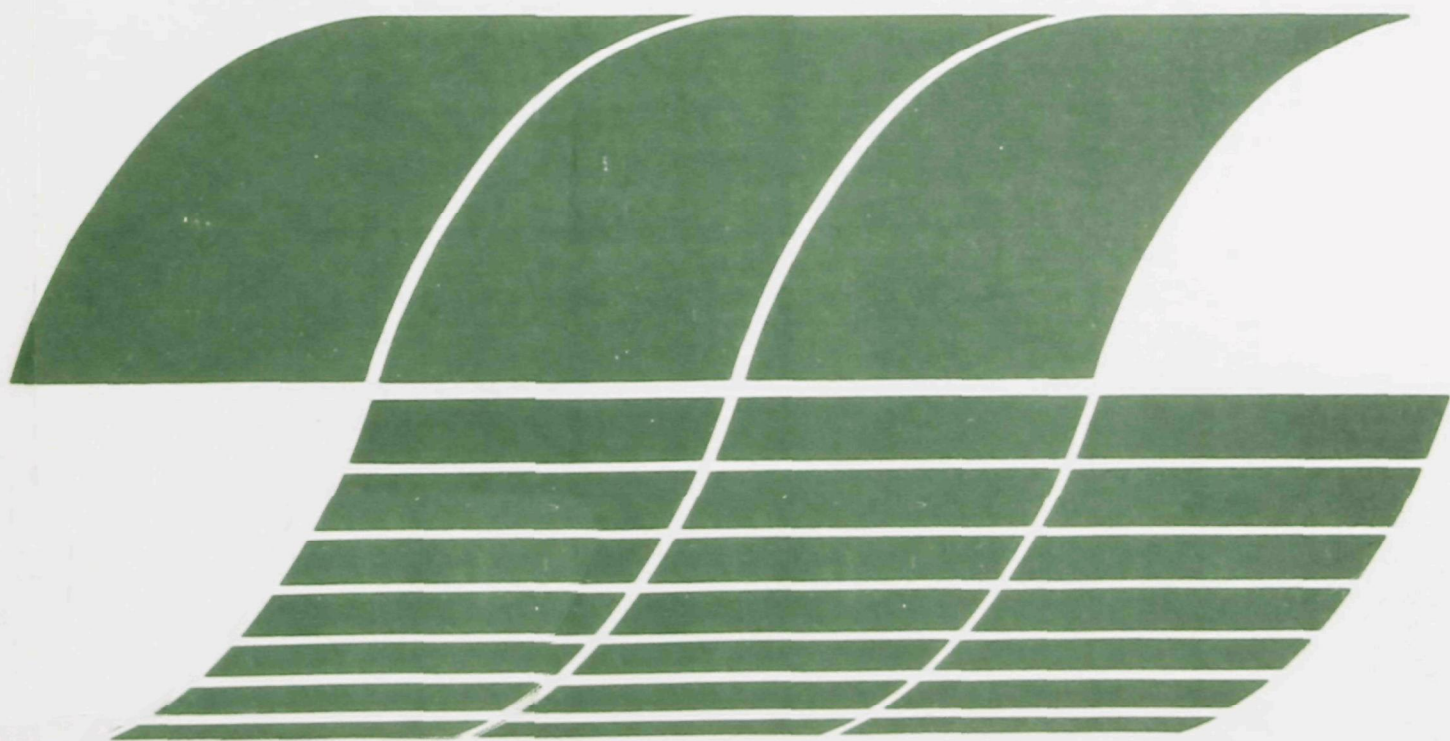




# Enhanced $\text{SO}_3$ Emissions from Staged Combustion

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**January 1979**

# **Enhanced SO<sub>3</sub> Emissions from Staged Combustion**

by

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## ABSTRACT

Staged combustion is a recognized, effective means for lowering  $\text{NO}_x$  emissions. Examination of the staged combustion process suggests however that the high CO levels produced in the first stage may pump a sufficient level of oxygen atoms into the second stage to result in increased (enhanced)  $\text{SO}_3$  formation. Experiments were carried out in a small two-stage combustor which allowed for an examination of  $\text{SO}_3$  formation under similar single- and two-stage conditions. The experiments show that although staging can cause enhanced  $\text{SO}_3$  formation, the enhancement is of short duration, and is dependent on the air/fuel ratio of each stage and the delay interval between the first and second stages. Kinetic analysis yields a value of  $k_1 = 7.4 \times 10^{14} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  for the reaction  $\text{SO}_2 + \text{O} + \text{M} = \text{SO}_3 + \text{M}$  and  $k_2 = 1.5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  for the reaction  $\text{SO}_3 + \text{O} = \text{SO}_2 + \text{O}_2$  ( $T = 1685 \text{ K}$ ). The kinetic analysis also shows that enhancement of  $\text{SO}_3$  formation in staged combustion can occur. However, the experimental results suggest that the enhancement may only be a transient phenomenon dependent on several combustion variables.

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## ACKNOWLEDGMENT

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## SECTION 1

### INTRODUCTION

Staged combustion has proved to be an effective combustion modification technique for lowering  $\text{NO}_x$  emissions. Whether carried out as a direct two-step process, i.e., as a fuel-rich stage followed by a fuel-lean stage, or by a biased firing process where fuel-rich and fuel-lean zones exist in the combustor, the process has been quite effective in reducing thermal  $\text{NO}_x$ , and possibly equally effective in reducing fuel-nitrogen  $\text{NO}_x$ . This report considers the effect of staging on other combustion pollutants, specifically on combustion-generated sulfur trioxide.

