.	
V _a	Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for	
	SO ₂ .	
V _{m(std)}	Volume of gas sample measured by the dry gas meter corrected to	
	standard conditions, dscm (dscf).	
V_{soln}	Total volume of solution in which the H_2SO_4 or SO_2 sample is	
	contained, 250 ml or 1000 ml, respectively.	
V _t	Volume of barium standard solution titrant used for the sample, ml.	

V_{tb} Volume of barium standard solution titrant used for the blank, ml.

CHAPTER 1 INTRODUCTION

1.1 Background

Coal is the most readily available and presently least expensive fossil fuel resource in the world. About ninety percent of the earth's fossil fuel reserves are coal, of which the United States holds about twenty-five percent [1]. Due to availability, low cost, and the known problems of alternative energy sources, it seems certain that coal will remain the major fuel for electric power production in the United States [1]. However, contemporary methods of coal combustion have drawbacks due to the production of various pollutants including fly ash, metal fumes, and gaseous emissions such as the sulfur oxides, unburned and partially burned hydrocarbons, NO_x , carbon monoxide; and greenhouse gases such as N_2O , and CO_2 .

A major concern of late has been acid rain, which is largely caused by SO₂ emissions from the combustion of coal. It has been found that approximately 68% of SO₂ present in the atmosphere comes from coal burned at stationary sources such as power-generating plants [2]. The SO₂ combines with moisture in the atmosphere to form dilute solutions of sulfuric acid or "acid rain". Acid can be carried in snow, rain, or fog. Sulfur dioxide can also undergo dry deposition, which results in internal plant damage when uptake from the soil occurs. Generally, a pH of 5.6 has been used as the baseline in identifying acid rain, although there have been many debates over the acceptance of this value. Natural buffer systems can handle the natural acidity of rain, but the increased load of acid rain is sometimes impossible to overcome in the areas where limestone is not readily available. Acid rain damages forests, crops, lakes, and lives of fish. Lakes undergo dramatic changes as the acidity increases. As the pH level of water in lakes decreases to about 6.0, crustaceans, insects, and some plankton groups begin to disappear. Further decrease of pH to about 5.0 causes changes in the lake's plankton structure. Less desirable moss species and plankton to invade, which in turn causes fish populations to decline. The most desirable fish populations especially the trout and salmon, followed by walleye, bass, and pike, are the first populations to disappear. At pH below 5.0, the carp die, the bottom is lined with undecayed matter, and the shoreline is predominantly covered by moss. Waterfowl and other species dependent on the lake system for their livelihood are also affected.

Likens [3] has reviewed the known effects of acid rain on plant-soil systems. Controlled laboratory and field studies have demonstrated decreased productivity, necrosis of leaves, nutrient loss from foliage and soil, weathering of leaf surfaces, and altered pathogenicity of plant parasites. Acid rain has a high potential for producing environmental stress through additive or synergic action in combination with other factors, such as gaseous pollutants.

There are many approaches available for abatement of SO_2 . The control of SO_x emissions in industries has historically been accomplished through physical processes e.g., scrubbers etc [5]. The method of flue gas desulfurization via wet scrubbing requires a high initial capital investment. On the other hand, dry scrubbing processes are more economically feasible than wet processes for similar SO_2 removal rates due to less expensive process involvement.

Fly ash or particulate matter produced during the coal combustion process is also potentially hazardous if emitted in to the atmosphere. The effect of inhalation of particulate matter on human health is related to injury or damage to the lungs or other surfaces of the respiratory tract. Because particulate matter of much smaller size may exert a toxic effect either directly, because of its influence on the tissue in the respiratory system, or because of the toxic material adsorbed on the particle surface. Early studies of the retention of particulate matter showed that particles larger than about 1µm in diameter were either trapped in the upper respiratory system or were not inhaled at all, and that particles below 1µm in diameter were not effectively retained in the lungs. But several recent studies indicate that particles below 1µm in diameter may have a greater irritant potential than larger particles, perhaps due to the large number of such particles in the respired atmosphere.

Control of particulates is commonly done using electrostatic precipitators. Fly ash from the combustion of coal is charged by ions from a corona discharge, and an applied electric field causes it to move perpendicularly to the air flow and deposit on the collecting plates of the electrostatic precipitator. Particles that have resistivity between 10^4 - 10^7 ohm-cm are called low resitivity, which are difficult to collect since they are easily charged and lose their charge upon arrival at the collection electrode. This happens very fast and the particles can take on the charge of the collection electrode. Low resistivity particles thus bounce off the plates and become restrained in the gas stream. On the other hand, particles with resistivity between 10^7 - 10^{10} ohm-cm are termed as normal resitivity which do not rapidly lose their charge upon arrival at the collection electrode. These particles slowly leak their charge to ground and are retained on the collection plates by intermolecular adhesive and cohesive forces. This allows a particulate layer to be built up, which then can be collected most efficiently. However, an electrostatic precipitator requires a specific range of ash resistivity, generally 10^9 - 10^{10} ohm-cm, to operate properly. Particles that exhibit resistivity higher than 10^{10} ohm-cm are difficult to charge thus forming a repelling layer of ash on the plates [4].

However, in an attempt to comply with the new regulations restricting SO_2 and particulate emissions implemented by 1990 Clean Air Act Amendment, power industries have begun to switch from high sulfur to low sulfur coals to reduce SO_2 emissions. It is obvious that combustion of high-sulfur coal, which contains 2.5% sulfur or more, causes higher SO_2 emissions than the low-sulfur coal which contains less than 1% sulfur. Therefore, using low sulfur coal could be an easy solution to reduce SO_2 emission. But it is unfortunate that low sulfur coals generally have a higher ash content which eventually causes high particulate emission. In addition, when low sulfur coals are burned, natural SO_3 levels in the combustion products are reduced to the point that they no longer can create enough H_2SO_4 to sufficiently reduce the resistivity. Therefore, the higher resistivity ash is harder to collect and creates unacceptable particulate emissions.

1.2 Benefits of Increased Sulfur Reactivity

Fly ash resistivity depends primarily on the chemical composition of the ash, the ambient gas temperature, the water vapor, and SO₃ present in the flue gas. In general, the higher the levels of SO₃ in the flue gas, the lower the fly ash resistivity [6]. The performance of the electrostatic precipitator tends to increase at lower fly ash resistivities. Therefore, the presence of SO_3 is very important and increases the collection efficiency of the electrostatic precipitator because it naturally combines with moisture in the flue gas to create sulfuric acid. This sulfuric acid is deposited on fly ash particles to form a thin conductive film which lowers the electrical resistance of the ash, allowing it to be readily collected by the electrostatic precipitator. The amount of SO_3 generated in the flue gas depends on the furnace conditions as well as on the sulfur content of the coal.

In addition, the presence of SO₃ in the flue gas enhances the sulfur capture when dry sorbent is injected in the gas stream because SO₃ is more reactive than SO₂ in limestone and lime [7]. Therefore, the conversion of SO₂ to SO₃ should lead to improved sulfur capture by dry scrubbing processes. The typical collection efficiency of dry scrubbers are 65% with a Ca: S ratio of 2:1.

Previous research on the formation of SO₃ in the flame gases were conducted to reduce the level of SO₃ in an attempt to reduce the corrosion and deposits in boiler furnaces, and metal losses in air heaters. The homogeneous superequilibrium of SO₃ were observed when SO₂ passes through a flame in the presence of excess O₂. While this superequilibrium condition has been studied, little data exist about the effects of free stream gas temperature as opposed to flame temperature on this process. SO₃ in industrial combustion systems causes sulfuric acid to form and corrode metal surfaces at temperatures below the acid dew point. This work proposed to investigate whether the presence of SO₃ through conversion of SO₂ to SO₃ could increase sulfur capture levels in an injected dry sorbent. Unlike the previous research, this study is concerned solely with the formation of SO₃ in flame gases and does not discuss its formation due to catalytic oxidation by stationary surfaces over which the gases pass. Another area of examination was the effect of the conversion to SO_3 on capture in the dry sorbents. Therefore, emphasis were given to identify the factors that enhance the formation of SO_3 at a lower temperatures rather than reducing its level.

In this experiment, a pre-mixed methane flame was used to promote the conversion of SO_2 to SO_3 in a drop tube furnace with a free stream gas temperatures ranging from 450-1000K. It was found that the amount of SO_3 formed in flames depends on factors that provide oxygen atoms. Additionally, the level of capture would indicate the usefulness of this conversion to practical applications, such as dry scrubbing.

In brief, this thesis proposes to address both improved SO_2 capture in sorbents and improved fly ash collection using natural gas combustion. It also explores the possibilities to increase SO_3 concentration even at flue gas temperature as low as 450K, which is typical of post air-heater flue gas temperatures at pulverized coal power plants.

1.3 Organization of the Thesis

This thesis consists of five chapters and relevant appendices. Chapter 2 presents the overall review of literature regarding natural gas combustion with sorbent injection and previous researchers' suggestions about the kinetics and mechanism of SO₃ formation and decomposition. Chapter 3 explains the general experimental facilities that are used to simulate the sulfur capture mechanism and the description of experimental setup for collection of solid and gas samples. Chapter 4 explains the experimental techniques for sampling and the procedure of analyzing both the solid and gas samples.

Chapter 5 discusses the experimental results obtained from the sorbent tests and gas sampling tests. It also represents the verification of the assumption using the experimental results to predict the concentration of SO_3 and its duration of existence and finally Chapter 6 concludes with a summary, and outlines recommendation for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Sulfur Oxides (SO_X)

The oxides of sulfur, SO_2 or SO_3 , are collectively called SO_x . They are generally released as the by-product of combustion of sulfur-containing fuel. SO_2 is the most common and available form of SO_x and is a non-explosive, colorless gas with a characteristic irritating, pungent odor. Similarly, SO_3 is a non-combustible, colorless gas, that is dangerously reactive and has a characteristic pungent odor. SO_3 reacts with water to form sulfuric acid. In addition, it reacts exothermically with alkaline materials, organic compounds, metallic powders, nitrates, chlorates, carbides, and cyanides.

Other sulfur oxides are sulfur monoxide, SO, its dimer, $(SO)_2$, and disulfur monoxide, S₂O. These are too unstable or reactive to appear as products of combustion in the ordinary sense, but they are known to occur as intermediates in appropriate circumstances.

Sulfur in the form of organic and inorganic compounds commonly accounts for several percent by weight of fuels burnt in power industries and other large industrial plants. The predominant sulfur-containing product formed by the combustion or slow oxidation of sulfur compounds and elementary sulfur is almost invariably sulfur dioxide. Even when oxygen is present in large stoichiometric excess, SO₃ is seldom found in amounts greater than a few percent of the SO₂, where SO₃ largely forms via:

$$SO_2 + \frac{1}{2}O_2 \xleftarrow{\kappa_1} SO_3$$
 (2.1)

The theoretical yield of SO_3 at a specified temperature can be calculated if the equilibrium constant k_1 is known. Theoretical conversion of SO_2 to SO_3 in flue gases at different temperatures and excess air levels was studied by Bodenstein [8]. From his work it was found that at high temperatures experienced in flames, one would expect that the reaction would proceed very quickly indeed, but only to give a very small equilibrium yield of SO_3 . Conversely at low temperatures, a low rate of reaction with a high possible yield occurred.

In most cases SO₃ appears in combustion products at room temperature as H_2SO_4 . The reaction of SO₃ with water in gas phase is very rapid. However, the equilibrium is such that at atmospheric pressure the H_2SO_4 is completely dissociated to SO₃ and water above about 500°C [9].

Molecules and radicals such as CS, SO, and HS if present in flame are considered as "labile" or "intermediate" species as distinct from "stable" products such as SO_2 , SO_3 and carbonyl sulfide. If a strictly thermodynamic criterion of stability is adopted any species may be "labile" in the sense that it is present in the system in higher or lower concentration than the equilibrium value. It was also found by Cullis and Mulcahy [9] that SO, HS etc., in common with other species such as H and OH, are frequently present in super-equilibrium concentrations during combustion of sulfur compounds in flame gases.

