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EVALUATION OF COMBUSTION PROCESSES FOR PRODUCTION OF FEEDSTOCK CHEMICALS FROM AMMONIUM SULFATE AND AMMONIUM BISULFATE

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ABSTRACT

The combustion of ammonium bisulfate and ammonium sulfate solutions in hydrocarbon/air flames was studied under varied flame conditions. The objective of the study was to optimize the recovery of sulfur value from aqueous waste streams containing these salts. Combustion of ammonium sulfates yielded different sulfur species such as sulfur dioxide (SO₂), hydrogen sulfide (H₂S), and carbonyl sulfide (COS). The types of sulfur species obtained and their yields were dependent on the flame stoichiometry. When combustion was carried out in stoichiometric flames or in flames with excess oxygen, the sulfur present in the salts was quantitatively converted to SO₂. However, these flames also produced nitrogen oxides (NO_x) above the 200ppm level. Combustion of ammonium sulfates in the sub-stoichiometric (oxygen-deficient) flames resulted in the formation of reduced sulfur species, particularly H₂S. This species accounted for nearly 90% of the total sulfur present in the salts. Introduction of a secondary air stream in cooler regions of the combustor led to quantitative oxidation of H₂S and other reduced species such as COS to SO₂. The SO₂ obtained through the secondary oxidation contained nitrogen oxides at comparably lower levels.

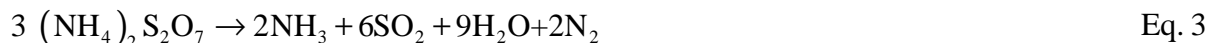
Key words: *combustion, ammonium sulfate, ammonium bisulfate, sulfur species*

INTRODUCTION

Several million tons of ammonium sulfate ((NH₄)₂SO₄) and several thousand tons of ammonium bisulfate (NH₄HSO₄) are produced annually during varied chemical manufacturing processes such as the production of lactam, methionine, and methionine hydroxy analog (HMB), an animal feed additive. A substantial portion of ammonium sulfate (AS) is used as fertilizer; however, due to concerns for sulfate buildup this use is coming under increased scrutiny, especially in developed countries. As a result, a significant portion of the ammonium sulfate production is disposed of as waste. The high acidity of the ammonium bisulfate (ABS) limits its industrial application, and essentially all of this salt is disposed as waste in deep wells at considerable cost to industry. Furthermore, this practice may lead to a potential long-term environmental problem. The problem can be reduced or eliminated by converting the ammonium bisulfate/sulfate into feedstock chemicals such as sulfuric acid and methanethiol. Both of these chemicals are used in methionine and HMB synthesis. A few processes for the conversion of ammonium sulfate and ammonium bisulfate have been reported in the literature.

A thermal process for the degradation of ammonium sulfate to ammonia and sulfur dioxide was first reported in the mid 1940s (Dixon, 1944). Similar processes have been reported by other researchers (Halstead, 1970; Kiyoura and Urano, 1970). The chemical transformations that occur

during these processes are depicted in Equations 1–3.



Thermal degradation leads to the decomposition of AS to ABS with the release of ammonia at temperatures ranging between 200–400°C. Subsequent thermal treatment of ABS results in the formation of ammonium pyrosulfate ((NH₄)₂S₂O₇). The decomposition of ammonium pyrosulfate leads to the release of ammonia (NH₃), sulfur dioxide (SO₂), molecular nitrogen (N₂), and water (H₂O). The conversion efficiencies of 15% and 45% have been reported for NH₃ and SO₂, respectively (Montgomery, 1962). Enhanced recovery of NH₃ from (NH₄)₂SO₄ has been obtained in the presence of alkali sulfates (Bonfield and Bohn, 1966; Hüter, 1963). In such treatments, aqueous AS was first dehydrated at 300°C and then converted to ABS with the release of NH₃. The ABS was transferred to a second chamber, mixed with alkali sulfates, and heated to 500°C. The treatment resulted in the formation of alkali pyrosulfate and the release of additional NH₃. The mixed salt melt was then transferred to a third chamber maintained at 900°C, where the alkali pyrosulfate was decomposed to alkali oxide and SO₂.

A combustion-based thermal process for generation of NH₃ and SO₂ from dry NH₄HSO₄ has been described (Hirabayashi et al., 1980). These researchers introduced finely divided ABS into a combustion chamber and reacted it with combustion gases from an oxygen-deficient flame. The reaction was carried out at temperatures ranging between 700–900°C. Approximately 82% of the total ABS nitrogen was converted to NH₃, while 90% of the total ABS sulfur was converted to SO₂. A small portion (5%) of the ABS sulfur was converted to SO₃.

A process for the treatment of AS-containing wastewater was reported in a 1992 patent (Becker, 1992). In this process, AS-containing wastewater was introduced directly into a natural gas/air flame through a centrally located nozzle. It was reported that essentially all of the AS sulfur was converted to SO₂, whereas all of the AS nitrogen was converted to N₂. Combustion of AS solution in an oxygen-deficient flame was also reported. In this case, AS-containing wastewater was introduced into a sub-stoichiometric flame. The term “sub-stoichiometric” or “oxygen-deficient” flame in present context refers to fuel-rich flames. The temperature of the flame was reported to be around 1000°C. H₂S was found to be the principle sulfur species. Combustion of ABS in stoichiometric and sub-stoichiometric flames has been modeled (Gill and Associates, 1996). This model suggested that a waste stream containing high concentrations (50 to 70%) of ABS (w/w basis) can be treated efficiently and economically through combustion.