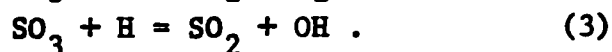
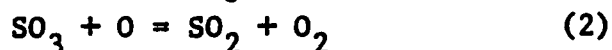
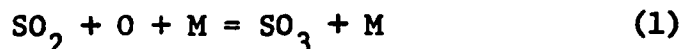
In looking at the two-stage process, one can rationalize reduced  $\text{NO}_x$  emissions at least partially in terms of a reduced concentration of oxygenating species in the fuel-rich first stage combined with a significantly lower temperature in the oxygen-rich second stage. At first glance then one might logically expect that inasmuch as the formation of  $\text{SO}_3$  in combustion occurs by an O-atom process,  $\text{SO}_3$  emissions from staged combustion would also be reduced. Data in the literature however suggest the contrary, namely that the two-stage process might actually cause an increase in the concentration of sulfur trioxide in the flue gas stream. This obviously, of pronounced, would be objectionable from an operational point of view if it contributed to increased corrosion problems in boilers, and from an environmental point of view if it contributed to increased sulfate emissions. The purpose of this study was to explore the effect of staging on  $\text{SO}_3$ , first to determine if staging had an effect, especially if it could cause an increase, i.e., enhancement, of  $\text{SO}_3$  relative to single stage firing, and second to examine the effects of staging on  $\text{SO}_3$  formation kinetics.

### THERMODYNAMICS AND KINETICS

Equilibrium calculations for ratios of  $\text{SO}_3$  to  $\text{SO}_2$  as a function of temperature and excess air are well established. If equilibrium conditions were to prevail under staged firing one could logically expect that, as excess air was reduced, the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  would also be reduced. Strict thermodynamic criteria are not applicable to flames however. Although equilibrium conditions may prevail at high temperatures, as gases cool, reaction rates decrease and equilibria may be frozen. It is also recognized that sulfur-containing species may take up a quasi-equilibrium (partial equilibrium) distribution, quite different from true equilibrium (1). Also,  $\text{SO}_2$  is an effective agent for the recombination of both hydrogen and oxygen atoms (2) and might readily influence the effect of first stage processes on the oxidation steps in the second stage.



Kinetically the formation of SO<sub>3</sub> in an oxygen atom process is best described by the mechanism (3,4)



Rate data for Reaction 1 are quite variable; the data suggest a value of  $k_1 = 1.0 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  (5) at room temperature with little or no activation energy required for the reaction. For Reaction 2, Merryman and Levy obtained

$$k_2 = 2.8 \times 10^{14} \exp(-12,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

in the temperature range 1480 to 1550 K, and

$$k'_2 = 6.5 \times 10^{14} \exp(-10,800/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$$

in the temperature range 825 to 1325 K. The latter  $k'_2$  value takes into consideration Reaction 3, whereas the former does not. Rate values for Reaction 3 have not been obtained experimentally; however, Fenimore and Jones (6) estimate the ratio of  $k_1/k_2$  or  $k_1/k_3$  to be of the order of  $10^4 \text{ cm}^3 \text{ mole}^{-1}$ .

#### ENHANCED SO<sub>3</sub> EMISSIONS

Four sources of data suggest that a potential increase in SO<sub>3</sub> might result from staged combustion. The first comes from a study by Hedley (7) where he showed SO<sub>3</sub> was considerably in excess of thermodynamic equilibrium. The second comes from studies of the authors (8) where some of the SO<sub>2</sub>-SO<sub>3</sub> kinetics were developed. The third and fourth, from studies of Dooley and Whittingham (3) and of Gaydon (9), identify the importance of CO oxidation kinetics on SO<sub>3</sub> kinetics.

At the time of Hedley's studies no special attention was directed to the use of staged combustion for NO<sub>x</sub> control. However, in the course of bringing forth his evidence on the formation of SO<sub>3</sub> at levels considerably above equilibrium he describes a one-dimensional controlled mixing experiment and (although this is not presented as such in his paper) he states: "If combustion took place under stoichiometric or fuel-rich conditions then no trioxide formation took place. When less than stoichiometric air was used, the unburnts in the gases consisted solely of carbon monoxide with SO<sub>2</sub> but no SO<sub>3</sub>. When the remaining excess air was injected into these gases, the maximum amount of SO<sub>3</sub> formed was greater than that formed when this additional air was included with the initial combustion air, the overall excess of air being the same in both cases."

This observation and its potential impact on the effects of staging on  $\text{SO}_3$  formation then became closely tied to the effect of CO oxidation kinetics in the second stage production of  $\text{SO}_3$ . The CO effect is best borne out in Figures 1 and 2 where one notes the highest conversion of  $\text{SO}_2$  to  $\text{SO}_3$  in sulfur-bearing CO flames (3,8). When one couples (1) the observations in Figures 1 and 2 with (2) Gaydon's observations of high concentrations of oxygen atoms in CO flames and with (3) the O-atom mechanism for  $\text{SO}_3$  formation in combustion, Hedley's statements on the enhancement of  $\text{SO}_3$  in staged firing appear quite consistent. Basically then  $\text{SO}_3$  formation is an oxygen atom process, and the question to be addressed is "what is the effect of staging on the oxygen atom concentration?" and its corollary, "what is the effect of staging on  $\text{SO}_3$  formation?"