2.2 Flue Gas Desulfurization (FGD) Process

Flue gas desulfurization process is a common technique to minimize SO_X emissions in utility industries. This process is classified as either recovery or throwaway. The throwaway process produces a waste stream that must be disposed.

The recovery process is designed to convert SO_X into valuable by-products such as elemental sulfur, sulfuric acid, ammonium sulfate, and high quality CaSO₄ (gypsum). These systems are usually more expensive than the more common throwaway systems. FGD technologies include wet scrubbing techniques which use sodium or calcium-based sorbents such as hydrated lime or limestone, and dry scrubbing techniques, in which a lime or alkaline slurry is brought in contact with flue gas in a spray dryer. The dry FGD systems generate a dry product, usually a powder, for simpler disposal than the wet system.

Limestone injection is complicated by the three different types of reactions that must take place - calcination, absorption, and oxidation [5]. The calcination or thermal decomposition of $CaCO_3$ to active CaO occurs in the furnace at temperatures around 2000° F via:

$$CaCO_3 (s) \longrightarrow CaO (s) + CO_2 (g)$$
 (2.2)

The lime (CaO) then absorbs SO₂ via:

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3$$
 (2.3)

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow CaSO_4(s)$$
 or (2.4)

$$CaO(s) + SO_3(g) \longrightarrow CaSO_4$$
 (2.5)

Calcination is necessary for good SO₂ absorption because the reaction of SO₂ with CaCO₃ is extremely slow at the temperature below which CaCO₃ is stable (~1400° F). Thus limestone must be injected at the point at where the temperature is high enough (on the order of 1500-2100° F) to give an adequate calcination rate.

The direct reaction between SO_2 and the sorbent such as $Ca(OH)_2$ occurs according to the following reaction:

$$Ca(OH)_2(s) + SO_2(g) \longrightarrow CaSO_3(s) + H_2O(g)$$
 (2.6)

A bench-scale integral experiment for FGD was performed by Ben-Said [10] to investigate the effect of inlet SO₂ concentration, flue gas relative humidity, and limestone particle size to test the SO₂ removal performance of a 2 inch diameter by 6- inch deep fixed-bed reactor. The results indicated that more SO₂ removal for a longer period of time was achieved as the flue gas relative humidity was increased. Therefore, the presence of water in the flue gas has significant effect on the SO₂ removal efficiency [10].

2.3 Fly Ash Resistivity

When pulverized coal granules are burned, particles carried in suspension in the flue gases are called fly ash. These are formed from the inert or inorganic residue of the coal as well as small amounts of carbon or coke particles from the incomplete combustion of coal. The amount of fly ash emitted from a furnace depends mainly on the amount and composition of the coal burned, on the furnace design, and on furnace operation.

Fly ash is generally collected in the electrostatic precipitator before it leaves the exhaust stack. The ash aerosols are charged by ions from a corona discharge, and an applied electric field causes them to move perpendicularly to the airflow and collect on the walls of the electrostatic precipitator. Resistivity is also related to the ability of a particle to take on a charge. In most industrial applications, the resistivity of the particle is such that the charge on the particle is only partially discharged upon contact with the grounded collection electrode. A portion of the charge is returned and contributes to the intermolecular cohesive and adhesive forces which hold the particles to the surfaces. The dust layer builds up a thickness between 0.03 to 0.05 inch on the collection plate. If the dust layer becomes too thick, it is possible for the accumulated layer to act as an insulator, reducing the flow of the electric filed lines. The layer of collected fly ash usually falls into a hopper when the plates are vibrated by mechanical shock known as 'rapping'.

The fly ash resistivity is the dc resistance between the opposite parallel faces of a portion of the fly ash having unit length and unit cross-section. The unit of fly ash resistivity is ohm-cm. The fly ash resistivity for good precipitator operating range is 10^9 - 10^{10} ohm-cm at normal exhaust gas temperature of about 130° C. Particles that exhibit high resistivity are difficult to charge. Once they are finally charged they do not readily give acquired negative charge upon arrival at the collection electrode. As the dusts layer builds up on the collection electrode, the layer and the electrode form a high potential electric field. The surface of the dust layer is negatively charged, the interior is neutral, and the collection electrode is grounded. This causes a condition known as back corona or reverse ionization [6].

Utilities that have switched low sulfur coal in order to reduce the emission of SO_2 have seen particulate collection problems due its increased electrical resistivity. When low sulfur coals are burned, natural SO_3 levels are reduced to the point that they no longer can create enough H_2SO_4 and reduce ash resistivity. In addition, low sulfur coals especially from the Power River Basin have higher ash content per mass of coal, leading to even greater ash collection difficulties.

It has been found that the addition of conditioning agents, e.g. SO_3 or NH_3 is beneficial in reducing fly ash resistivity. Although NH_3 promotes ash agglomeration rather than reducing resistivity, however, the addition of conditioning agents reduces fly ash resistivity and helps to overcome reverse ionization effect within a precipitator. Flue gas conditioning is an effective way of collecting fly ash where the controlled injection of small quantities of SO_3 into the flue gas stream reduces the resistivity of the fly ash and permits its collection in the existing precipitator. However, it is questionable that if regulations require to reduce SO_X emissions, why would someone try to inject them. Fortunately only small amount of SO_3 are needed to combine with moisture in flue gas to create H_2SO_4 which is deposited on fly ash particles and forms a thin conductive layer and lower the electrical resistance of the ash.

From the report presented by Altman [11] on a field study for reduction of resistivity using flue gas conditioning, it was observed that the lower the inlet temperature of the precipitator the lower the resistivity. It was found that at 7-14 ppm of SO₃ injection at the precipitator inlet at a temperature of 153° C, the concentration of SO₃ was 1.4 -1.7 ppm in the exhaust gas stream, where the difference between the observed concentration and the injected quantity indicated that a large amount of SO₃ transformed to SO₂. The resistivity at a temperature of 153° C with a similar injection rate was found as low as 1×10^{8} to 1×10^{9} ohm-cm.

Although enhancing fly ash collection via flue gas conditioning is a viable technique, it may require a large initial capital investment. However, the generation of SO_3 via natural gas cofiring using SO_2 in the flue gas could be an easier and cost effective way of reducing ash resistivity as compared to that of injecting externally

generated SO₃. Therefore, the kinetics on homogeneous formation and decomposition mechanism of SO₃ are needed.

2.4 Sulfur Leveraging Through Natural Gas CoFiring

Cofiring is a process of simultaneous firing of natural gas and pulverized coal in a coal-fired utility boiler's primary combustion zone. It is a low-capital cost, lowrisk technology. Cofiring coal with sulfur-free natural gas dilutes the sulfur content in the stack gases. In addition, cofiring is expected to become more widely used to meet impending CO_2 emissions regulations. The combined effects of cofiring was studied in five different pilot projects cosponsored by EPRI and GRI. The summary report concluded that cofiring can be used to trim emissions of SO_X , NO_X , CO_2 , and particulates, and to improve stack opacity. In addition, it was seen that SO_2 and particulates reduced in direct proportion to the amount of coal displayed by sulfurfree, ash-free gas. The incremental reduction in opacity was reduced up to 3% with 10% cofiring. However, it was observed that at a full-scale operation with cofiring at 10-15% might result in reductions in power plant efficiency of about 1% [14].

Results from field studies conducted at Cheswick Power Station (Duquense Light Company) to examine the effects of cofiring coal with natural gas on sulfur emissions showed a reduction in SO_X emissions greater than the reduction expected by displacement of coal. This enhanced reduction of sulfur emissions, known as sulfur leveraging, was believed to result from increased sulfur capture in coal ash [12]. Cofiring experiments at the Northeast Power Station (Public Service Company of Oklahama) showed a significant increase in the sulfur retained in the ash [13]. In a review study on sulfur leveraging, Kramlich [15] reported that natural gas combustion may increase the reactivity of the sorbent with sulfur gas or increase ash surface area and hence may increase the reactivity of sorbent metals in ash [16]. According to Hura et.al [17], limestone activation increases significantly when limestone is processed by flame. Their results suggest that a natural gas flame could increase sulfur capture in ash by increasing calcination [16]. The degree of sulfur capture may increase during calcination through exposure to high temperatures. However, prolonged exposure to very high temperatures can reduce the ability of sorbent to capture sulfur. For example, sulfur capture by CaO is optimal at 1250 K, but a prolonged exposure to temperature above 1250 K cause CaO to sinter or become less reactive due to a decrease in internal pore area.

The idea that sorbent reactivity can also be enhanced by increasing surface area was suggested by Kramlich [15]. A reaction between sorbent and sulfur creates a coating on the sorbent surface. To continue further sulfur capture, the remaining sulfur containing gas must diffuse through the coating. For otherwise equivalent sorbent particles, one with a small surface area is more rapidly coated, while one with a porous structure and a large internal surface area will have more surface area available to capture sulfur. The flame from gas cofiring may increase the heating rates of a coal particle, which increases its internal surface area, and in turn, may increase its reactivity [16].

The effects of cofiring natural gas and coal on sulfur retention in ash was studied by Bayless [18] in a drop tube furnace under various gas compositions, furnace temperatures, and particle residence times to investige the factors affecting sulfur leveraging. Experimental evidence was provided that increased levels of SO_3 were responsible for the observed sulfur leveraging.

2.5 Kinetics and Mechanism of Homogeneous SO₃ Transformations

When a sulfur compound is introduced into a hydrogen, carbon monoxide, or hydrocarbon flame burning with excess oxygen, a few percent of the SO₂ becomes oxidized to form SO₃[8]. This is brought about by labile species participating in the flame reactions. The SO₃ concentrations are, temporarily, greater than equilibrium concentration as found from Eq. 2.1 and is termed as superequilibrium SO₃. Superequilibrium of SO₃ observed previously amounted from 1-2% up to 8% in case of the observation performed by Levy and Merryman for the SO₂ present in the flue gases [19].

The three possible reactions by which SO₃ could be formed in a combustion system are [20]:

(1) Reaction of SO with molecular oxygen early in the flame,

$$SO + O_2 \longrightarrow SO_3$$
 (2.7)

(2) Reaction of SO₂ produced in the flame with atomic oxygen available in the flame and the immediately post-flame region,

$$SO_2 + O \longrightarrow SO_3$$
 (2.8)

(3) Reaction of SO₂ by molecular oxygen on steel surfaces and at lower temperatures where equilibrium is more in favor of SO₃,

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$
 (2.9)

A study on these reactions showed that SO_3 was formed early in flame by Eq. 2.7 but that SO_3 was dissociated as the temperature went higher in the flame. Eq.2.9 showed

insignificant production of SO₃ for the short residence time in practical combustion systems [20]. According to Levy [21] reaction by Eq. 2.9 is of minor importance in H₂S flame as the homogeneous gas-phase reaction between SO₂ and O₂ is very slow at temperatures below 1000° C. Eq. 2.8 accounted essentially for all SO₃ found beyond the flame front.

The experiment conducted by Hedley [22] indicated that the combustion of carbon monoxide in the presence of SO_2 produced more SO_3 . In examining the mechanism by which CO is converted to CO_2 during combustion, it was found that for each molecule of CO oxidized to CO_2 , one atom of oxygen was consumed in the process but two were produced. Thus each time a single CO molecule burns, a surplus of oxygen atoms released into the system, which collide with an SO_2 molecule and form excited SO_3^* molecules [22] as Eq. 2.10 shown below:

$$SO_2 + O \longrightarrow SO_3^*$$
 (2.10)

This SO_3^* has six vibrational degrees of freedom over which the excess energy may be spread. If the environment of this activated molecule is amenable to its stable existence, then this excess energy could be removed by a third body collision to give normal SO₃ by the following scheme:

$$SO_3 + M \longrightarrow SO_3 + M$$
 (2.11)

Therefore, the principal reaction of an oxygen atom with SO_2 is generally considered to be the major source of SO_3 formation in the combustion process [21] and reaction occurs as a termolecular process via:

$$O + SO_2 + M \xleftarrow{k_{12}} SO_3 + M$$
 (2.12)

The difference between Eq. 2.8 and 2.12 is that SO_2 in Eq. 2.12 reacts with atomic oxygen in flames where the atomic oxygen concentration is relatively high as compared to the oxygen concentration considered in Eq. 2.8. Flame-produced SO_3 depends on the availability of oxygen atoms, which in turn must come from other flame reactions. Because the SO_2 level with sulfur-bearing fuels is invariably greater than the oxygen atom concentration, the amount of SO_3 formed in flames depends on factors that provide oxygen atoms.