The objective of the present study was to experimentally examine the feasibility of a combustion-based process for the recovery of ABS sulfur as sulfur dioxide or hydrogen sulfide. Three sets of experiments were conducted to achieve this objective. The initial experiments involved the conversion of ABS to SO_2 in flames with stoichiometric and excess air. The conversion of ABS to H_2S in oxygen-deficient flames and the generation of a NO_x -free, SO_2 gas stream through a two-stage combustion process involved production of H_2S in an oxygen-deficient flame followed by a low-temperature oxidation of H_2S to SO_2 .

EXPERIMENTAL

All combustion experiments were carried out in a combustor designed and fabricated in our laboratory.

Combustion setup

The combustor consisted of a commercial burner and a refractory-lined combustion tube.

Burner: A commercially available nozzle-mix burner (Eclipse ThermJet 150) was used in all experiments. The burner can deliver up to 158 kJ of thermal energy per hour with a gaseous hydrocarbon fuel. The burner assembly was mounted on a 6mm-thick stainless steel plate placed at the bottom of the combustion chamber.

Fuel: Liquefied propane gas (LPG) was used as the fuel in all but a limited number of experiments, in which methane was used as the fuel. LPG and methane were obtained from a local commercial supplier. The fuel flow rate was regulated with a calibrated mass-flow controller.

Air: House compressed air was used as the oxidant. Its flow was regulated with an in-line pressure regulator in tandem with a calibrated, standard orifice plate and a water manometer. The pressure difference across the plate was measured and used for determining the air-volume flow rate into the burner.

Combustion chamber: The combustion chamber consisted of a stainless steel pipe (210 cm x 35 cm i.d. with a 1.5mm wall thickness) lined with 7.5 cm-thick layer of Kaolite refractory. The inner dimensions of the combustion chamber were 210 cm x 20 cm. One side of the chamber wall was lined with a set of 13, 12 mm ports; and another set of 13, 25 mm diameter ports was placed on other side, perpendicular to the 12mm ports. The spacing between ports of both sizes was 15.2cm. The smaller (12mm) ports were used for placement of thermocouples, while the larger (25mm) ports were used for sampling the flue gas. The flue gas samples were drawn through quartz tubes (6mm o.d. X 2 mm i.d.) placed along the central axis of the combustion chamber. The larger ports were also used for viewing the combustor operation. A cross-sectional view of the combustor is shown in Figure 1.

Combustion of aqueous ABS and AS

The combustion of aqueous ABS was evaluated under varied flame stoichiometry. For a fuel

flow rate fixed at 7.9 L min^{-1} , a stable flame was obtained with air flow between 130 to 220 L min^{-1} , corresponding to flame stoichiometry of 50% to 110% , respectively. For the two-stage operation, a ceramic restrictor with a 10cm opening was placed 60cm above the flame, Figure 2.

The salt solutions were pumped, at flow rates between 1 to 10mL min^{-1} , into the combustion chamber with a microprocessor-controlled, dual-piston pump (Model LC-6A, Shimadzu). Pumps with higher flow capacity, either a dual-piston pump (Model Series 3, Perkin-Elmer Instruments) or a diaphragm pump (Model LMI, Milton Roy), were used for introducing larger volumes of salt solutions. The maximum ABS solution feed rate used in the present study was 50mL min^{-1} , which corresponds to the introduction of 32g ABS min^{-1} . The salt solutions were delivered into the flame through a centrally located quartz tube and formed fine mist with the aid of a small (5 L min^{-1}) auxiliary air stream.

Analysis of product gases

Determination of combustion gases: The combustion gases (H_2 , O_2 , N_2 , CO , CH_4 and CO_2) were sampled through quartz sampling tubes located at different positions along the length of the chamber. The gas sample was drawn through a six-port sampling valve with a 0.5mL loop. The sampled gas from the valve was introduced into a gas chromatograph (Model 8700, Perkin Elmer Instruments) equipped with a thermal conductivity detector (TCD). The flue gas constituents were separated with a column consisting of a stainless steel tube ($2.4\text{m} \times 2\text{mm i.d.}$) packed with Carbosieve S (100-120 mesh, Supelco Inc.) and monitored with the TCD. Helium was used as the carrier gas, and its flow rate through the column was maintained at 25mL min^{-1} . The separation of gases was facilitated by temperature programming the GC column oven linearly from 40°C to 250°C at $20^\circ\text{C min}^{-1}$. The TCD was operated with the filament current set at 150mA . The detector signal was processed with a PC-based chromatography data system (Turbochrom, Perkin Elmer Instruments). Individual gas components were identified and quantitated with commercial reference gas standard mixtures (Scotty II Mix 218, 234 and 237, Alltech Associates).

Determination of sulfur gases: Sulfur gases formed during the combustion were determined with a GC (Model Autosystem, Perkin Elmer Instruments) equipped with a flame photometric detector (FPD). A rotary valve with a fixed volume (0.5mL) loop was used for introducing the gas sample into the GC. The sulfur gases present in the gas sample were separated with a column consisting of a stainless steel tube ($2.4\text{m} \times 2\text{mm i.d.}$) packed with mixed Porapak stationary phase (80% Porapak Q and 20% Porapak N, Alltech Associates). The separated gases were monitored with the FPD. Helium was used as the carrier gas, and its flow through the column was maintained at 30mL min^{-1} . The GC oven temperature was kept constant at 100°C during the separations. The detector response was calibrated with sulfur gas standards obtained from Matheson Gas Products.