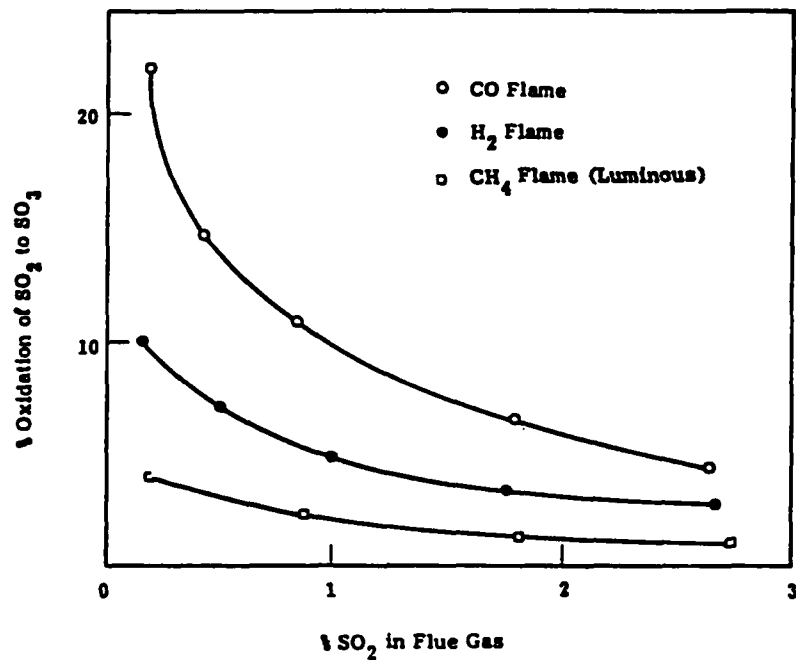


Figure 1. Oxidation of SO<sub>2</sub> in Flames From Different Fuel Gases(3)

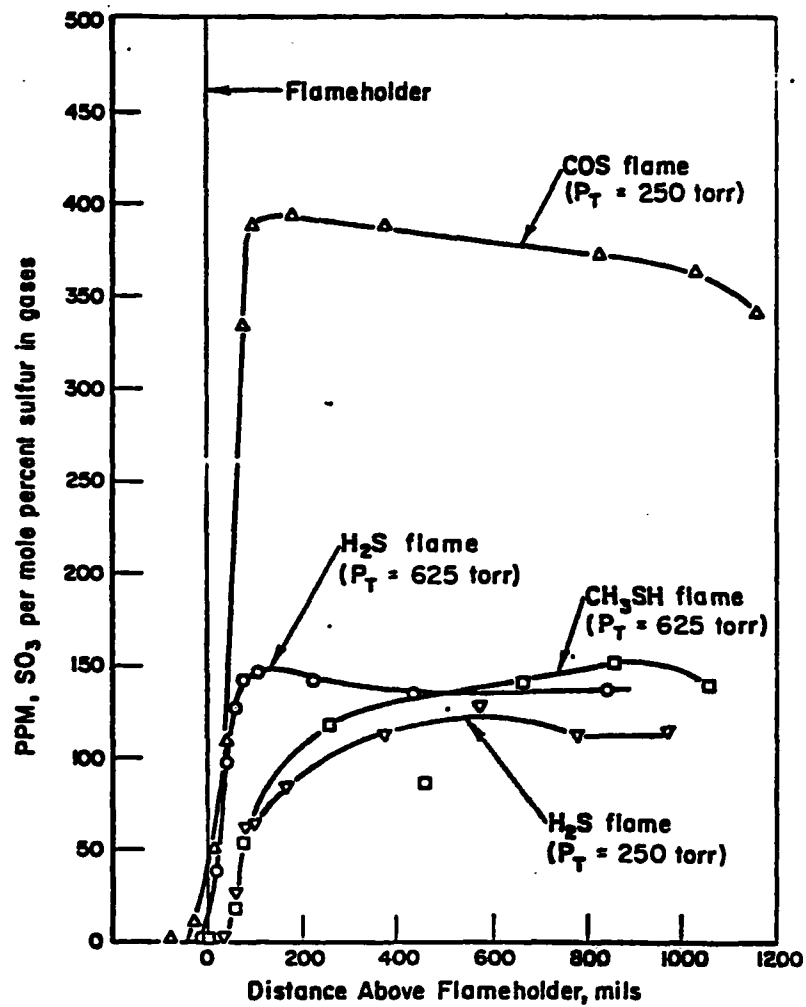


Figure 2. SO<sub>3</sub> Profiles in H<sub>2</sub>S, COS, and CH<sub>3</sub> SH Flames(8)

## SECTION II

### EXPERIMENTAL

A quartz tube burner which allowed one to establish stable methane- $\text{H}_2\text{S}$  flames within desired fuel-air ratios was used. Two inlets were provided above the flame (first stage) for adding air to complete the combustion process (second stage).  $\text{SO}_3$  was then sampled at various positions downstream of the secondary air. Figure 3 is a sketch of the burner tube and the insulated postflame reaction chamber with the various sampling ports.

#### Burner System

The primary burner tube was constructed of quartz (13 mm I.D.) and produced a laminar flow bunsen-type flame ( $L/D > 60$ ). The reaction chamber surrounding the burner tube was 18 mm I.D., also quartz. This chamber contained several temperature and sampling ports spaced from 3-1/2 to 5-1/2 cm apart in the early postflame zone increasing to about 12-1/2 cm apart in the far postflame zone (Figure 3). These spacings provided appropriate time intervals for collecting the  $\text{SO}_3$ . The reaction chamber was externally heated (Chromel "A" wiring) to control second stage temperatures. Total chamber length was approximately 80 cm, providing a maximum gas residence time of about 250 msec.

Secondary air was introduced at positions F and G shown in Figure 3. The jets at F and G were at 6-1/2 cm and 46 cm above the first-stage burner rim, respectively. Temperatures at the secondary air entrance ports were generally above 950 C. Temperature profiles in the postflame gases were obtained with silica-coated Pt-Pt/10 percent Rh thermocouples.

#### Analytical

Gas samples were removed at various locations above the flame via a quartz sampling probe.  $\text{SO}_3$  was removed from the gas as  $\text{H}_2\text{SO}_4$  using a Goksoyr-Ross type (micro) collection apparatus and was determined colorimetrically by the barium chloranilate procedure.  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{SO}_2$  were also measured, mainly for purposes of confirming and comparing postflame combustion conditions and sulfur oxide levels with calculated cold gas compositions.