A study by Hedley [22] on the formation of SO_3 in flames was performed by spraying sulfur doped liquid fuel into the combustion products obtained by burning a fuel at about 1300° C that is similar but sulfur free. Figure 2.1 shows that in such cases the



Figure 2.1 Formation of SO₃ in a Hydrocarbon Flame (after Hedley)

initial yield of SO₃ exceeded the maximum theoretical yield calculated from the thermodynamic considerations. But as combustion proceeded, the amount of SO₃ present gradually decreased until equilibrium levels were reached.

Figure 2.1 shows that the amount of SO_3 present in the gas following interaction with a flame was very much in excess of the theoretical equilibrium concentration. According to thermodynamic considerations, the consecutive reaction for the formation and decomposition of SO_3 are represented as follows from the study performed by Hedley [22]:

$$SO_2 + O \xrightarrow{k_{13}} SO_3^*$$
 (2.13)

$$\operatorname{SO_3}^* \xrightarrow{k_{14}} \operatorname{SO_2} + \frac{1}{2} \operatorname{O_2}$$
 (2.14)

where both reactions were assumed to be first order with the rates dependant solely on concentration of O and SO_3^* respectively. The duration of the superequilibrium effect is dependent on the concentration of radicals and the temperature of the gas stream following the flame reaction zone.

The superequilibrium of SO₃ thus found was very short lived in this study due to the high temperature, which increased the rate of thermal decomposition of SO₃. But the product of this dissociation could be SO₂ with oxygen atoms or molecules, and in the case of molecular products, SO₂ and O₂ each could retain some of the energy initially gained which eventually could be removed by third body collision. In addition, the decomposition of SO₃ can occur through the backward reaction as shown in Eq. 2.10 which is highly dependent on temperature.

However, simple equilibrium calculations underestimated SO_3 concentration at high temperatures and overestimated SO_3 concentrations at low temperatures. As a result, considerable investigation was done to determine a more accurate description of the behavior of SO_3 under transient and steady conditions. The decomposition of SO_3 may occur by the following mechanisms [22] as shown in Eq. 2.15 and 2.16,

$$O + SO_3 \xrightarrow{k_{15}} O_2 + SO_2$$
 (2.15)

$$H + SO_3 \xrightarrow{k_{16}} OH + SO_2$$
 (2.16)

As reviewed by Cullis and Mulcahy [11] an overall rate constant for SO₃ (k_{SO_3}) destruction was given as,

$$k_{SO_3} \equiv k_{15} + k_{16} \frac{[H]}{[O]} = k_{12} \frac{[SO_2][M]}{[SO_3]}$$
(2.17)

where, the range of k_{SO_3} could be determined from the assumed behavior of k_{15} .

The effect of oxygen concentration on the formation of SO_3 was studied by Barrett, Hummell, and Reid [20] in a 25 cm in diameter tubular non-catalytic reactor and the results suggested that the degree of conversion of SO_2 to SO_3 increases with the increasing amounts of oxygen fed to the flame over and above that required stoichiometrically for complete combustion of fuel to steam and CO_2 . Figure 2.2



Figure 2.2 Effect of Excess Air on the Formation of SO₃ in a Hydrocarbon Flame

shows that the effect of excess air on the quantity of SO₃ formed in the stainless-steel combustor. Combustion air was varied to investigate SO₃ formation from combustion with slightly less than stoichiometric air to combustion with nearly 30 percent excess air. Figure 2.2 shows that virtually no SO₃ was detected when the ratio of oxygen to fuel was equal to 1 or less than the stoichiometric value. Increasing the excess oxygen from 0 to 1% caused a sharp increase in the amount of SO₃, further addition of oxygen causing only a relatively small increase. Since the oxygen was added as air, with a consequent dilution of the flame by nitrogen, the later case may be a consequence of the lower flame temperature [9].

In general the effect of gas temperature on SO₃ reactions is not well understood, especially at low temperatures. It was speculated by Cullis and Mulcahy [9] that some fraction of SO₂ converted to SO₃ found at low temperature is an artifact of the temperature at which the equilibrium by Eq. 2.1 becomes 'frozen' as the gases cool and, in principle, could occur equally well with a catalytic and non-catalytic mechanism. In addition, there is reason to believe that an intense flame-front could generate enough O radicals to produce the enhancement, at even lower free stream temperature [12]. The conditions that result from lower temperatures could also reduce the concentration of O radicals from temperature driven O₂ dissociation downstream of the flame. Thus the destruction of SO₃ via Eq. 2.19 would be retarded. In addition, the lower temperature should reduce the rate at which the SO₃ thermally degrades. Coupling these effects could lead to an increase in residence time for the converted SO₃, thus increasing the possibilities of practical application.

CHAPTER 3 EXPERIMENTAL FACILITY

3.1 Overview

The objective of this work was to examine the conversion of SO₂ to SO₃ using a perpendicularly introduced methane flame at free stream gas temperatures of 1000K, 650K, and 450K. The two goals for this study were to determine if sulfur reactivity could be increased at low temperatures and to quantify the effect of temperature. Experiments were performed to determine whether the conversion process of SO₂ to SO₃ would increase capture levels in an injected dry sorbent. The theory behind these experiments as described in section 2.4 was that if SO₂ were converted to SO₃, the more reactive SO₃ would be more easily captured in the dry sorbents. Additionally, the level of capture would indicate the usefulness of this conversion to practical applications, such as dry scrubbing. Experiments were then performed to quantify the level of SO₃ conversion in each of the examined temperature ranges as a function of O₂ concentration using EPA method 8.

The Sulfur Reactivity Experimental Facility described in this section, is shown in Figure 3.1. The SREF can be used for solid sampling experiments where both the primary and secondary reactors were used with helium quenched sampling probe. Samples were collected at the bottom of the combustor tube and the percentage of sulfur capture by sorbent injection from solid samples was measured by chemical analysis using the LECO analyzer.



Figure 3.1 Schematic of the Sulfur Reactivity Experimental Facility

Figure 3.1 represents the schematic of the SREF used for both solid sampling

and gaseous sampling which contained the following instruments:

- Primary and Secondary Reactor
- Water Cooling System
- Sorbent and Natural Gas Injection Probe
- Propane Gas Lighter
- Helium Quenched Extraction Probe
- Rotameter Board and Vacuum Pump

The reactor facility allows the user to collect samples under well-controlled

conditions of flow, temperature, and composition. The simulated conditions typical of

an exhaust gas stream in a power plant were achieved by using the characteristics

summarized in Table 3.1

Table 3.1 Operating Characteristics of the Furnace Setup				
<u>Operating C</u>	haracteristics	Measured Quantities		
Gas Temperature	450 K to 1000 K	Temperature Profile		
Excess Oxygen	0 to 200%	% S capture & SO ₃ concentration		
Percentage CH_4 0 to 4%		% S capture & SO ₃ concentration		
SO ₂ concentration	500 ppm to 5000 ppm	% S capture & SO ₃ concentration		
Gas Velocity	0.677 to 2.032 m/sec	Residence time		

The first stage of a two-stage electrical resistance-heated reactor preheated the sulfur bearing gas stream to the approximate temperature of the secondary furnace limit quenching effects. A 1.25-inch reaction tube made of stainless steel to minimize SO_3 catalyzation was used in both the primary and secondary reactor [18].

In the secondary furnace, a pre-mixed methane flame, controlled by varying methane and oxygen concentration, was directed perpendicularly to the flow field. In case of solid sampling experiments, the particle size of the sorbent (Ca $(OH)_2$) ranging from 25-45µm was collected using the vibrated screen. Sorbents were injected into the reaction

tube downstream of the flame using preheated nitrogen to fluidize an aerosol stream of sorbent through a horizontal tube covered by the sorbent injection probe as shown in the Figure 3.1. Sorbent and capture products were isokinetically sampled using a heliumquenched, water-cooled probe. The injected sorbent reacted with the gas mixture and the reactants were collected to quantify the sulfur capture percentage.Once collected, the samples were analyzed for sulfur content to indicate the extent of increased capture because of the flame.

The SREF can also be used to perform gas sampling which uses both the reactors, sulfuric acid mist sampling train, the gas chromatograph, and online data acquisition systems. The concentration of SO₃ was measured from the gas samples characterized by EPA Test Method 8 via wet chemistry. The Figure 3.2 represents the experimental setup





25
of this wet chemistry. The gas chromatograph provided simultaneous on-line measurement of sulfur content from the exit gas stream. The gas sampling was performed by replacing the sorbent sampling probe with a 1/4th-inch stainless steel tube that has flexibility in positioning at any axial location inside the secondary reaction tube. The gas stream was transported via a heated sample line for analysis of sulfur species, including SO₃ content, by a gas chromatograph with a flame photometric detector and a wet chemistry technique [23].

Figure 3.2 shows EPA Test Method 8 Setup for gas sampling and is called the sulfuric acid mist sampling train, which included some or all of the following equipment:

- Computer Gateway 2000
- Gas Chromatograph HP5890 plus
- Midget Impinger
- Filter
- Silica Gel Drying Tube
- Vacuum Pump
- Rotameter
- Dry Gas Meter
- Borosilicate Glass Probe
- Dial Thermometer
- Variable Height Extraction Tube
- Adjustable Thermal Tape
- Reagents

The following sections describe the design of the reactors and sampling train in detail. The section first describes the basic design of the solid sampling setup and then subsequently discusses the apparatus and techniques used to measure concentration of SO_3 , and percentage of sulfur capture in sorbent.

3.2 Reactor Design

Joining the main tube located at the center of both the primary and secondary

reactor formed the heating chamber of the reactor. These main tubes were two stainless

steel cylindrical tubes of 1.25-inch diameter at the primary and secondary; one of those was 113 cm long surrounded by the primary and the other was 76.2 cm long surrounded by the secondary reactor as shown in the Figure 3.1 by dark lines. The gas mixture was pre-heated in the primary reactor to prevent quenching effects and was elevated to a higher temperature in the secondary reactor.

3.2.1 Primary Reactor

The primary furnace was used to pre-heat the gas mixture to prevent the thermal shock of the gas stream, where temperatures up to 1200° C could be generated. A schematic representation of the primary reactor is provided in Figure 3.3. The major components of this reactor were:

- Heating Elements
- Alumina (Al₂O₃) Board
- Alumina Matting Insulator
- Lindberg Controller
- Combustor Central Tube
- Combustor Frame
- Secondary Combustor Base
- Sensing Plug

The secondary reactor was situated on the top of the secondary base and the central tube of the combustor was connected with the main tube of the secondary reactor. The base of the secondary combustor has a hole to let the gas mixture pass from secondary through the tube. Solid samples were collected under this secondary base using the helium quenched extraction probe. A three way tube connector was used to provide connection between different gas bottles e.g. SO_2 , N_2 etc. and the reactor tube. The horizontal heating elements were the major source for raising temperature which were controlled by the primary controller connected by the cable from the reactor.



Figure 3.3 Primary Reactor and Apparatus

The temperature control of the primary reactor was performed by a microprocessor based controller as shown in Figure 3.4. The control panel was an individual unit (Lindberg) manufactured by General Signal. The input current (220V dedicated line at 50/60 Hz) was provided to the furnace and the sensor which was connected with both the controller and furnace gave feedback through digital display unit to control the temperature and other parameters e.g. proportional band, cycle time etc.