Determination of particulates: The weight of particulate matter formed during combustion was determined gravimetrically by sampling a known volume of flue gas from a selected port

through a pre-weighed glass microfiber filter (Whatman GF/A, 3.7cm diameter). The filter was dried to a constant weight in a desiccator. The weight difference of the filter before and after sampling was used for estimating particulate matter in the flue gas.

RESULTS AND DISCUSSION

Combustion of ABS and AS in oxidative flames

The oxidative combustion experiments were carried out with a fixed-fuel flow rate (7.9 L min⁻¹) while varying the airflow rate from 188 - 207 L min⁻¹. These flow rates correspond to flame stoichiometries of 100 - 110%. The temperatures and flue gas composition were monitored with and without the aqueous salt solutions at selected positions along the height of the combustor chamber. The flue gas compositions obtained in the oxidative regimes are summarized in Table I. The flue gas composition in the absence of ABS conformed to the expected values and yielded a good fit with estimated equilibrium values. The introduction of ABS solutions into the combustor led to the appearance of SO₂; however, it had little effect on the flame temperature or the concentrations of the other dry flue gas constituents. A slight increase in the NO_x concentration was observed in experiments carried out in flames with 104 % and 110% stoichiometric airflows. The small increase indicated that only a small fraction (<0.1 %) of ABS nitrogen was converted to NO_x, while most of the ABS nitrogen was converted to molecular nitrogen.

The change in SO₂ concentration observed with a fixed ABS input and varied air input is shown in Figure 3. The solid line in the figure depicts the calculated SO₂ concentration, assuming 100% conversion of ABS sulfur to SO₂. A good agreement between the measured and the calculated values was observed. The highest SO₂ concentration was obtained when the airflow rate was 4% in excess of the amount required for complete combustion of fuel (propane). This observation can be attributed to the additional oxygen necessary for the degradation of ABS, Equation 4.



Thus, ~0.014 M O₂ (0.34 L min⁻¹) will be required for the combustion of 0.055M of ABS (50% solution @ 10mL min⁻¹), an increase of 0.87% above the amount required for complete combustion of the fuel. Further increase in oxygen (air) flow does not facilitate ABS combustion but does lead to dilution of SO₂ concentration in the flue gas. The oxygen requirement will increase with an increase in the ABS feed rate.

The effect of a change in the ABS input on the operation and the efficiency of ABS to SO₂ conversion was monitored. ABS input was varied either by increasing the flow rate of a fixed concentration (50% w/w) solution or by changing the ABS concentration of solutions and introducing these at a fixed flow rate (10mL min⁻¹). In the first case, the ABS input was varied from 6.4 - 32g min⁻¹ (10 to 50mL min⁻¹), while in the second case the ABS amount was varied from 3.2 - 9.6g min⁻¹ (solution concentration of 25% to 75%).

An increase in ABS solution flow rate into the combustor resulted in an increase in SO₂ concentration. However, the increase was linear only at flow rates <30 mL min⁻¹. Further increase in the solution flow rate did not result in a corresponding increase in the SO₂ concentration (Figure 4). This deviation did not result from insufficient energy for evaporation and decomposition. Combustion of 0.323M of propane yielded sufficient energy to vaporize water and decompose ABS. In fact, combustion of ABS is slightly exothermic. The energy output of the combustor and energy requirements for vaporization and decomposition of the ABS solutions revealed that even at the high ABS solution feed rate of 50 mL min⁻¹, there are nearly 200 kJ min⁻¹ of excess energy. An examination of the salt-solution feed tube revealed that inefficient conversion at high flow results from the nonuniformity of solution introduction by the diaphragm pump used in these experiments. This pump delivered salt solutions in spurts instead of a continuous and uniform stream. An improved solution introduction and atomization system would be required to fully exploit the combustion process at higher flow rates. Despite some difficulties in pumping a highly viscous solution of 75% ABS, a quantitative conversion of ABS to SO₂ was obtained in all experiments during which the ABS input was varied by changing the solution concentration (25-75%) while maintaining a constant flow rate (10 mL min⁻¹).

The optimization of the ABS feed-to-fuel ratio was carried out through experiments in which the ABS input was held constant (6.4 g min⁻¹) while the fuel (propane) input was varied from 3.9 to 8.4 L min⁻¹. These experiments were carried out at a constant flame stoichiometry by adjusting the airflow rate with the fuel flow rate. SO₂ concentrations in the flue gas were measured and plotted as a function of fuel input (Figure 5). At the lowest fuel input, the ABS feed-to-fuel (propane) ratio was 1164 g ABS/m³ propane. This value is more than an order of magnitude higher than the feed-(AS) to-fuel (methane) ratio reported in the BASF patent (Becker, 1992).