#### Flame Conditions

Three flame compositions were probed in detail for  $\text{SO}_3$  profiles in this study. The compositions were

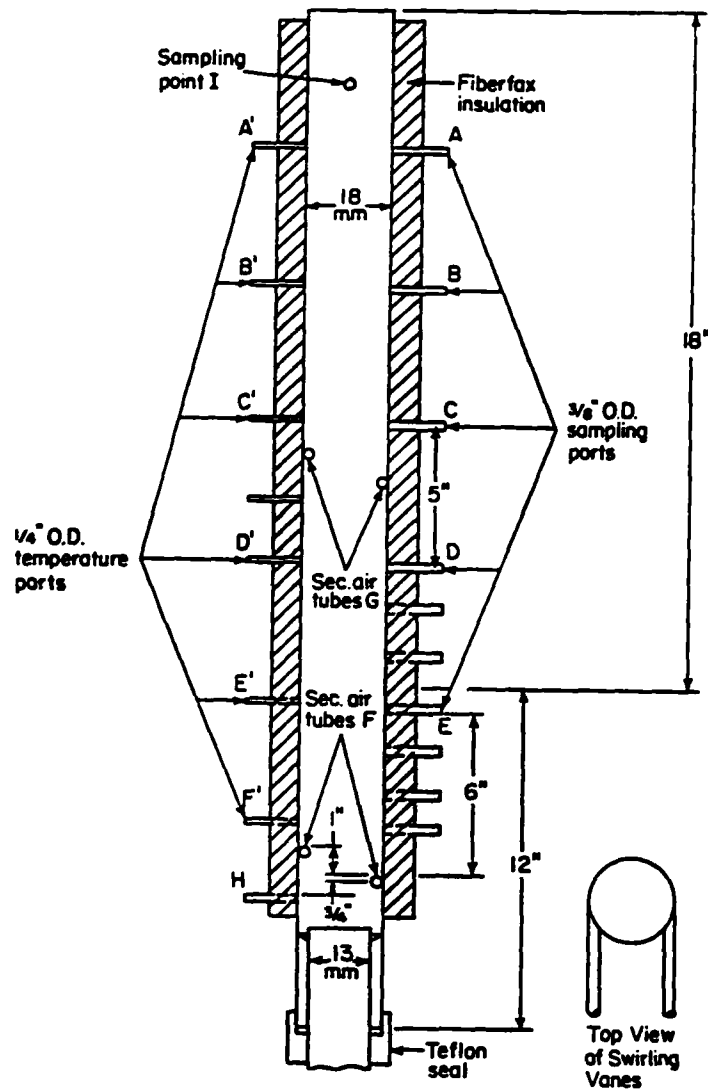


Figure 3. Quartz Tube, Two-Stage Combustor

Mole Fraction (Cold Gases)			
Gas	Single Stage $\phi_s = 1.1$	Two-Stage*	
		1st Stage $\phi_1 = 0.95^*$	1st Stage $\phi_1 = 0.90^*$
CH <sub>4</sub>	0.087	0.099	0.104
O <sub>2</sub>	0.191	0.189	0.188
N <sub>2</sub>	0.720	0.710	0.706
H <sub>2</sub> S	0.0015	0.0017	0.0017

\* In the second stage,  $\phi_2 = 1.1$ ; mole fractions were the same as in the single stage firing.

Equivalence ratios, defined as

$$\phi = [\text{Air/Fuel}]/[\text{Air/Fuel}]_{\text{stoich}},$$

are expressed as  $\phi_s$ ,  $\phi_1$ , and  $\phi_2$ , i.e.,  $\phi_s$ , single stage;  $\phi_1$ , first stage; and  $\phi_2$ , second stage. In all experiments the second stage firing introduced sufficient air that  $\phi_2$  was comparable to  $\phi_s$ .

Total cold gas flow rate for each flame was maintained at 205 cc/sec and the SO<sub>2</sub> level was kept constant at 1500 ppm (after addition of secondary air in the two-stage firings).

## SECTION III

### RESULTS

The results obtained from this study are discussed mainly in relation to the "enhancement" (i.e., the increase) in  $\text{SO}_3$  from two-stage combustion as compared to similar single-stage firings. The maximum  $\text{SO}_3$  level observed in each mode of firing is used as a basis for evaluating the enhancement phenomenon, if any. Since the enhancement effects are observed to be conditional, one should keep in mind the specific experimental parameters leading to the observed increase in  $\text{SO}_3$  over single-stage firings and the transient nature of the observed increase. Also, it is clear that the results obtained from this study are derived from a homogeneous gas-phase system.

Figures 4, 5, and 6 summarize the major findings in this study. It should be noted that residence time for the two-stage flames in these figures refers to the time between the introduction of secondary air and the  $\text{SO}_3$  measurement position. Also, the  $\Delta t$  on the above figures refers to the delay time before adding the secondary air. The mid-flame position was used as zero time for the single-stage firings (and for calculating  $\Delta t$ ).

CO levels for single-stage combustion were about 1100 ppm just above the flame and less than 50 ppm at the exit of the reactor tube. CO levels for first-stage firing ( $\phi_1 = 0.95$ ) were 15,000-17,000 ppm, and these dropped to 135-260 ppm near the second stage exit. Exploratory experiments showed that the addition of secondary air at about 850 C resulted in slow reaction rates and produced considerably less  $\text{SO}_3$  than when the air was added at 950 C. Therefore, the higher temperature was maintained at the secondary air entrance ports for all two-stage combustion experiments carried out in this study. The higher temperature is also more in line with single-stage conditions and produces better burnout.