Figure 3.4 Lindberg Primary Controller

3.2.2 Secondary Reactor

After the gas stream was preheated, the reactions with a methane flame occurred inside of the stainless steel tube placed at the center of the secondary furnace as shown in Figure 3.5. The U shaped $MoSi_2$ heating elements were able to generate temperatures up to 1700° C. A variable transformer called secondary controller was used to control the temperature inside the reactor.



Figure 3.5 Schematic of the Secondary Reactor

Figure 3.5 represents secondary reactor which included the following major

components:

٠,

- a) Heating Elements: Four U-shaped MoSi₂ heating elements having highly brittle properties.
- b) Aluminum Straps: Six 50A Straps to connect between the terminal and elements.
- c) Holding Clamps: Four spring steel clips to hold the elements and the straps together.
- d) Element Holder: Four element holders to keep the elements in the same vertical position.
- e) Alumina Board: Used to enclose the heating chamber
- f) Alumina Matting: For insulation between the Alumina board and the furnace casing.

The side walls of the reactor as shown in the Figure 3.5 was made by alumina board in the middle, aluminum plate at the outer shell, and alumina matting as insulator at the innermost layer. The location of the methane and sorbent injection port was kept by dimensions shown in the figure.

The secondary control unit had three transformers of which two were: 3.24 KVA, 1:5 step down, 1Ø, and 50-60 Hz; and the other transformer known as Main Unit had a variable dial which was used to set different voltage as required. This main transformer had 120V input current option with 0-140V output and 3.1 KVA power generation capability at 50-60 Hz by a single phase. As the objective of this setup was to achieve higher current at lower voltage, the connection was done in parallel. In order to achieve required temperature, a multi purpose meter were used to read the instant current and voltage of the heating elements.

3.3 Solid Sampling Apparatus

3.3.1 Water Cooling System

Figure 3.6 represents the closed loop water cooling system. The system consists essentially a water pump in conjunction with water container. The system was designed to re-circulate water and consisted of a water containing bucket, inlet tubing, outlet tubing, and 35 foot head water pump.

Re-circulated water was used for cooling all the probes e.g. natural gas injection probe, sorbent injection probe, and sampling probe. The cooling of the probes with circulating water was performed to achieve a lower temperature for the probe surface which in turn gave safer probe handling and longer life of the probe. The water was supplied through a water container which contained both the inlet and outlet valves. As shown in Figure 3.6, the water from the probes was sent back to the container for recirculation and shown by the arrows in the figure.





3.3.2 Natural Gas Injection Probe

The gas injection probe was designed to inject a pre-mixed natural gas and air at a desired rate by controlling the flow rate through rotameters. Figure 3.7 represents the gas mixture injection probe made with precise geometric size and shape. The similar type of probe was also used for sorbent injection process. The probe was built from stainless steel to protect from high temperature and corrosion.



Figure 3.7 Schematic of Gas and Sorbent Injection Probe

the water at room temperature and provided a continuous cooling to the gas mixture in the inner shell. The cold water from the container was supplied through the inlet port and the outlet of the water jacket was connected with the water container to keep a constant water re-circulation. A rotameter was connected with the probe to measure the gas flow rate at the point before the gas mixture enters the inner shell.

3.3.3 Sorbent Injection Setup

The sorbent injection setup used the same type of probe as the natural gas injection probe (Fig. 3.7). The sorbent injection probe was designed to deliver the sorbent at a desired rate via gaseous entrainment into the reaction tube. Sorbent was injected approximately 200 mm downstream of the methane flame by entraining 25-45 μ m Ca(OH)₂ particles in N₂ gas stream from the bottom of the fluidized bed. The gaseous flow rate was controlled via a rotameter, by changing the pressure of the gas container. The sorbent flow was kept constant to a pre calibrated value by controlling the flow rate of the N₂ gas and using variable vibrator. The probe was designed for continuous recirculation of water from the container as in the case of natural gas injection probe.

Among many other components the setup entailed the following:

- Water inlet and outlet tubing
- Fluidized Sorbent Bed and Sorbent
- L-shaped injection tube
- VariableVibrator
- Rotameter and N₂ gas bottle etc.

A glass tube as shown in Figure 3.8 contained the dry sorbent on a filter bed. The bed contained a bottom tube for injection of N_2 gas, which caused the sorbent particle to fluidize. The L-shaped stainless steel tube for sorbent injection which was located at the top of the bed carried the fluidized particle and injected sorbent inside the secondary reactor tube.

The flow rate of the sorbent injection was also kept approximately uniform for the entire period of sampling operation by providing a variable vibration effect on the bed. The vibration effect helped to avoid the sorbent sticking with the glass tube and also created an extra swirl which provided an uniform sorbent flow. The vibration from the



vibrator was transferred to the bed through the fixture attached to the glass tube.

Figure 3.8 Schematic of the Fluidized Bed

A plastic retainer as shown in Figure 3.8 at the top of the glass container was used to keep the sorbent particles inside the bed. The hole at the center of the retainer was used to hold the injection tube as shown in Figure 3.8.

3.3.4 Helium Quenched Sampling Probe

A helium quenched sampling probe as shown in Figure 3.9 was designed to collect samples of sulfur products with the help of very fine mesh. Samples were extracted using a vacuum pump through the copper tubing attached to the lower end of the probe. The quenching was accomplished through a number of helium injection ports at the tip of the inner circumference of the probe, which helped to draw the combustion products properly and to minimize further reactions in the sample. The water cooling system served as the actual heat sink for quenching. The components of the sampling probe were:

- Helium carrying tube connected with Helium gas bottle
- Fine fabric mesh (preferably 325 mesh)
- Copper tubing connected with a vacuum pump



Figure 3.9 Schematic of the Sampling Probe

3.3.5 Gas Flame Lighter

The gas flame lighter shown in Figure 3.10 was used to ignite the premixed gas from gas injection probes. This setup consisted of a propane gas bottle that worked as a lighter and a 30 inch long stain- less steel vertical tube that was inserted completely inside the secondary reactor tube during lighting. After turning the knob for required gas flow, a separate lighter was used to ignite the flame, which was then inserted inside the reactor tube to ignite the gas mixture.



Figure 3.10 Schematic of the Gas Flame Lighter

3.3.6 Flow Rate Measuring Board

The flow rate measuring board shown in Figure 3.11 consisted of rotameters for SO_2 , CH_4 , air, and N_2 to measure and control the flow rates. Two more rotameters for He and N_2 were mounted to a separate stand. The roatmeter for N_2 in the board was provided

to control the amount N_2 used in the main gas mixture. The other one was dedicated for sorbent fluidization.



Figure 3.11 Schematic of the Rotameter Board

The experimental flow rates for SO₂, CH₄, Air, and N₂ were 0-3000 cm³/min, 0-1000 cm³/min, 0-20,000 cm³/min, and 0-30,000 cm³/min respectively. Flow meters were selected in such a way that they were dedicatedly used to measure a specific type of gas flow rate. Each meter was marked from 0 to 150 to obtain the particular flow rate in cm³/min. All the meters were pre-calibrated before connecting to the corresponding gas tube. The float inside the tube showed the rate of flow for any particular condition and the flow rate was controlled by adjusting the regulatory valve.

3.4 Gas Sampling Apparatus

A schematic of the gas sampling train specified by EPA Method 8 (EMTIC) is shown in Figure 3.2. The sulfuric acid mist sampling train was employed to separate sulfuric acid mist (including SO₃ in the absence of other particulate matter) and SO₂ emissions from the furnace. Collaborative tests performed by EPA show that the minimum detectable limits of the method are 0.05 mg/m³ for SO₃ and 1.2 mg/m³ for SO₂.

In this method, a gas sample was extracted approximately isokinetically from the gas mixture through 0.25-inch tubing connected to the sampling train. The sulfuric acid mist (including SO₃) and the SO₂ was separated using a midget bubbler and impingers in the sampling train. The concentration of H_2SO_4 (including SO₃) and SO₂ were measured separately by the titration method using barium perchlorate and thorin indicator.

The overall sampling train including the apparatus has shown in the Figure 3.2. The impingers were placed in an ice bath and the major apparatus used in the train are described in the following sections.

3.4.1 Probe Liner

To prevent visible condensation during sampling a 12-cm quartz glass tube packed with Pyrex Wool was connected with the midget bubbler as shown in Figure 3.2 via an L-shaped glass joint. The temperature of the probe liner was controlled by a variable Thermolyne controller connected to heating tape.

3.4.2 Impingers

Four 30-ml midget impingers of borosilicate glass were placed as shown in Figure 3.2. The first impinger, called midget bubbler, was used to collect gas samples for the detection of H_2SO_4 including the SO₃ acid mist. The second and the third impingers were used to measure SO_2 amounts in the gas stream. The impingers were connected with joints to provide a positive seal against leakage. The first impinger contained 30 ml of 80 percent isopropanol to capture the H₂SO₄ mist and SO₃ [15]. The second and third impingers contained 30 ml of 3 percent hydrogen peroxide to capture SO₂ from the gas stream [15]. Finally, the fourth impinger, which was kept free from any solution, was connected with a silica gel drying tube to dry the gas sample as shown in the Figure 3.2. *3.4.3 Filter*

The filter was placed between the first and second impingers to remove small smoke particles from the gas mixture. Made of glass fiber filters without an organic binder, the filter was rate to capture at least 99.95% of particles to the size of 0.3 μ m. The filter material was chosen for its non-reactivity with SO₂ or SO₃.

3.4.4 Vacuum Pump

A $\frac{3}{4}$ HP rotary vane, oilless vacuum pump was placed after the needle valve to collect the gas samples. The pump used a single phase motor with and thermal overload protection, suitable to work at a maximum temperature of 104° F. The vacuum pump featured a free vacuum capacity of 4.5 cubic feet per minute and the exit of the pump was connected with a dry gas meter.

3.4.5 Dry Gas Meter

A dry gas meter was placed after the vacuum pump to measure the sample volume. The dry gas meter was equipped with a temperature gauge i.e., dial thermometer. The meter had a capacity of 0.1 cubic feet per revolution which could easily be read from the meter. Moreover, the exit of the meter was connected directly to the exhaust of the room to maintain a healthy atmosphere inside the laboratory. A variable height extraction tube completed the connection between the solid sampling setup with the gas sampling train. The tube had a splitter and allowed a sample to be drawn through the sampling train with or without the gas chromatograph in order to have online sampling facilities for future work.

3.4.6 Water

De-ionized distilled water was used for every step in the analysis where required to conform to ASTM specification D1193-77 [24].

3.4.7 Silica Gel

The sample gas passed through the drying tube prior to enter the pump and meter. The drying tubes packed with 6 to 16 meshes of silica gel was used as desiccants to dry up the exit gas and hence protected the pump and meter.

3.4.8 Isopropanol, 80 percent

80 ml of 100 percent Isopropanol with 20 ml of deionized distilled water was used to prepare 80 percent Isopropanol and was used in the first impinger to capture SO₃ and sulfuric acid mist.

3.4.9 Hydrogen Peroxide, 3 percent

100 ml of 30 percent hydrogen peroxide were diluted to one liter with de-ionized, distilled water according to the test Method 8, and was used for the second and third impinger. Fresh 3 percent hydrogen peroxide was prepared before running every sample. *3.4.10 Thorin Indicator*

1-(o-arsonophenylazo) 2-napthol-3, 6-disulfonic acid, disodium salt was used as thorin indicator for titration of the sample after their collection from the impingers.

CHAPTER 4

TEST PROCEDURE AND SAMPLE COLLECTION

4.1 General Steps of Sample Collection

In every test performed, the following general procedures were used in the operation of the sulfur reactivity experimental facility. Two different procedures were followed for sample collection through solid sampling and gaseous sampling and are discussed in this chapter.