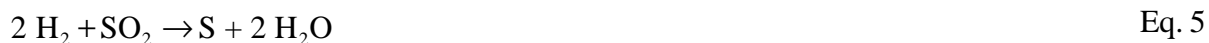
The AS to SO₂ conversion efficiency was also monitored at different AS and propane inputs. Due to lower solubility of AS in water, the maximum concentration of AS in solution used in these experiments was 25% (w/w). These experiments were conducted with the AS solution flow rate of 10 mL min⁻¹. The results obtained at two different propane inputs are summarized in Table II. The measured SO₂ concentration in the two cases was found to be 0.6 and 0.5 percent. These values were nearly the same as the calculated values. This indicates a complete conversion of AS sulfur to SO₂ during the combustion. It should be pointed out that complete conversion was achieved at a salt-to-fuel ratio of nearly 770 g AS/m³ propane. This value also compares favorably to the 150 g AS/m³ methane ratio reported in the BASF patent (Becker, 1992).

Combustion of ABS and AS in oxygen-deficient flames

Combustion of ABS and AS in oxygen-deficient flames was evaluated with intent to produce hydrogen sulfide. Hydrocarbon flames sustained under sub-stoichiometric conditions are known to yield flue gas species such as CO, H₂, methane, and other lower alkanes, as well as elemental

carbon. These species can facilitate the reduction of SO_2 to H_2S and COS (Kohl, 1983). The formation of COS and H_2S from SO_2 involves reduction of sulfur from a S^{+4} to a S^0 or a S^{-2} state. The extent of reduction is dependent on the availability of reducing species. The SO_2 can also be reduced to S^0 by elemental carbon leading to the formation of CO . A secondary reaction involving CO and elemental sulfur leads to the formation of COS . Yet, another reaction between elemental carbon and sulfur can also yield carbon disulfide (CS_2). These reactions are depicted in Equations 5 - 9.

Primary reactions:



Secondary reactions:



Analyses of the flue gas obtained during ABS and AS combustion in oxygen-deficient flames showed that the reactions depicted above occur to a degree under different flame conditions (Table III). SO_2 was the most abundant species in stoichiometric flames and flames with oxygen deficiency less than 20%. When the oxygen deficiency was 30% or higher, the principal sulfur species were COS and H_2S . The change in the measured concentrations of sulfur species resulting from a change in the oxygen input is shown graphically in Figure 6. The H_2S concentration increased initially with a decrease in oxygen input but remained constant thereafter. The concentration of COS was relatively unaffected by the change in air input under the oxygen-deficient regime used in the present study. The flue gas samples for these measurements were collected through sampling tubes located 150cm above the flame.

Concentrations of sulfur species obtained at various points along the length of the combustor are shown in Figure 7. Measurements showed that the SO_2 concentration was highest in the immediate vicinity of the flame and decreased downstream; conversely, the concentrations of H_2S and COS increased in regions away from the flame. It is likely that the SO_2 reduction is catalyzed by Al_2O_3 of the refractory lining inside the combustor chamber. The reduction was very effective, and near quantitative conversion was achieved near the exit end of the combustor tube.

The apparent discrepancies between the measured and calculated concentrations of sulfur

gases in the oxygen-deficient environment are in part due to the differences in the FPD response for sulfur gas standard mixtures in helium and the sulfur gases in flue gas. The flue gas from oxygen-deficient flames contains significant amounts of residual methane and other hydrocarbons (Table III). The residual hydrocarbons in gas streams are known to quench S_2 emission in the FPD and decrease its signal for the sulfur species (Kapila et al., 1989).

Two-stage combustion

Another set of experiments was carried out to explore the feasibility of obtaining NO_x -free SO_2 . These experiments involved the use of a two-stage combustion process. The first-stage combustion was carried out in a manner analogous to the oxygen-deficient combustion described in the previous section. The combustor was operated with the propane and airflow rates set at $7.9L\ min^{-1}$ and $122L\ min^{-1}$, respectively. This airflow rate was 64.8% of the flow rate needed for complete combustion of propane (stoichiometric combustion). Combustion of ABS in such flame led to the formation of H_2S , COS , H_2O , and molecular nitrogen. To obtain a NO_x -free SO_2 stream, H_2S and COS were oxidized to SO_2 . The process was facilitated by separating the “reductive” and the “oxidative” zones with a ceramic baffle. A secondary air stream ($10\text{-}50L\ min^{-1}$) was introduced through a 25mm port located just above the baffle. The flue temperature in this zone was approximately $750^\circ C$ and led to fast and efficient oxidation of H_2S and COS to SO_2 . The overall reactions occurring during the process are depicted in Equations 10 and 11.



Concentrations of product gases were monitored in gas samples collected through the sampling port located 150cm above the flame. The measurement showed that the relative concentrations of H_2S , COS , and SO_2 were dependent on the secondary airflow. In the absence of the secondary air, H_2S was the most prevalent sulfur species. Introduction of a secondary airflow at rates greater than $25L\ min^{-1}$ led to the formation of SO_2 , Figure 8. The highest SO_2 concentration was obtained when the secondary airflow rate was approximately $34L\ min^{-1}$. Due to lower overall gas flow, the SO_2 concentration obtained in these experiments was in fact higher than the SO_2 concentration obtained during the single-stage oxidative combustion. A further increase in the secondary airflow resulted in the dilution of SO_2 in the flue gas, leading to a decrease in the SO_2 concentration.

NO_x concentrations were found to be less than 30ppm under all two-stage combustion regimes, and considerably below the 100 - 270ppm NO_x concentrations observed during the single-stage oxidative combustion. The results demonstrate that the two-stage combustion approach can lead to generation of NO_x -free SO_2 from AS- and ABS-containing waste streams.