#### Axial $\text{SO}_3$ Profiles

The data in Figure 4 show the effects of two-stage combustion and the effects of time of addition of secondary air on  $\text{SO}_3$  formation. The two-stage firings, Curves B and C, show a transient enhancement of  $\text{SO}_3$  production, relative to single-stage firing, Curve A. The effect, although it does not appear pronounced here, occurs in the early second stage region and is about 9 percent at the maxima. This is discussed in more detail later. The  $\text{SO}_3$  patterns change as the reactions continue in the downstream gases. No enhancement of  $\text{SO}_3$  is observed beyond about 90 msec residence time. As seen in the figure, the flue gases emerging from the reactor after 150-200 msec contain the same amount of  $\text{SO}_3$  regardless of the firing mode.

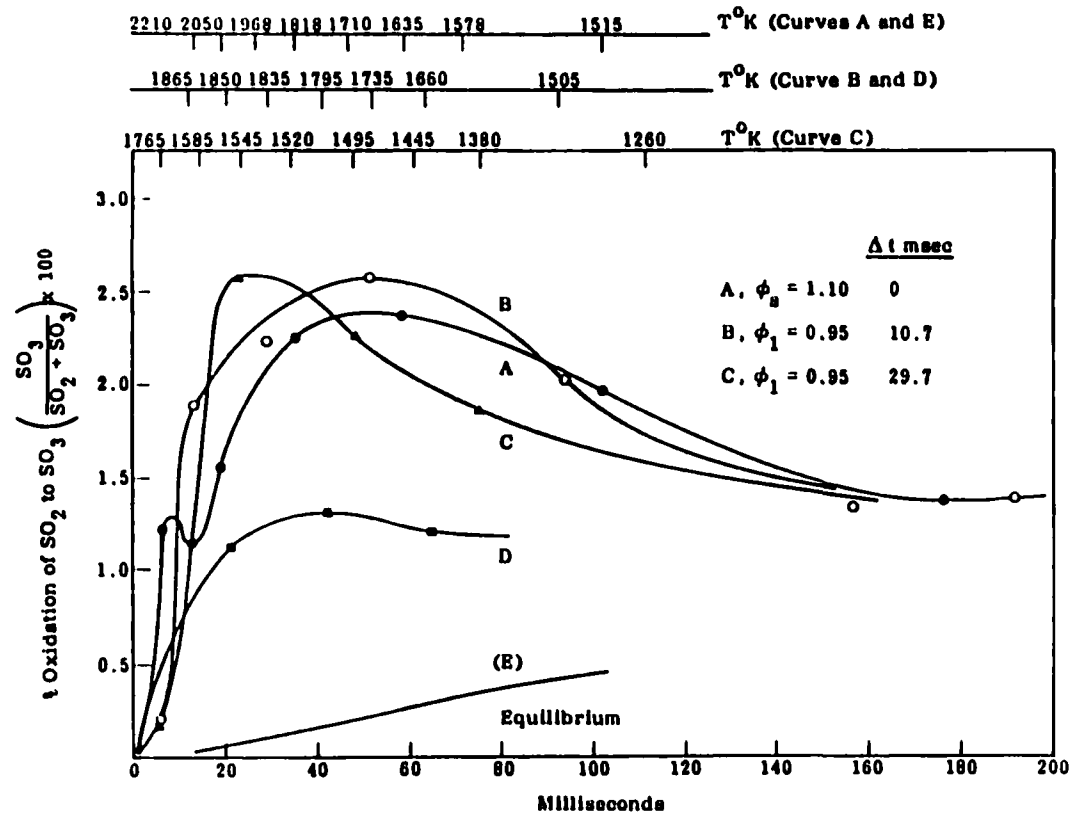


Figure 4. Oxidation of  $\text{SO}_2$  in Single and Staged Combustion,  $\phi_1 = 0.95$ ,  $\phi_s = \phi_2 = 1.1$ .  $\Delta t$  is the Delay Time Before Addition of Secondary Air



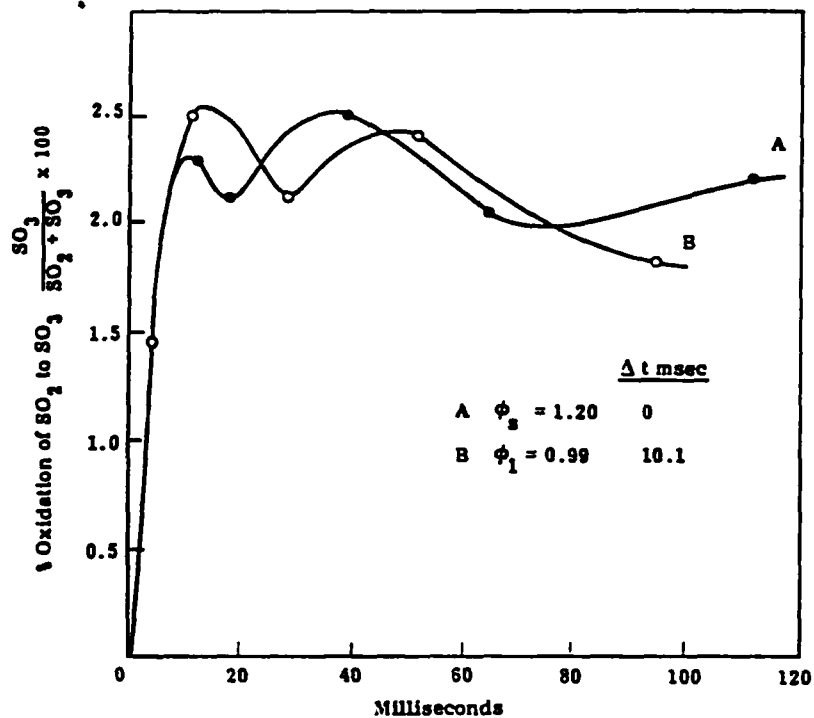


Figure 5. Oxidation of  $\text{SO}_2$  in Single and Staged Combustion,  $\phi_1 = 0.99$