Experiments were performed by first establishing a flow of nitrogen, oxygen, and SO_2 through the primary furnace of the SREF. In the secondary reactor, the gas flow could then pass through a flame perpendicularly to the tube's major axis. Experiments were conducted to examine the effects of gas stream temperature, CH_4 concentration, O_2 concentration and SO_2 residence time on gas-phase SO_2 to SO_3 conversion. In the experiments, SO_2 concentrations were maintained at 2000 ppm, the approximate level of SO_2 emissions from the combustion of a medium sulfur high-volatile bituminous coal, and gas velocities of 1.016 m/s were also consistently maintained. Excess O_2 levels (the level of O_2 in the combustion products compared to stoichiometric levels) ranging from 0-30% natural concentration was set at either 0% or 4%, and free stream temperatures of 1000K, 650K, and 450K were used.

For the sorbent-based capture experiments, a hydrated lime sorbent was injected via gaseous entrainment into the reaction tube approximately 200 mm downstream of the flame. This distance was chosen to minimize flame effects, such as calcination or sintering, on the sorbent. A fluidized feeding system was used to deliver the sorbents into the tube at the rate of approximately 16.7 mg/min. A water-cooled, helium-quenched probe was used to collect the sorbent for sulfur analysis. Care was taken to assure that samples are collected using the same sorbent flow and duration. The samples were analyzed after they were collected for sulfur content using a Leco S-32 Sulfur Determinator.

After the sorbent injection tests were performed to indicate viability and usefulness of the general process, gas sampling for SO₃ analysis was initiated. During gas sampling, of course, no sorbent material was introduced into the system to foul the gas lines. The inlet to the heated gas sampling line was placed at various axial positions in the secondary furnace to draw gas via the use of a vacuum pump. The gas sample was then split between a gas chromatograph and a wet-chemistry set-up to quantify all sulfur species in the stream.

SO₃ detection was done via wet chemistry (EPA Method 8) using the apparatus shown in Fig. 3.2. A drawn sample was collected in hydrogen peroxide solution and tested for SO₃ content by use of barium perchlorate trihydrate [Ba (ClO_4)₂·3H₂O]. The sample was titrated and analyzed via pH spectrum . This information was then used to determine the concentration.

4.1.1 Primary Controller Adjustment

To begin with, the overhead power switch and the power of the primary controller were turned on. For the various temperatures- 450K, 650K, and 1000K different parameters were set using the scroll button on the panel of the display unit, which continuously showed the set point temperature and the actual temperature on the panel. The parameters settings e.g. A_1 , A_2 , Pb, ti, td, AP, Hc, HL etc., were performed according to the instructions provided by the Eurotherm manual [25].

The parameters, each of which had different values, were set according to the initial test conducted for setting three variables in the control parameters. This was common for every step before starting with each temperature. The initial parameter setting was as below:

The proportional band, Pb % = 0.50, Integral time, ti = OFF Derivative time, td = OFF Cycle time, Hc = 0.3 Approach, AP = 1.00 Setpoint, = As required.

For example, to set an overall required temperature of 1000K, the temperature of the primary was set as 700K and the following procedures were followed.

The *UP* button was pushed to set the temperature of the primary furnace at 700K, which was located at the right side of display panel. The other parameters were set after pulling the bottom panel and when the scroll button was depressed, different parameters e.g. A_1 , A_2 , Pb, ti, td, AP, Hc, HL etc. were displayed one after another in a sequence. After depressing the scroll button when any of the above parameters were displayed, the *UP/DOWN* button was depressed to set that parameter by choosing the above-mentioned values. Once the above steps were done, the temperature profile of the furnace was measured after about 20-30 minutes by inserting a thermocouple inside the vertical stainless tube of the furnace, which is located at the center of both the reactors.

4.1.2 Secondary Controller Adjustment

After the primary controller was fixed, and set at the required temperature, the secondary controller was cranked up by turning the power switch *ON*. The dial indicator of the main transformer was set at zero because a sudden increase of voltage by an

increasing variable dial meter of the main transformer could cause a severe thermal shock in the heating elements. In fact, as the resistance of the heating elements varied with the temperature, their properties changed gradually with the increase of current. A sudden increase in current caused an abrupt change in property and consequently the element became more brittle and hence could not be used anymore after such an operation. Therefore, the voltage was increased by an increment of 5V every time at a 10-12 minute interval. Meanwhile, the reading of voltage and current were measured across each of the secondary transformers and also the current reading was measured at both the input and output end of the transformers. The voltage, current, and temperature were read using Amprobe multimeter and the Omega thermocouple meter.

The inside temperature of the secondary reactor was taken by inserting thermocouple from the bottom of the reactor and a temperature profile with and without the natural was created and is shown in Fig. 4.1, 4.2, and 4.3. The height from the bottom of the reactor was chosen such that it started from zero with a 4-cm increment to measure the temperature inside the reactor. It should be noted that the region from 0-24 cm is above the flame.

In addition, the terminal clamps were separated from each other to avoid unnecessary heat generation at the contact surface. The voltage was increased gradually as long as the required temperature was achieved. It was found that the transformer efficiency decreased if the dial was set to more than 85% of the total transformer capacity.

The temperature profile at 1000K, 650K, and 450K has shown below in Figures 4.1, 4.2, and 4.3 respectively.



Figure 4.1 Temperature Profile of the Secondary Reactor at 1000K



Figure 4.2 Temperature Profile of the Secondary Reactor at 650K



Figure 4.3 Temperature Profile of the Secondary Furnace at 450K

It is clear from the profiles that the temperature at every condition is higher for 4% natural than 0% natural case. However, the difference between them is not very significant for the 1000K case as shown in Fig. 4.1. The temperature difference is maximum approximately at the center of the tube which is about 20-30 cm above the bottom of the secondary tube. After reaching the maximum point, the characteristics of the profile for 4% natural case is such that it goes down and becomes equal to the temperature for 0% natural as the distance from the bottom increases. The maximum attainable temperature with natural for all the conditions were almost 1000K, 650K, and 450K respectively.

The temperature was checked after 1-2 hours of the above operations and as soon as it reached the desired temperature the sampling task was taken into consideration. Tests on the temperature characteristics and the variac reading showed that a variac dial setting of 25-28 gives a temperature of 450K inside the secondary reactor without the natural flame. Also in case of natural flame a setting of 15-18 provides the required temperature. However, for 1000K and 650K without natural flame, the variac settings were kept at about 45-50 and 34-38 and in the case of natural flame it was about 32-35 and 24-28 respectively. Although this type of rule of thumb was used for an approximation it was always double-checked by measuring the exact temperature using the thermocouple.

4.2 Solid Sampling

These samples constituted an important part of the experiments in this investigation. In fact, most of these tests were performed to study the amount of sulfur capture via sorbent injection. The effect of natural gas flame on the ability to capture sulfur was studied by varying the percentage of natural in each test series. Moreover, the effect of sulfur capture was observed by changing one particular parameter in each test, while the others were left unchanged. These parameters included: (1) concentration of SO₂ (ppm); (2) temperature of the gas stream; (3) velocity of the gas mixture; (4) percentage of excess oxygen; and (5) percentage of CH₄ in the gas mixture. A matrix as shown in Appendix A.2 was constructed for different combinations of these parameters to select each experimental condition and samples were collected on the basis of the randomly chosen condition from the matrix.

For any chosen condition, similar steps were performed for every single case except adjusting natural flow rate in the case of sampling in the presence of natural gas flame. The following are the steps, which were followed while collecting solid samples.

First of all, a mesh fabric measuring 2 inches by 2 inches was cut and inserted inside the helium-quenched extraction probe with a thin stick/tube to collect the reactants. The helium-quenched probe was set on the floor with a clamp stand aligned with the exterior part of the tube of the secondary furnace and the junction was sealed with alumina plaster to prevent leakage. When the extraction tube below the extraction probe was connected with the inlet end of the vacuum pump, the whole setup turned into a single unit without any leakage in the interface and the setup was completely fixed for further sampling.

As the reactor temperatures were set earlier, the flow rates for different gases were set in these following steps. Before proceeding further the condition chosen from the matrix was considered and depending on the condition, two separate steps were followed to set the gas flow rates and are discussed in the following sections.

4.2.1 Non-Flame Sampling Procedure

Using different types of rotameters to inject gases in the mixture, the flow rates were controlled for different gases. The injection of air was performed at the beginning and gas having 2% SO₂ and 98% N₂ as balance was injected at the final stage of injection. The reason for this choice was to save SO₂ consumption. During the intermediate stage of injection, N₂ and O₂ were injected either simultaneously or one after the other.

After the setup was prepared according to the foregoing steps, air was injected and the flow rate that was determined from the matrix was set using the rotameter, which was pre-calibrated for airflow rates. The similar technique was followed to set the flow rate of N_2 , O_2 , and SO_2 respectively according to the condition of the matrix.

The injection of sorbent required special care. The mass flow rate was precalibrated and the fluidization was performed using N_2 gas flow from the bottom of the bed. Ca $(OH)_2$ produced by Sigma Chemicals Inc. was selected as the sorbent, and consists of approximately 99% Ca $(OH)_2$. This sorbent was injected through an L-shaped stainless steel tube that was inserted horizontally inside of the combustor tube. Adjusting the flow rate of N_2 and the variable power vibrator controlled the mass flow rate of sorbent. While collecting samples, special attention was given to make sure that the vibrator was providing adequate agitation in the sorbent tube to confirm sufficient fluidization of sorbent.

After completion of all these preparations, the vacuum pump was turned on and kept open for 30 minutes to collect the solid part of the reactants absorbed on to the mesh.

The collected solid samples were then labeled according to the corresponding conditions and stored for further analysis. The whole group of samples collected in this manner were then analyzed using LECO sulfur analyzer, which provided the percentage of sulfur capture by sorbent.

4.2.2 With Flame Sampling Procedure

The effect of natural gas flame on the sulfur capture ability of the sorbent was studied by injecting different percentages of natural gas and excess oxygen into the gas mixture. Once the primary and secondary reactors were prepared as previously mentioned, the air and natural flow rates were adjusted according to the chosen matrix. The mixture was lit using a propane lighter, which was inserted from the bottom reactor tube. The flame was observed for 5-10 minutes to make sure that the flame was steady.

The next step was to set the other gas flow rates e.g. N_2 , SO_2 etc. and the same procedure was followed for the case in which solid sampling might be used without natural flame to adjust these flows. Once, the gas flow rates were adjusted, the sorbent fluidization and the collection of samples were performed in the same way explained earlier.

4.3 Gaseous Sampling

These tests constituted the quantitative part of the entire investigation. These tests were performed to reveal the degree of conversion from SO_2 to SO_3 . As a result, the gas in the secondary furnace was sampled at five locations: the flame, 100, 200, 300, and 400 milliseconds down stream of the flame. Excess oxygen was maintained at 10%, initial SO_2 concentration was set at 2000 ppm, and gas velocity was set at 1.016 m/s.

Moreover, the quantification of SO_3 was studied by analyzing the gaseous samples and the locations of existence were predicted from the previous researcher's results. It was expected that the SO_3 would exist way below the center of the flame and gaseous samples were collected at different locations of the reactor tube with an interval of 10 cm (equivalent to 100 milliseconds) starting from the center of the flame to further below the flame.

As in solid samples, two different conditions were considered where one was without the natural flame and the other is in the presence of natural flame. Samples were collected using the sulfuric acid mist sampling train. The experimental procedure for both cases is described in the following sections.

4.3.1 Non- Flame Sampling Procedure

All these samples were collected through the sulfuric acid mist sampling train. In fact, the gaseous samples were pulled using the vacuum pump through the sampling train and samples were collected for different locations inside the secondary reactor.