It should be pointed out that despite a two-year operation in a harsh acidic environment, no damage to the structural integrity of the combustor chamber and burner assembly has been observed. This points to the basic soundness of the concept. However, a detailed economic assessment of a commercial-scale process has not been carried out.

CONCLUSIONS

Combustion of ammonium sulfates in hydrocarbon/air flames was evaluated as a means to recover sulfur as SO_2 or H_2S . Results showed that an oxygen-rich combustion could be used for efficient conversion of ABS or AS to SO_2 . An oxygen-deficient flame can be used for converting ABS or AS to H_2S . The latter can be easily oxidized to a NO_x -free SO_2 gas stream in a two-stage process. The process holds considerable potential for treatment of highly acidic ABS produced as a by-product in methionine and methionine hydroxy analog synthesis.

ACKNOWLEDGEMENT

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REFERENCES

- Becker, R., Method for the Thermal Workup of Residues that Contain Ammonium Sulfate, Particularly of Wastewater that Contains Ammonium Sulfate, 1992, German Patent 4,101,497.
- Bonfield, J.H., and F.L. Bohn, Production of Sulfur Dioxide, 1966, U.S. Patent 3,282,646.
- Dixon, P., Formation of Sulphamic Acid During the Thermal Decomposition of Ammonium Sulphate, 1944, Nature, 154, p. 706.
- Gill and Associates, July 1996, Modeling of Ammonium Sulfate – Bisulfate Combustion, FruCon, Inc., St. Louis, MO. Communication through FruCon, Inc.
- Halstead, W.D., Thermal Decomposition of Ammonium Sulphate, 1970, J. Appl. Chem, 20, pp. 129-132.
- Hirabayashi, T., Process for the Recovery of Ammonia and Sulfur Dioxide from a Contaminated Ammonium Salt of Sulphuric Acid, 1980, U.S. Patent 4,208,390.
- Hüter, L., and U. Reichau, Verfahren zur Gewinnung von Ammoniak und Schwefelsäure aus Ammoniumsulfat und/oder –hydrogensulfat bzw, aus deren Lösungen in Wasser oder Schwefelsäure, 1963, German Patent 1,151,492.
- Kapila, S., D.O. Duebelbeis, S.E. Manahan, and T.E. Clevenger, 1989, “Flame Photometric Detectors” in Environmental Analysis Using Chromatography Interfaced with Atomic Spectroscopy, R.M. Harrison, and S. Rapsomanikis, Editors, John Wiley and Sons, New York, pp. 76-95.
- Kiyoura, R., and K. Urano, Mechanism, Kinetics, and Equilibrium of Thermal Decomposition of Ammonium Sulfate, 1970, Ind. Eng. Chem. Process Des. Develop, 9, pp. 489-494.

Kohl, A., Sulfur Dioxide Reduction Process, 1983, U.S. Patent 4,396,594.

Montgomery, J.C., Apparatus for Decomposing Solid Ammonium Sulfate, 1962, U.S. Patent 3,047,369.

Table I. Flue gas composition with and without ABS in oxidative flames.

Flame Stoichiometry	100	104	110
Air Flow (LPM)*	188	196	207
Propane Flow (LPM)*	7.9	7.9	7.9
Flue gas composition resulting from combustion of propane without ABS; concentrations are in volume percents (dry gas basis - DGB).			
H₂	0	0	0
O₂	1.2	2.0	4.6
N₂	84.7	84.8	84.0
CO	0.7	0.1	0
CH₄	0	0	0
CO₂	13.4	12.8	11.3
NO_x (ppm)	106	130	130
Flame Temp (°C)	1318	979	1100
Flue gas composition resulting from combustion of propane with 50% (w/w) ABS introduced at 10mL min ⁻¹ . Concentrations are in volume percents (DGB).			
H₂	0	0	0
O₂	1.9	2.9	4.8
N₂	83.2	83.6	83.5
CO	1.7	0.7	0
CH₄	0	0	0
CO₂	13.3	12.8	11.6
NO_x (ppm)	106	240	160
H₂S (ppm)	<10	<10	<10
COS (ppm)	<10	<10	<10
SO₂	0.73	0.88	0.73
Flame Temp (°C)	1318	1295	1290

*Flow rates measured at ambient temperature and pressure.

Table II. Compositions of flue gas from combustion of ammonium sulfate (AS).

AS sol. Concentration (percent w/w)	25	25
% Stoichiometry	104	110
Air input (LPM)	127	167
Propane (LPM)	5.2	6.3
	% Volume (DGB)	
H ₂	0	0
O ₂	7.9	9.0
N ₂	84.3	84.9
CO	0	0
CH ₄	0	0
CO ₂	8.0	6.1
SO ₂ Experimental	0.6	0.5
SO ₂ Theoretical	0.6	0.47
Flame Temperature (°C)	1220	1250

Table III. Flue gas composition with and without ABS in reductive flames.