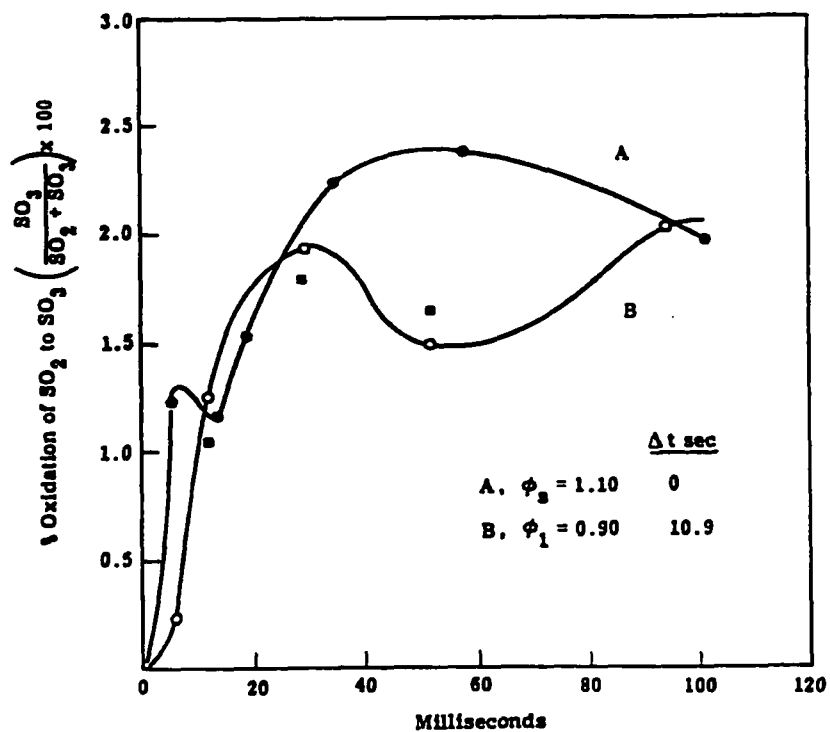


Figure 6. Oxidation of  $\text{SO}_2$  in Single and Staged Combustion,  $\phi_1 = 0.90$

Curves B and C in Figure 4 present  $\text{SO}_3$  data obtained from adding the secondary air at two different positions in the postflame gases. Comparison of these two curves shows that altering the distance between the burner head and the introduction of secondary air produced some changes in the shape of  $\text{SO}_3$  curves, particularly in the 40-150 msec range. Although maximum  $\text{SO}_3$  levels are nearly the same in either of the two-stage modes of firing, the depletion of  $\text{SO}_3$  appears to occur more rapidly when the addition of secondary air is delayed several msec (Curve C). The initial rate of  $\text{SO}_3$  formation is less, however, when the secondary air is delayed. Curve C has an initial rate of  $\text{SO}_3$  formation of about 5500 ppm/sec while the rate from Curve B is about 7000 ppm/sec. The difference is likely due to temperature effects.

Curve D in Figure 4 presents a calculated  $\text{SO}_3$  profile for a single-stage process and is discussed further in the kinetics discussion later in this report.

Figure 5 compares single- and two-stage firing at an overall equivalence ratio of 1.2. Enhancement effects here, where  $\phi_1$  is barely substoichiometric, are negligible.

The effect of operating the first-stage equivalence ratio at  $\phi_1=0.90$  is shown in Figure 6. No enhancement of  $\text{SO}_3$  is observed at this lower equivalence ratio. In fact, less  $\text{SO}_3$  is formed in the postflame gases of this two-stage process than in the single-stage process, at least in the mid-region of the postflame zone probed.

#### Radial Profiles

In the course of developing the data for Figures 4-6, a question was raised as to the effects of mixing patterns and the possible time dependence of these patterns on the early postflame chemistry. Radial probings were therefore carried out for  $\text{SO}_3$ ,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  at various positions in the secondary combustion region. In essence, mixing across the tube was completed within 10 msec after the addition of secondary air.

## SECTION IV

### DISCUSSION

#### General Observations

##### Enhancement--

The data presented here tend to confirm Hedley's observation that staged combustion can enhance  $\text{SO}_3$  formation. However, our results indicate 1) that the effect may not be a severe effect, 2) the enhancement is of short duration, the  $\text{SO}_3$  appearing to approach steady state conditions about as rapidly as in single-stage combustion, and 3) the enhancement effects and its duration are dependent on the air/fuel ratio of each stage and the delay interval in the addition of secondary air.

##### Time Delay Effects--

It is obvious that delaying the addition of secondary air to the point where the temperature is below that required to produce favorable conditions (mainly O-atoms) for  $\text{SO}_2$  oxidation will prevent further  $\text{SO}_3$  formation. It follows that the formation of  $\text{SO}_3$  would therefore decrease with decreasing temperature at the secondary air ports. Barrett, et al., have commented on this effect in their examination of the formation of  $\text{SO}_3$  in a small combustor using single- and two-stage firing modes (10). They concluded from their studies that the addition of secondary air at temperatures below about 950 C would likely produce little or no additional  $\text{SO}_3$ . This is not supported in the present study. Adding the secondary air at about 850 C produced less  $\text{SO}_3$  than when the air was added at higher temperature, and no enhancement of  $\text{SO}_3$  was observed at the lower temperature. Nevertheless, about 10 ppm of  $\text{SO}_3$  was formed with the addition of secondary air at 850 C and the  $\text{SO}_3$  continued to increase slowly to about 15 ppm  $\text{SO}_3$  in the postflame gases. Thus, the "nonreactive temperature limit" may be somewhat lower than that observed by Barrett, et al.