To begin with, both the reactors were adjusted for a particular temperature setting and the gas flows were adjusted at the corresponding rotameters from the flow meter board according to the chosen matrix. The adjustable stainless steel tube, which can slide over a vertical tube setup inside the secondary reactor, was set at the 400 milliseconds' position i.e. approximately at 40 cm below the flame point. The other end of this tube was connected to a 0.25 inch copper tube which was wrapped with adjustable thermal tape to avoid condensation of the gas mixture. The open end of the copper tube was connected with the sulfuric acid mist sampling train setup. The sampling required the same EMTIC NSPS test instruction that was followed throughout the entire procedure. The sampling equipment was maintained according to the procedures described in APTD-0576. First of all, the filters were inspected with the naked eye for flaws or pinhole leaks. They were dessicated at about 25° C and at ambient pressure for at least 24 hours. They were weighed at intervals of at least 6 hours to establish a constant weight, i.e., ≤ 0.5 mg change from their previous weight before being were set at the exit of the midget bubbler. The crushed ice around the impingers was placed inside the ice bath. 30 ml of 80% isopropanol in the bubbler and 100 ml of 3% hydrogen peroxide in both the second and third impingers were placed at the beginning of the preparation. A portion of each reagent was retained for use as a blank solution. About 200-g silica gel was placed in the fourth impinger. All the impingers and the tubes together with the copper tube and vacuum pump were previously connected as shown in Fig. 3.2.

Following this setup, the initial reading of the wet test flow meter, rotameter, and dial thermometer were recorded. The vacuum pump was turned *ON* after adjusting all the flows and initial time was recorded for further calculation. The gaseous residue from the samples was sent in to the atmosphere using an exhaust pipe connected at the exit tube of the wet test flow meter. After running the samples through the impingers for at least 30 minutes, the pump was turned *OFF* and the samples were recovered for further analysis.

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

The solutions from the second and third impingers were transferred to a 1-liter graduated cylinder. The impingers, all connecting glassware between the filter and silica gel impinger were rinsed with water to dilute to 1 liter. The solution was transferred to a storage container and the level of liquid on the container was marked and sealed.

The analyses for containers No.1 and 2 were performed separately according to the EMTIC NSPS test method and the calculation for concentration of SO_2 and H_2SO_4 were done later.

4.3.2 With Flame Sampling Procedure

The sampling procedure with natural flame is similar to that of the non-flame sampling procedure except for the injection of natural gas into the reactor. The natural gas level and the percentage of excess oxygen were set at the rotameters, according to the conditions chosen from the matrix. After setting the natural and excess oxygen levels, the lighter was used to create flame and the setup was prepared for further gas sampling. Once the flame was lit the sampling followed the same procedures as previously described for the non-flame case.

4.4 Analysis of Gas Samples

Before analyzing the samples, container No. 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 to reach a pink end point using 0.0100 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 No.2 the solution was mixed thoroughly in the container by holding the contents of the second and 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 0.0100 N barium perchlorate. The titration was repeated with a second aliquot of sample and average titration values were taken into account. Also, the blanks were 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.

CHAPTER 5 EXPERIMENTAL RESULTS

This chapter presents the experimental results obtained from both solid and gaseous sampling for various conditions. Solid samples were collected from both flame and non-flame conditions using a helium-quenched extraction probe after the reaction occurred between the sorbent and gas mixture. The experiments on solid samples using natural gas flame were conducted to verify whether the presence of natural gas flame enhanced the sulfur capture in sorbent. Similarly, the gaseous samples were collected for both flame and non-flame conditions using EPA Method 8 to identify and quantify the level of SO₃ that generated in both flame and non-flame conditions. In Section 5.1, results of the solid samples at different temperatures for flame and non-flame conditions are presented and discussed. The measured level of SO₃ generated in the reaction is reported in Section 5.2.

5.1 Sorbent Capture Studies

The sulfur capture experiments were conducted initially without natural gas reburning to determine baseline sulfur capture levels for differing free stream temperatures and oxygen concentrations. These levels were compared to the results of sulfur capture with 4% natural gas combustion for approximately the same free stream temperature and oxygen concentration in the baseline case. The result was used to indicate the possible increase in sulfur reactivity due to the reactions caused by the natural gas flame. The operating conditions of furnace temperature, excess oxygen, and flame vs. non-flame were examined to determine their effect on sulfur capture. Although a fraction of the combustion products consisted of water, no separate test was performed to investigate its effect on the sulfur capture. The experimental results for sulfur capture as a function of temperature, excess oxygen level, and natural gas flame is presented. In Figures 5.1, 5.2, and 5.3, where the mass percentage of sulfur in the sorbent is plotted versus excess oxygen for both non-flame and flame conditions. These figures represent three different free stream temperatures 1000K, 600K, and 450K. Two different curves at each temperature represent the sulfur capture for flame and non-flame condition. Each data point represents the mass percentage of sulfur in sorbent where the sulfur capture levels were found consistent in trend at all three temperatures but different in magnitude.

The effect of excess oxygen was examined by varying excess oxygen in the combustion chamber for both flame and non-flame cases. The amount of excess oxygen for both the non-flame and post-combustion case was same. As shown in Figures 5.1, 5.2, and 5.3, the sulfur capture remained almost the same for non- flame condition at different excess oxygen levels. But the sulfur capture level increased with an increase in excess oxygen for the flame case up to 10.5% at 450K. It was found that maximum sulfur capture took place when excess oxygen was in the range of 5-15%, except the 650K case where the maximum capture was found at 30% excess O_2 as shown in Fig. 5.2. But as the temperature went down to 450K the sulfur capture increased again at 5-15% excess oxygen level as shown in Fig. 5.3. When no excess oxygen was present for the reburning case, no change in sulfur capture levels was noted as compared to non-flame case. This



Figure 5.1 Sorbent Capture Results at 1000K



Figure 5.2 Sorbent Capture Results at 650K



Figure 5.3 Sorbent Capture Results at 450K
result indicated that excess oxygen was required for increased sulfur capture levels. In theory, because SO₃ is more reactive than SO₂, the level of sulfur capture should be higher when SO₃ comprises a greater fraction of the overall sulfur balance [29]. If SO₃ forms as a result of oxygen radicals forming from the natural gas flame, a higher level of sulfur capture in the sorbent should result assuming all other conditions are same. The observed behavior was found consistent with the assumption of SO₃ formation from SO₂ by interaction with oxygen radicals resulting from the hydrocarbon flame and that SO₃ reacted more rapidly with sorbent than SO₂.

The observed dependence on excess O_2 was also consistent with the literature. However, one result was somewhat different from previous homogeneous sulfur conversion studies. While previous studies indicated that 1% excess O_2 should be sufficient for optimal conversion, nearly 5% was required for maximum capture, as the data indicated no statistically significant increase above the level of 5% excess oxygen.

The effects of furnace temperature on the sulfur capture were also studied and shown in Figs. 5.1, 5.2, and 5.3. For each temperature 1000K, 650K, and 450K, the level of sulfur capture was greater when there was a natural gas flame versus no flame. Fig. 5.1 shows sulfur capture at 1000K, where sulfur capture increased about 37.7% at an excess oxygen level of 5% as compared to the baseline capture. The maximum level of sulfur capture took place at 450K as shown in Fig. 5.3 where about 43.7% higher sulfur capture was seen at 30% excess oxygen with 4% natural gas flame compared to the non-flame case. Although the general speculation is that the rate at which SO₂ is absorbed by sorbent is much less at 450K compared to 1000K. However, it is clear that the total sulfur absorbed at 450K was larger in this experiments than at 1000K. The most plausible

explanation for this phenomenon would be a greater concentration of SO_3 at 450K than at 1000K. Capture of SO_3 by the sorbent is less temperature dependent than SO_2 , and occurs much more rapidly than capture of SO_2 . A higher SO_3 level would then translate to a higher total level of sulfur capture in the sorbent, even at a lower temperature.

For all these results, it may be speculated that the large percentage increase in sulfur capture resulting from the natural gas flame is exaggerated in these experiments compared to what might be observed in practical systems. This may be due to the short residence time of the sorbent in this system. Because SO₃ reacts much more quickly with sorbents than SO₂, a short residence time scenario could produce a larger percentage increase in capture than a longer residence time system. However, despite the exaggeration, the results strongly indicate that more reactive SO₃ forms as a result of a flame and that the increased reactivity leads to increased sulfur capture in sorbents.

5.2 Measured SO₃ Level

While the results shown in Figs. 5.1, 5.2, and 5.3 are of value in showing the increase in capture resulting from interaction with a flame, the degree of conversion from SO_2 to SO_3 is not revealed. As a result, the gas in the secondary furnace was sampled at five locations: the flame, 100, 200, 300, and 400 milliseconds downstream of the flame to measure SO_3 concentrations. As shown in Figs. 5.4, 5.5, and 5.6, the measured concentration of SO_3 is plotted versus the different sampling locations inside the secondary reactor for temperatures of 1000K, 650K, and 450K. The zero time point was referenced to the flame tip. The excess oxygen was maintained at 10%, initial SO_2 concentration was set at 2000 ppm, and gas velocity at peak gas temperature was set at 1.016 m/s for all three temperatures. SO_3 concentration was quantified using a gas



Figure 5.4 Measured SO₃ Concentration at 1000K



Figure 5.5 Measured SO₃ Concentration at 650K



Figure 5.6 Measured SO₃ Concentration at 450K

chromatograph with a flame photometric detector and EPA test Method 8, as discussed earlier with an error of \pm 5 ppm.

The effect of natural gas flame on the formation of SO₃ was examined by collecting samples at both flame and non-flame conditions as shown in Figs. 5.4-5.6. All three temperatures showed that the concentration of formed SO₃ was higher with a natural gas flame than without, which showed that the presence of a natural gas flame significantly promotes the homogeneous conversion of SO₂ to SO₃. Further, for all three temperatures the SO₃ stayed above equilibrium from 0-300 milliseconds except for 450K where the superequilibrium state of the SO₃ occurred for an extended period of time compared to the results discussed in the literature review. The peak concentration of SO₃ occurred at less than 100 milliseconds downstream from the flame, which was consistent with the results of Hedley [22] at higher temperatures.

The percentage of SO₂ to SO₃ conversion, in excess of the base (0% natural gas) case, is 3.5% for a free stream temperature of 1000K, and decreases to 3.3% at 650K and 3.0% at 450K as shown in Figs. 5.4-5.6. The conversion percentage was found by calculating the ratio of differential concentration of SO₃ between the flame and non-flame case to the initial concentration of SO₂. The decrease in conversion percentage at lower temperatures may be due to the decreased oxygen radicals near the flame. Because at lower gas temperatures, the flame temperatures for otherwise similar conditions is lower, reducing the rate of CO production and associated oxidation, reducing the availability of O radicals. Although the conversion percentage at lower temperatures is less, however, the concentration of SO₃ measured at 450K is higher for both flame and non-flame cases as compared to 1000K and 650K. This contradicts with the fact that the higher the

temperature, the higher the rate of formation of O radicals which occurs through the following dissociation:

$$O_2 \longleftrightarrow 2O$$
 (5.2)

In addition, as the Eq. 5.2 is highly temperature dependent, it can be considered that the amount of O radicals at 1000K would be higher than 450K and thus the concentration of SO₃ should be higher as well. However, the consequent effect of higher temperature may increase the rate of backward reaction of Eq. 5.2 and the dissociation of SO₃ to SO₂ through the backward reaction as shown in Eq. 2.10. These combined effects in turn could decrease the concentration of SO₃ at higher temperatures.

It is important to note that there is still considerable conversion of SO_2 to SO_3 even at 450K. At this temperature, virtually no dissociation of O_2 takes place; instead, the only significant source of oxygen radicals is from the combustion of natural gas. Therefore, while free stream temperatures are too low to generate significant oxygen radicals through dissociation at 450K, the presence of an energetic hydrocarbon flame can apparently generate enough radicals to convert a significant percentage of SO_2 to SO_3 .

In addition, the rate at which SO₃ decomposes back to SO₂ apparently decreases at lower temperatures. Comparing the results of Hedley [22] with those presented in Figs. 5.4-5.6, it is apparent that the lower the free stream temperature, the greater the duration of the superequilibrium event. In fact, at 450K, SO₃ levels remained above those found without a flame for up to 400 milliseconds. Extended duration of the superequilibrium state of SO₃ (Eq. 2.19) was likely facilitated by the low concentration of oxygen radicals to attack the SO₃ in the region following the flame.