Flame Stoichiometry	50	60	70
Air Flow (LPM)*	103	108	140
Propane Flow (LPM)*	8.4	7.7	8.4
Flue gas composition resulting from combustion of propane without ABS. Concentrations are in volume percents (dry gas basis - DGB).			
H₂	5.3	3.4	2.5
O₂	0.9	0.7	0.9
N₂	77.3	79.4	80.6
CO	7.1	6.5	3.9
CH₄	1.3	1.1	0.3
CO₂	7.9	8.7	11.7
NO_x (ppm)	<30	<30	40
Flame Temp (°C)	950	979	1100
Flue gas composition resulting from combustion of propane with 50% (w/w) ABS introduced at 10mL min ⁻¹ . Concentrations are in volume percents (DGB).			
H₂	5.3	3.4	2.5
O₂	0.9	0.7	0.9
N₂	77.3	79.4	80.6
CO	7.1	6.5	3.9
CH₄	1.3	1.1	0.3
CO₂	7.9	8.7	11.7
NO_x (ppm)	<30	<30	45
H₂S	0.79	0.8	0.77
COS	0.18	0.17	0.17
SO₂	<0.05	<0.05	<0.05
Flame Temp (°C)	1238	1243	1260

*Flow rates measured at ambient temperature and pressure.

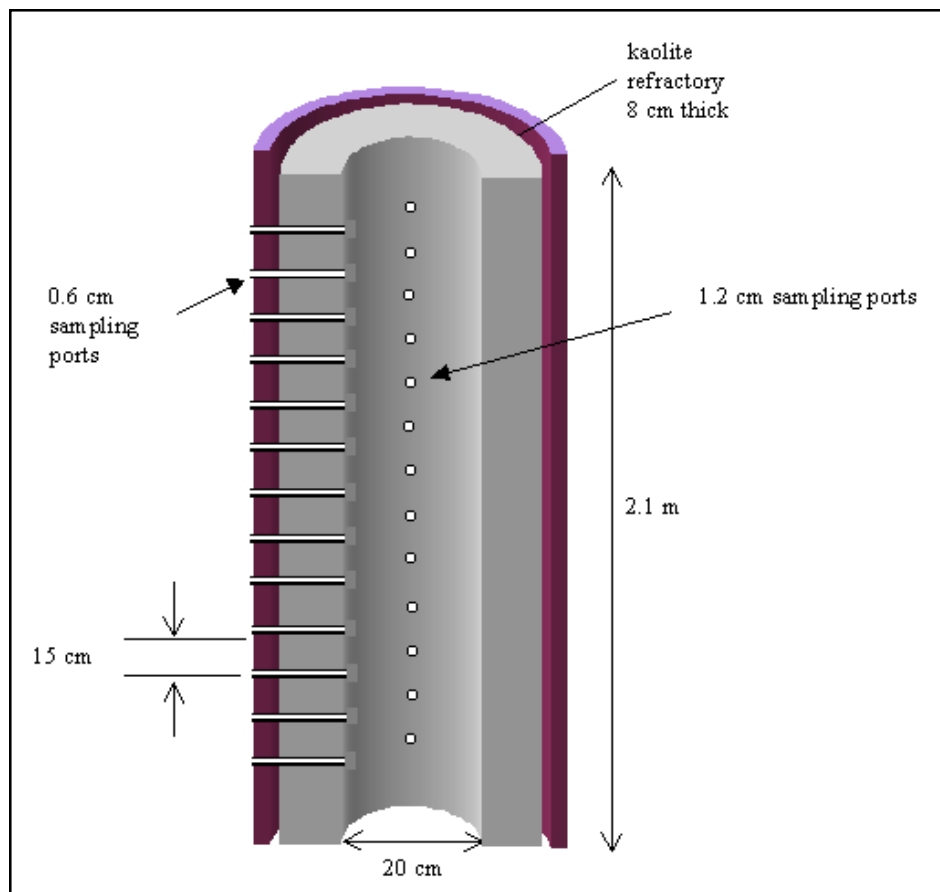


Figure 1. A cross-sectional view of the combustion chamber.

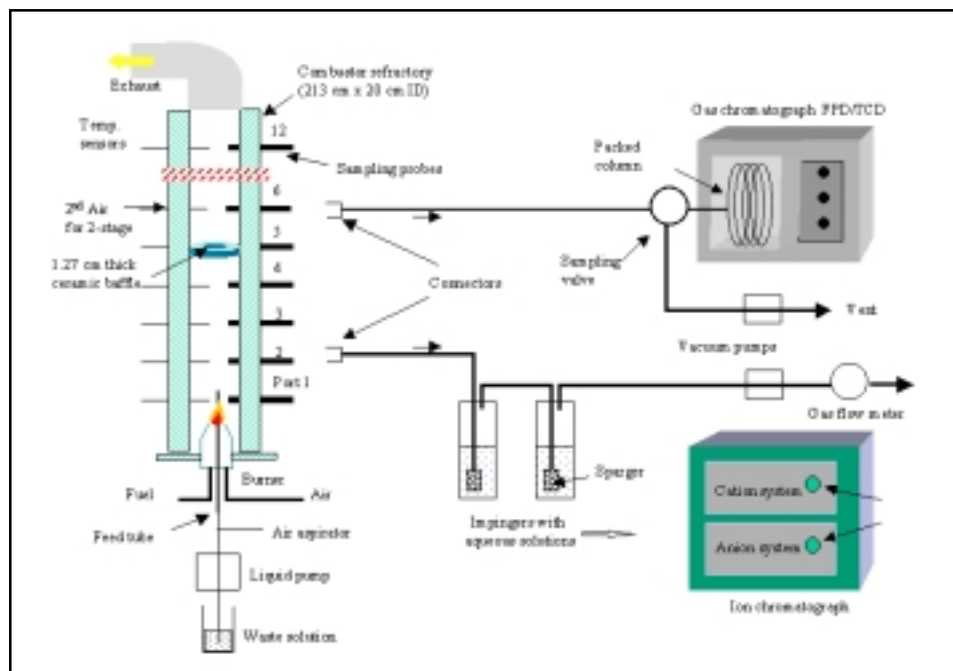


Figure 2. A schematic of the combustor and instrumentation used for the analysis of flue gas components.