##### Air/Fuel Ratio Effects--

The trends in the  $\text{SO}_3$  data observed at the different equivalence ratios used in this study (Figures 4-6) can be rationalized to some extent by the following considerations.

In considering the ultimate effects of different air/fuel ratios on  $\text{SO}_3$  production in two-stage combustion, one might expect an increase in  $\text{SO}_3$  production in the second stage with decreasing air/fuel ratio in the

first-stage firing. This can be reasoned on the basis of an increase in CO concentration with decreasing air/fuel ratio in the first stage, followed by a greater enhancement of SO<sub>3</sub> from the CO oxidation chemistry in the second stage. (No SO<sub>3</sub> is observed in the first stage at  $\phi_1 < 1.0$ ). However, the temperature also influences the chemistry here, limiting the effect of the air/fuel ratio in the first stage. As the air/fuel ratio reaches well below stoichiometric, the temperature of the first stage decreases. Also, a larger amount of secondary air is needed to restore the second stage to the desired overall equivalence ratio. Further cooling of the gases takes place with a resulting overall reduction in the rate of CO oxidation, a lower O-atom concentration, and hence less SO<sub>3</sub> formation. The SO<sub>3</sub> data of Figures 4 and 6 tend to confirm this line of reasoning.

On the other hand, approaching stoichiometric conditions in the first-stage would increase the flame temperature to near a maximum, resulting in an increase in the CO oxidation, thus leaving less CO to be oxidized in the second stage. This could, within limits, lead to less SO<sub>3</sub> formation relative to a richer first-stage firing. Data from the present flame probings do not show any enhancement in SO<sub>3</sub> formation in a two-stage process at  $\phi_1 = 0.99$  (Figure 5).

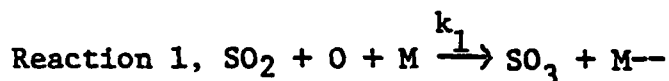
The SO<sub>3</sub> data from this study indicate that optimum enhancement occurs in the region  $0.99 > \phi_1 > 0.90$ .

#### SO<sub>3</sub> Fluctuation--

The data in Figures 4, 5, and 6 show an interesting, as yet unexplainable but repeatable, discontinuity as SO<sub>3</sub> approaches its maximum. The authors have observed similar fluctuation in their microprobing of H<sub>2</sub>S flames, which they attributed to the oxidation of SO (11). Although a positive explanation is lacking at this time, the discontinuity may reflect some mixing and/or wall effects. Assuming that the fluctuation is real, it could mean that the rate of SO<sub>3</sub> formation is being reduced momentarily. This reduction may be brought about by excess CO molecules or H atoms present early in the second stage or by excess O-atoms just above the premixed single-stage flame.

#### Kinetics

The present study provides further confirmation of specific rate constants for the formation and depletion of SO<sub>3</sub>. Also, analysis of the rate data further emphasizes the fact that staged combustion can enhance SO<sub>3</sub> formation.

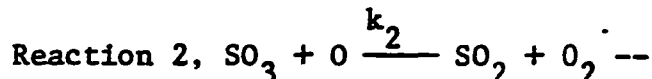


Analysis of the single stage data allow one to calculate a value for  $k_1$ . Assumptions used in the calculation include:

1. There is negligible depletion of  $\text{SO}_3$  via Reaction 2
2. The O-atoms are equilibrated
3. Diffusion velocity corrections can be ignored.

The inclusion of Assumptions 1 and 2 in calculating  $k_1$  are partially validated in using the initial  $\text{SO}_3$  formation rate, and realizing that the  $\text{SO}_3$  formation occurs in the postflame gases, respectively. In the case of item number three, diffusion velocity corrections are small in the early postflame gases relative to the high convectional velocity arising from the reactor design.

Taking these assumptions into account the calculated early rate of formation of  $\text{SO}_3$  from the data of Curve A, Figure 4, is approximately 7000 ppm  $\text{SO}_3/\text{sec}$ . At a constant level of 1500 ppm  $\text{SO}_2$  and at a maximum flame temperature of 2250 K, where the equilibrium O-atom level equals 430 ppm, one obtains a value of  $7.4 \times 10^{14} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  for  $k_1$ , if M is given an intermediate value of 0.5. The results are in fair agreement with the room temperature value of  $1 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  reported by Cullis and Mulcahey (5). If  $k_1$  is temperature dependent, the experimental value is likely to be low.



$k_2$  is readily evaluated under steady state conditions with Reaction 1. Evaluating this rate equation at the maximum in the  $\text{SO}_3$  versus time curve, Curve A, Figure 4, gives

$$k_1 (\text{SO}_2) (\text{O}) (\text{M}) = k_2 (\text{SO}_3) (\text{O})$$

or

$$\frac{k_1}{k_2} = \frac{(\text{SO}_3)}{(\text{SO}_2)(\text{M})}$$

The latter relationship thus becomes independent of the O-atom concentration. Substituting the ratio of  $\frac{\text{SO}_3}{\text{SO}_2}$  from the experimental data at the maximum in the

Curve A and setting  $\text{M} = 0.5$  gives

$$\frac{k_1}{k_2} = \frac{.024}{0.5 (P/RT)} = 6.6 \times 10^3 \text{ cm}^3 \text{ mole}^{-1} \text{ (at 1685 K)}.$$

This value of  $k_1/k_2$  agrees well with Fenimore and Jones<sup>(6)</sup> estimate of  $10^4 \text{ cm}^3 \text{ mole}^{-1}$ .