CHAPTER 6 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary and Conclusions

This study was concerned with the effects of gas stream temperature on the homogeneous conversion of SO_2 to SO_3 via natural gas reburning. Experiments on different operating characteristics were performed in a non-catalytic stainless steel combustor, simulating conditions of a cooled exhaust gas stream from a power plant. Temperature of the gas mixture, excess oxygen, presence of natural gas involved in reburning, and the concentration of SO_2 gas were varied and the effects on sulfur content in sorbents and gas phase SO_3 levels were studied.

Results from experiments on sulfur capture in an injected dry sorbent indicated that sulfur capture levels increase when the natural gas flame is present in a gas mixture containing 2000 ppm SO₂. Results also indicated that the percentages of sulfur capture in sorbent increases as the free stream gas temperatures decrease. The percentage of sulfur capture in sorbent was maximum at 450K. This behavior was not expected because lower temperatures decrease the rate of sulfur capture in sorbents. However, this phenomenon might be explained if the lower temperatures were responsible for a larger amount of SO₃ being transported to the sorbent. Therefore, it was assumed that the increased level of sulfur capture was a result of homogeneous conversion of SO₂ to SO₃, which is more reactive with sorbent materials.

However, the degree of conversion of SO_2 to SO_3 was not truly revealed in the solid sampling experiments. As a result, gaseous sampling experiments were conducted

at the same conditions as the solid sampling experiments in the presence of natural gas flame with excess oxygen. Results showed that the peak percentage of SO₂ to SO₃ conversion is less for 450K compared to 650K or 1000K. This indicates that the lower temperature lowered the flame temperature reducing the rate of formation of O radicals. Further, at 450K, virtually no dissociation of O_2 ($O_2 \leftrightarrow 2O$) occurs. It is clear that the formation of O radicals in this reaction at 450K takes place due to the presence of natural gas flame. In contrast, at 1000K, the higher flame temperature produces more O radicals and hence the theoretical concentration of SO_3 should be more than 450K. However, due to the temperature difference between the flame tip and the gas mixture down stream of the flame, these O radicals have a tendency to associate to form O₂ molecule, which may reduce the rate of conversion of SO_2 to SO_3 and hence reduce the concentration of SO_3 . Because SO₃ formation is dependant on the concentration of O radical as discussed in the literature review in reaction shown by Eq. 2.12. It was clear that as the concentration of O radical increases the concentration of SO_3 . In addition, the rate of dissociation from SO_3 to SO₂ is less at lower temperatures as compared to higher temperatures. Also as the gas temperature decreases, the availability of O radicals decreases more rapidly with distance from the flame. The two effects (O radical reduction and less thermal decomposition) led to an increased duration at which SO3 exists above equilibrium state. In contrast, at 1000K, the rate of dissociation of SO_3 to SO_2 is more, as the reaction is highly temperature dependent, which obviously lowers the concentration of SO₃.

The SO₃ thus formed at lower temperatures helps CaO to capture sulfur at 450K more easily than 1000K. Because SO₃ is more reactive in sorbent than SO₂ and thus the capture level is higher for 450K case compared to the 1000K case as discussed in the

solid sampling results. However, the presence of H_2O has also significant effect on the sulfur capture mechanism. It increases the sulfur capture level as the presence of H_2O increases the gas relative humidity which in turn enhances the sulfur capture efficiency as discussed in solid sampling results. Therefore, for practical purpose we get both SO₃ and H_2O in the gas mixture and their effects help to capture sulfur. However, it is not critical at this juncture to quantify both effects, as both have positive effects on capture.

The data from the gas-phase measurements of SO₃ concentrations showed that the maximum SO₃ that formed at 450K could remain at superequilibrium levels upto 400 milliseconds. This is due to the lower rate of dissociation of SO₃ to SO₂ and reduced concentration of O radicals as discussed earlier. This is important because the greater the duration of superequilibrium SO₃, the longer the time in which the more reactive form of the sulfur can be absorbed by injected sorbent or used to condition fly ash. For example, if the superequilibrium state can be extended, even to only to a level of 5-10 ppm, the implications for reduced fly ash resistivity can be significant.

6.2 Recommendations

There are many possible areas of continued research in the effects of temperature on the homogeneous conversion of SO_2 to SO_3 using natural gas. Studies should be performed to determine the optimum level of natural gas use at which SO_3 conversion is maximum. While capturing sulfur in sorbent, results showed that the largest sulfur capture occurs when adding 4% methane by volume to the mixture. Sulfur capture with other percentage of methane addition (e.g. 1%, 2%, 3% etc.) were not examined.

It may also be possible to conduct experiments to determine the effects of excess oxygen on sulfur capture and SO₃ formation for other percentages of excess oxygen level.

An excess oxygen range of 0-2% with an increment of 0.1% in every step could be performed to investigate the optimum excess oxygen requirement for the formation of maximum SO_3 concentration and its duration of existence as well.

Other future works could be conducted to investigate the effect of SO_2 on sulfur capture. It was found in the literature review that the larger conversion percentage of SO_2 to SO_3 takes place at lower concentration of SO_2 . Therefore, the formation of SO_3 could be examined by varying the concentration of SO_2 in the gas mixture.

Another area of future work might be to investigate if SO₃ stays at superequilibrium state for more than 400 millisecond at 450K and other lower temperatures. This would require the collection of gaseous samples further below from the flame tip than the current sampling locations. This could be performed by developing a secondary reactor with a longer tube.

It may be of interest to determine the effects of flow characteristics in the formation of SO_3 and sulfur capture as well. The drop tube furnace used in this work does not simulate the actual flow characteristics of a practical flue gas cleaning system.

The flow rate and the volume involved in a practical process is much higher than the value considered here. Therefore, a larger diameter tube could be developed to perform the same experiment to investigate its effects on SO_2 to SO_3 conversion.

The ongoing modeling work could be used to compare and support experimental results found in this work. The ongoing project could determine the overall reaction rate constant for SO₃ (k_{SO_3}) destruction as shown in Eq. 2.21. As the rate constant is a function of Arhenius constant (A_r) and activation energy (E_a), so an assumed value of E_a would give the value of A_r when the rate constant is known from Eq. 2.21. The rate

constant could be determined when concentration of H and O radicals would be known using CHEMKIN [27]. Further, the rate constant would be determined from Eq. 2.21 for iteration using the known concentration of SO₂, N₂, and SO₃ found in the experimental data, when N₂ would be considered as a third body.

The last recommendation would be to extend the work on a more realistic gas mixture stream, that is, to include all other elements that are found in flue gases. Also some pilot projects might be arranged to test practical application.

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APPENDIX A EXPERIMENTAL CONDITIONS

A.1 Experimental Conditions

The matrix listed in appendix A.2 describes the setting of different desired experimental conditions. These conditions are the SO_2 concentration, the gas temperature, and the superficial gas velocity through the reactor, the percentage of excess oxygen, and the percentage of methane gas. Table A.1 shows the conditions that have been chosen for actual experimentation.

The first column contains the superficial velocity of the gas mixture in meter per second. The second column shows the volumetric flowrate in cubic centimeter per minute of the gas stream at room temperature, which is calculated, from the flowrate as shown in appendix B. Rest of the columns represent the flow rates of other injected gases e.g., different percentage of CH_4 gas, excess O_2 , excess N_2 , and air and all the flow rates are in milliliter per minute and the calculation has been shown in appendix B.

A2 Matrix for Data Collection

Temp (K) = Radius(m) = Pi = Room T (K)=	450 0.015875 3.141592654 296.3333333					
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 0% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	0	2542.613	16501.55938	12102.83788
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 2.5% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	0	2606.178325	16198.98843	12405.40883
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 5% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	0	2669.74365	15896.41749	12707.97977
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 10% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	0	2796.8743	15291.27559	13313.12167
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 15% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	0	2924.00495	14686.1337	13918.26356
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 30% e.a	Qn2 Excess	Qair
2.032 1.016 0.677	63565.32724 31782.66362 21178.01503	6356.532724 3178.266362 2117.801503	0 0 0	6610.79406 3305.3969 2202.51356	25741.41479 12870.70802 8576.248983	31467.37973 15733.68924 10483.96455
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 0% e.a	Qn2 Excess	Qair
2.032	63565.32724	6356.532724	2542.61309	5085.22618	30460.50482	24205.67661
1.016	31782.66362	3178.266362	1271.306545	2542.61309	15230.25241	12102.83831
0.677	21178.01503	2117.801503	847.1206013	1694.241203	10148.5048	8064.588124
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 2.5% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	1271.306545	2606.178417	14927.68145	12405.40927
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 5% e.a	Qn2 Excess	Cair
2.032	63565.32724	6356.532724	2542.61309	5339.487489	29250.22098	25415.96045
1.016	31782.66362	3178.266362	1271.306545	2669.743744	14625.11049	12707.98022
0.677	21178.01503	2117.801503	847.1206013	1778.953263	9745.275397	8467.81753

Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Q for 10% e.a	Qn2 Excess	Qair
2.032	63565.32724	6356.532724	2542.61309	5593.748798	28039.93715	26626.24428
1.016	31782.66362	3178.266362	1271.306545	2796.874399	14019.96858	13313.12214
0.677	21178.01503	2117.801503	847.1206013	1863.665323	9342.045991	8871.046936
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 15% e.a	Qn2 Excess	Qair
1.016	31782.66362	3178.266362	1271.306545	2924.005053	13414.82666	13918.26405
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Q for 30% e.a	Qn2 Excess	Qair
2032	63565.32724	6356 532724	2542 61309	6610 794033	23198 80183	31467 3796
1.016	31782 66362	3178 266362	1271 306545	3305 307017	11599 40092	15733 6808
0.677	21178 01503	2117 801503	847 1206013	2202 513563	7720 128366	10/83 96/56
Temp(K) =	650					
Radius(m) =	0.015875					
Pi =	3.141592654					
Room T (K)=	296.3333333					
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 0% CH4	Q for 0% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	0	1760.2706	11424.1562	8378.888056
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 0% CH4	Qfor 25% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	0	1804.277365	7333.197215	5862.335228
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 5% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	0	1848.28413	10586.2674	9216.776862
Velocity(m/s)	Qtotal@roomT	Qso2 fmtank	Q for 0% CH4	Q for 10% e.a	Qn2 Excess	Qair
2.032	44006.76502	4400.676502	0	3872.59532	17820.97957	21785.10895
1 016	22003.38251	2200.338251	0	1936 29766	8910,489784	10892 55447
0.677	14661 70271	1466 170271	0	1200 220842	5937 403113	7258 129329
0.011			v	1200.220042	0001.400110	
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 0% CH4	Q for 15% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	0	2024.31119	6090.53629	33515.55222
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0%CH4	Q for 30% e.a	Qn2 Excess	Qair
2.032	44006.76502	4400.676502	0	4576.70356	6090.53629	33515.55222
1.016	22003.38251	2200.338251	0	2288.35178	3045.268145	16757.77611
0.677	14661.70271	1466.170271	0	1524.817086	2029.179628	11166.35281

Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 2% CH4	Q for 30% e.a	On2 Excess	Qair
0.677	14661.70271	1466.170271	293.2340543	762.4085411	7319.121995	5583.176394
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Q for 0% e.a	Qn2 Excess	Qair
1.016 0.677	22003.38251 14661.70271	2200.338251 1466.170271	880.1353003 586.4681086	1760.270601 1172.936217	10125.07649 6746.729121	8797.832462 5862.335213
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Qfor 2.5% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	880.1353003	1848.284131	9706.132092	9216.776865
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Qfor 5% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	880.1353003	1848.284131	9706.132092	9216.776865
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Qfor 10% e.a	Qn2 Excess	Qair
2.032 1.016	44006.76502 22003.38251	4400.676502 2200.338251	1760.270601 880.1353003	3872.595321 1936.297661	16060.70896 8030.35448	21785.10895 10892.55448
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Qfor 15% e.a	Qn2 Excess	Qair
1.016	22003.38251	2200.338251	880.1353003	2024.311191	-12427.51044	50273.32835
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 30% e.a	Qn2 Excess	Qair
2.032 1.016 0.677	44006.76502 22003.38251 14661.70271	4400.676502 2200.338251 1466.170271	1760.270601 880.1353003 586.4681086	4576.703562 2288.351781 1524.817082	4330.265678 2165.132839 1442.711547	33515.55224 16757.77612 11166.35279
Temp (K) = Radius(m) = Pi = Room T (K)=	1000 0.015875 3.141592654 296.3333333					
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 0% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	0	1144.1758	7425.701959	5446.276808
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 2.5% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	0	1172,780195	7289.545039	5582.433728
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 0% CH4	Q for 5% e.a	Qn2 Excess	Qair
1.016	14302,19863	1430.219863	0	1201.38459	7153.388119	5718.590648

Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 10% e.a	Qn2 Excess	Qair
2.032	28604.39726	2860.439726	0	2517.18698	13762.14751	11981.81002
1.016	14302.19863	1430.219863	0	1258.59338	6881.074278	5990.904489
0.677	9530.106764	953.0106764	0	838.649394	4585.124972	3991.971115
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 15% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	0	1315.80217	6608.760438	6263.218329
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 0% CH4	Q for 30% e.a	Qn2 Excess	Qair
2.032	28604.39726	2860.439726	0	2974.85734	11583.6366	14160.32094
1.016	14302.19863	1430.219863	0	1487.42854	5791.818917	7080.15985
0.677	9530.106764	953.0106764	0	991.131102	3859.312042	4717.784046
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 0% CH4	Q for 100% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	0	2288.3516	1979.425151	10892.55362
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 2% CH4	Q for 10% e.a	Qn2 Excess	Qair
0.677	9530.106764	953.0106764	190.6021353	419.3246976	6390.508392	1995.985561
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 2% CH4	Q for 15% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	286.0439726	657.901137	9045.85459	3540.080205
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 2% CH4	Q for 30% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	286.0439726	743.7143288	9045.85459	3540.080205
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Q for 0% e.a	Qn2 Excess	Qair
2.032	28604.39726	2860.439726	1144.17589	2288.351781	13707.22717	10892.55448
1.016	14302.19863	1430.219863	572.0879452	1144.17589	6853.613583	5446.277238
0.677	9530.106764	953.0106764	381.2042706	762.4085411	4566.827161	3629.064656
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Q for 2.5% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	572.0879452	1172.780288	6717.456653	5582,434169
Velocity(m/s)	Qtotal @room T	Qso2 fmtank	Q for 4% CH4	Q for 5% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	572.0879452	1201.384685	6581.299722	5718.5911
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 10% e.a	Qn2 Excess	Qair
2.032	28604.39726	2860.439726	1144.17589	2517.186959	12617.97172	11981.80992
1.016	14302.19863	1430.219863	572.0879452	1258.593479	6308.98586	5990.904962
0.677	9530.106764	953.0106764	381.2042706	838.6493953	4203.920696	3991.971121

Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 15% e.a	Qn2 Excess	Qair
1.016	14302.19863	1430.219863	572.0879452	1315.802274	6036.671998	6263.218824
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 30% e.a	Qn2 Excess	Qair
2.032	28604.39726	2860.439726	1144.17589	2974.857315	10439.46082	14160.32082
1.016	14302.19863	1430.219863	572.0879452	1487.428658	5219.730412	7080.16041
0.677	9530.106764	953.0106764	381.2042706	991.1311035	3478.107765	4717.784053
Velocity(m/s)	Qtotal @room T	Qso2 fm tank	Q for 4% CH4	Q for 100% e.a	Qn2 Excess	Qair
2.032	28604.39726	2860.439726	1144.17589	4576.703562	2814.67269	21785.10895
1.016	14302.19863	1430.219863	572.0879452	2288.351781	1407.336345	10892.55448
0.677	9530.106764	953.0106764	381.2042706	1524.817082	937.7625056	7258.129312

APPENDIX B

CALCULATION FOR PARAMETER SETTING

B.1 Setting of Gas Velocity (\vec{V}_{gas}) :

$$\sum m_{in} = \rho (A \times \vec{V}_{gas})$$
 for N₂, O₂, SO₂, and CH₄

 $\therefore \vec{V}_{gas} \text{ in furnace} = \frac{m_{total}}{\rho_{new} \times Area} = \frac{\sum m_{in}}{\rho_{new} \times Area} \& \text{ Traverse length} = 20.32 \text{ cm} = 8"$

For Residence time, $\Delta t = 100$ millisecond = 0.100 sec

$$\vec{V}_{gas} = 2.032 \text{ m/sec}$$

For Residence time, $\Delta t = 200$ millisecond = 0.200 sec

$$\vec{V}_{gas} = 1.016 \text{ m/sec}$$

For Residence time, $\Delta t = 300$ millisecond = 0.300 sec

$$\vec{V}_{gas} = 0.677 \text{ m/sec}$$

B.2 Setting of Gas Mixture Flow Rate (Q):

Diameter of the Reactor Tube = 1.25 in.

$$\dot{Q}_{\text{heated}} = \mathbf{A} \times \vec{V}_{gas}$$
 i.e., $\Pi \cdot \left(\frac{1.25}{2} \times \frac{2.54}{100}\right) \cdot \left(\frac{1.25}{2} \times \frac{2.54}{100}\right) \cdot \left(2.032\right)$

Now,
$$Q_{\text{room}} = \frac{T_{room}}{T_{furnace}} \times Q_{\text{heated}}$$

B.3 Setting of Individual Flow Rate:

$$Q_{\rm SO2} = Q_{\rm room} \times {\rm p.p.m}$$

APPENDIX C

CALIBRATION OF SECONDARY REACTOR CONTROLLER

The secondary reactor controller has been constructed in the laboratory and two 1:5 step down transformer has been used to provide high current with low voltage. Both the transformers were connected in parallel with another variac, which has a dial indicator. The indicator shows the amount of input voltage and that increases the current and voltage in across the heating elements. The relationship between the voltage, current, and the internal resistance of the heating elements has been shown in table C.1. The table allows the user to set a desired amount of current passing through any elements using the table from the calibrated data.

Table C.1 :

Transformer Reading (%)	Time (min)	Output Current (Amp)	Voltage out (V)	Resistance (Ω)
10	0	26.5	1.42	0.053584906
10	2	23.5	1.46	0.06212766
10	5	23.3	1.47	0.063090129
10	8	23.4	1.47	0.062820513
20	9.5	40.2	3.22	0.080099502
20	11	36.1	3.29	0.091135734
20	13	35.7	3.29	0.092156863
20	15	35.6	3.3	0.092696629
30	17	49.5	4.99	0.100808081
30	19	42.7	5.1	0.119437939
30	20	42.5	5.1	0.12
30	21	42.5	5.1	0.12
35	22	49.1	6.09	0.124032587
35	23	45.9	6.15	0.133986928
35	24	45.9	6.15	0.133986928
35	26	45.8	6.15	0.134279476
35	29	45.7	6.15	0.134573304

Transformer Reading (%)	Time (min)	Output Current (Amp)	Voltage out (V)	Resistance (Ω)	
40	31	51.7	7.09	0.137137331	
40	31.75	48.7	7.13	0.146406571	
40	32	48.5	7.14	0.147216495	
40	32.5	48.5	7.139	0.147195876	
40	33	48.5	7.135	0.147113402	
40	34	48.4	7.14	0.147520661	
40	35	48.3	7.12	0.147412008	
40	39	48.3	7.11	0.147204969	
40	42.5	48.3	7.11	0.147204969	
45	43	53.9	8.02	0.148794063	
45	43.5	51.1	8.09	0.158317025	
45	44	50.8	8.1	0.159448819	
45	45	50.8	8.1	0.159448819	
45	53	50.8	8.08	0.159055118	

 Table C.1: Relationship between voltage, current, and the internal resistance of the heating elements

APPENDIX D

METHOD FOR DETERMINING SULFUR CONTENT IN SORBENT SAMPLES

The sulfur content in the reaction products has been determined using LECO-SC-32 sulfur analyzer. In this method, the sulfur is oxidized to sulfur dioxide during the combustion of the samples. An infrared (IR) cell is used to detect the total sulfur as sulfur dioxide. The sample analysis procedure is as follows:

- 1. Dry the samples at about 105 °C for at least one hour.
- 2. Weigh the sample (about 0.2 g) and enter the weight.
- Add about 1.5 g of Lecocel 763-266 and 0.5 g of Iron powder (V₂O₅) 501-078 and mix thoroughly with the samples.
- Press "ANALYZE" key; when message center displays "LOAD FURNACE", slide the boat into the furnace, and press "ANALYZE" key again to start integration.
- Calibrate the analyzer using a calibration standard and following steps 2 through 4.
- 6. Analyze samples using above procedure.

APPENDIX E GAS FLOW RATE SETTING

E.1 Adjustment of Calibration for Different Gases

The rotameters were adjusted using the calculation given below. The supplied Omega rotameters were calibrated based on air, or nitrogen gas at STP for the same float. However, as they were needed to use for other gases e.g., SO_2 , N_2 , CH_4 etc. the calculation given in appendix E.2 was used to convert the flow rates for different rotameters. The calibrated chart for all the rotameters based on tube numbers for different gases have been shown in appendix E.3.

E.2 Calcualtion for Flow Rate Setting of the Rotameter:



W = F_D
C_D =
$$\frac{8F_D}{\rho \cdot u^2 \cdot \pi \cdot d^2}$$
 where, d = Float Diameter

To eliminate u: $C_{D\times}R_e^2 = \frac{8F_D}{\rho \cdot u^2 \cdot \pi \cdot d^2} \times \frac{\rho \cdot u^2 \cdot d^2}{\mu^2} = \frac{8F_D \cdot \rho}{\pi \cdot \mu^2} = \frac{8W \cdot \rho}{\pi \cdot \mu^2}$

Where: d = Float Diameter,

 $\mu = \text{viscosity}$, and Re = 2.663 (C_D × R_e²)^{0.468}

Also,
$$R_e = \frac{\rho \cdot u \cdot d}{\mu}$$
 $\therefore \frac{\rho \cdot u \cdot d}{\mu} = 2.663 \left(\frac{8W \cdot \rho}{\pi \cdot \mu^2}\right)^{0.468}$
 $u = 4.125 \text{ W}^{0.468} \times \rho^{-0.532} \times \mu^{0.0634}$
 $Q_1 = Au_1$
 $Q_2 = Au_2$
 $\therefore \frac{Q_1}{Q_2} = \frac{u_1}{u_2} = \left(\frac{\rho_1}{\rho_2}\right)^{-0.532} \cdot \left(\frac{\mu_1}{\mu_2}\right)^{0.634}$
But, $\because \left(\frac{\mu_1}{\mu_2}\right)^{0.634} \approx 1$,
We can write, $\frac{Q_1}{Q_2} \approx \left(\frac{\rho_2}{\rho_1}\right)^{1/2}$
i.e., $\frac{Q_1}{Q_2} = \left(\frac{R_2T_2}{P_2} \times \frac{P_1}{R_1T_1}\right)^{1/2}$
 $\therefore \frac{Q_1}{Q_2} = \left(\frac{R_2}{R_1}\right)^{1/2}$ since, $T_2 = T_1$ and $P_2 = P_1$ for the entire experiment.

APPENDIX F

CALCULATION SO3 CONCENTRATION

The calculation of sulfuric acid mist including SO3 concentration were performed on the basis of the following equation.

$$C_{H_2SO} = K_2 \frac{N(Vt - Vtb) \frac{Vsol}{Va}}{Vm(std)}$$

Where:

$$K_2 = 1.081 \times 10^{-4} \text{ lb/meq}$$