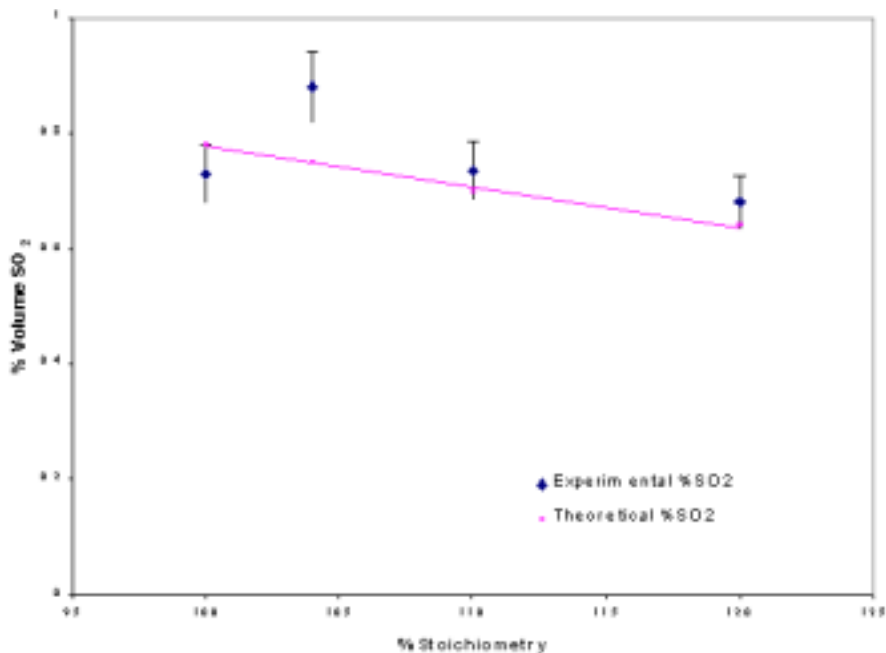


Figure 3. SO₂ concentration obtained through ABS combustion in oxidative flames at different flame stoichiometries.

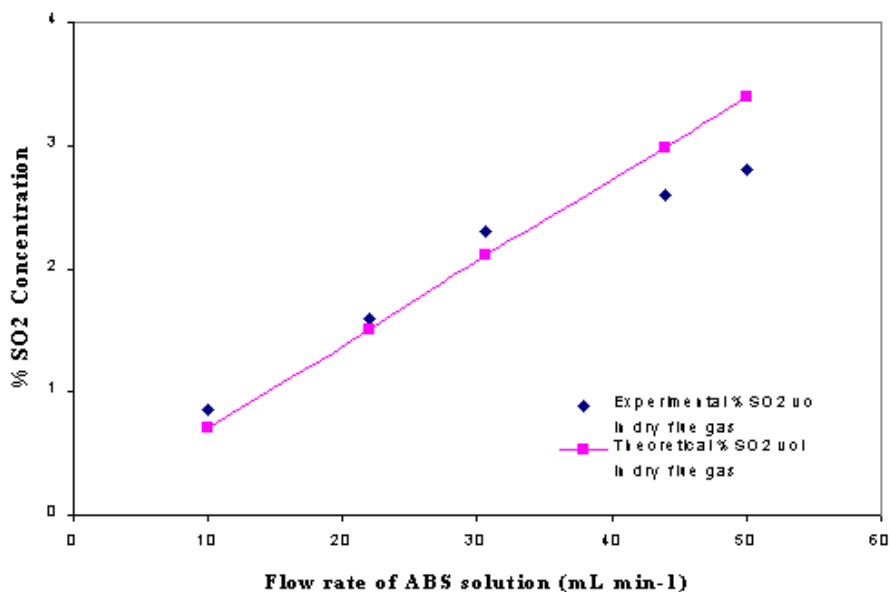


Figure 4. Calculated and measured SO₂ concentrations obtained from ABS combustion at varied ABS feed rates.