Setting  $k_1 = 1 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  in the above expression yields

$$k_2 = \frac{1 \times 10^{15}}{6.6 \times 10^3} = 1.5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

Comparing  $k_2$  with Cullis and Mulcahy's preferred value of  $1.2 \times 10^{12}$

$e^{\frac{-9500}{RT}} \text{ cm}^3 \text{ mole}^{-1}$  (5) yields

$$k_2 = 7.0 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \text{ at } T = 1685 \text{ K}.$$

Our  $k_2$  value is in good agreement with the literature value. As discussed below, however, the present work suggests a lower activation than that suggested by Cullis and Mulcahey.

#### Two-Stage Enhancement--

The preceding analyses for  $k_1$  and  $k_2$  were derived from the single stage flames where the calculations were carried out for the oxygen atoms under equilibrium conditions. Similar calculations were not carried out for the present two-stage experiments although the effect of temperature and various equilibria on the O-atom level in single and two-stage processes is discussed. Qualitative statements on the application of the kinetics of enhanced  $\text{SO}_3$  formation are given based on the similarity in Curves A and B in Figure 4.

Taking into consideration that the single-stage flames were at a higher temperature (2250 K) than the two-stage flames (1950 K), one notes first off, that in spite of the temperature difference, the initial  $\text{SO}_3$  rates and the  $\text{SO}_3$  maxima were similar. Inasmuch as the mechanism and kinetics will be the same for  $\text{SO}_3$  formation by either combustion process, the results provide qualitative evidence that the O-atom level in the lower temperature staged process was increased due to the combustion of CO in the second stage. Expressing  $k_1$  in the form (concentrations given in mole fractions)

$$k_1 = \frac{R_{\text{SO}_3}}{\left(\frac{P}{RT}\right)^2 (\text{SO}_2)(\text{O})(\text{M})},$$

calculations show that the O-atom level in the second stage would have to be 5.5 times the equilibrium level ( $\text{O}_2 \rightleftharpoons \text{O} + \text{O}$  at 1950 K) to produce the same rate constant,  $k_1 = 7.4 \times 10^{14} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$ , observed in the single-stage firing. Since this is not likely to occur, other O-atom sources are considered.

Using the reaction sequence involving CO oxidation



and assuming these reactions are equilibrated giving

$$(\text{O}) = K_{\text{eq}} \frac{(\text{CO}) (\text{O}_2)}{(\text{CO}_2)} \quad (I)$$

it is then possible to qualitatively account for a high O-atom level in the second stage combustion process. Taking the available CO, CO<sub>2</sub>, and O<sub>2</sub> flame data and calculating an O-atom concentration via Equation I, a value of 1910 ppm is obtained at 1950 K. This is considerably higher than the calculated 80 ppm O-atom from O<sub>2</sub> ⇌ O + O equilibrium at 1950 K, suggesting Reactions 4 and 5 are a good source of O atoms.

Since the O<sub>2</sub> concentration at the entrance to the second stage section will be close to that of the single stage process and since K<sub>eq</sub> decreases slowly with increasing temperatures, it appears from Equation I that the equilibrated O-atom levels depend primarily on the CO/CO<sub>2</sub> ratio. In the present studies, the (CO/CO<sub>2</sub>)<sub>1st stage</sub> to (CO/CO<sub>2</sub>)<sub>single stage</sub> ratio was measured in the early postflame zones of the single- and two-stage processes and found to be about 20 to 1. This high ratio would raise the O-atom level in the second stage section significantly above that in a single stage process under comparable conditions. The full potential of this ratio affect is not likely to occur, however, due to nonequilibrated conditions arising from the dependence of reaction rates on temperature. Nevertheless, the above reasoning can qualitatively account for the observed behavior of SO<sub>3</sub> in the different combustion systems.

Evaluating the ratio k<sub>1</sub>/k<sub>2</sub> at the maximum of Figure 3, Curve B, where O-atom effects cancel out gives

$$\frac{k_1}{k_2} = \frac{\text{SO}_3}{\text{SO}_2 (\text{M})} = 7.4 \times 10^3 \text{ cm}^3 \text{ mole}^{-1},$$

compared to  $6.6 \times 10^3 \text{ cm}^3 \text{ mole}^{-1}$  from the single-stage firing.

An attempt was made to calculate an SO<sub>3</sub> profile for a single stage process based on equilibrated O-atoms, O<sub>2</sub> ⇌ O + O, and on the lower temperature encountered in two stage process. This calculated profile is shown as Curve D, Figure 4. In carrying out this calculation the rate of Reaction 2 was found to be too slow to produce a maximum in the curve if Cullis and Mulcahey's activation energy of 9500 cal/mole was used. Reducing the activation energy to 7500 cal/mole yielded the profile and maximum of Curve D. This kinetic

analysis implies that, under comparable temperatures, SO<sub>3</sub> enhancement could be as much as 100 percent in staged combustion, although it appears to be only a transient condition.

One final comment is in order relative to the effect of CO concentration on SO<sub>3</sub> formation. The increase in SO<sub>3</sub> formation in the CO and COS flames noted earlier (Figures 1 and 2) were some 200 percent compared with SO<sub>3</sub> produced in methane or hydrogen sulfide systems. In the present study, on the other hand, experimental observations show an increase of some 10 to 25 percent, or based on kinetic analysis some 100 percent at best. The difference is probably a function of CO concentration in the various systems cited. CO levels in the flames of Figures 1 and 2 were some 5 to 10 times greater than the CO levels resulting from staged combustion. Hence if we accept the Semenov (12) mechanisms



for pumping oxygen atoms into Reaction 1, or the equilibrated reaction sequence represented by Equation I, we logically can expect a lesser effect in a staged combustion process than in a direct CO oxidation process.

## CONCLUSIONS

It is concluded that SO<sub>3</sub> enhancement can take place in staged combustion, but it appears to be a transient phenomenon and its effect may be less severe than one would predict from currently accepted kinetic considerations for CO and SO<sub>2</sub> oxidation mechanisms.



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