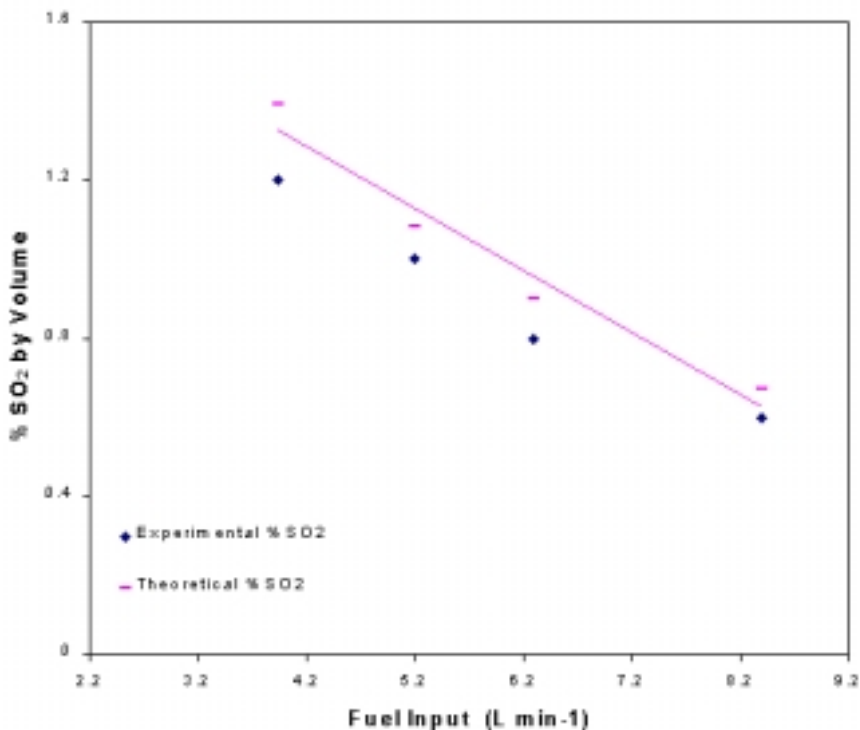


Figure 5. Measured and calculated SO₂ concentrations obtained from ABS combustion at varied fuel flow rates.

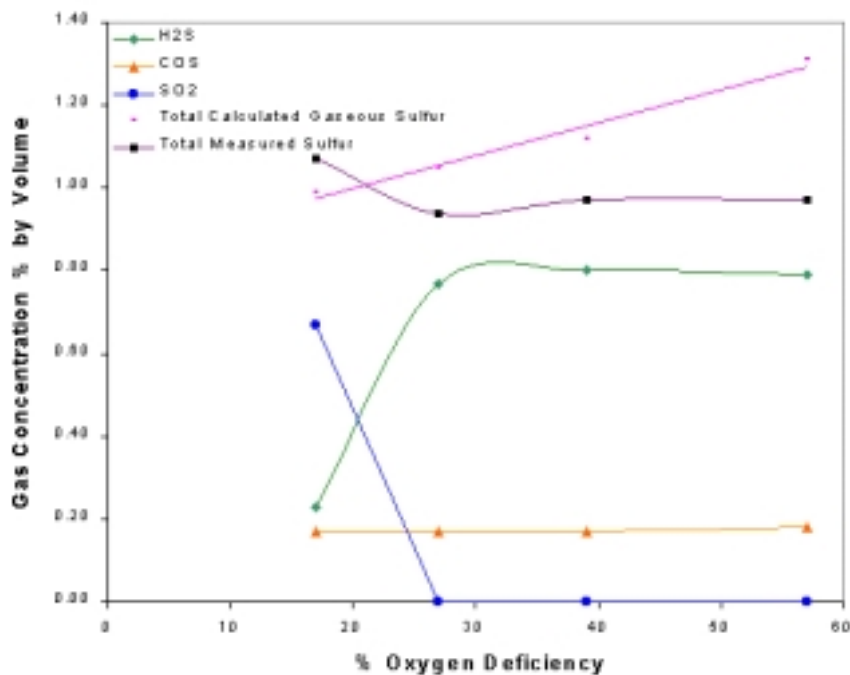


Figure 6. Measured SO₂/H₂S/COS concentrations obtained from ABS combustion in reductive flames at varied oxygen deficiencies.

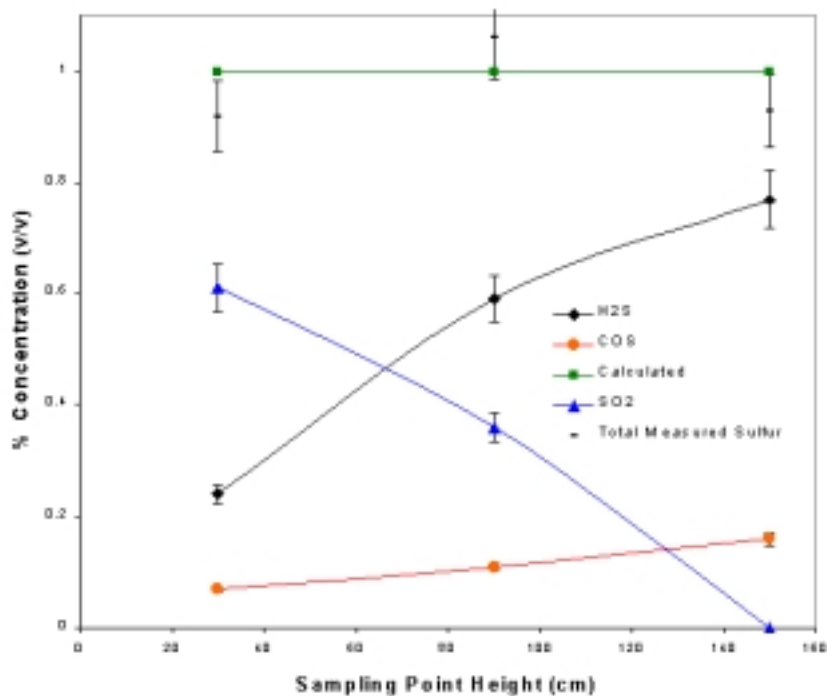


Figure 7. Measured and calculated SO₂/H₂S/COS concentrations obtained from ABS combustion in reductive flames at different sampling points along the length of the combustor.

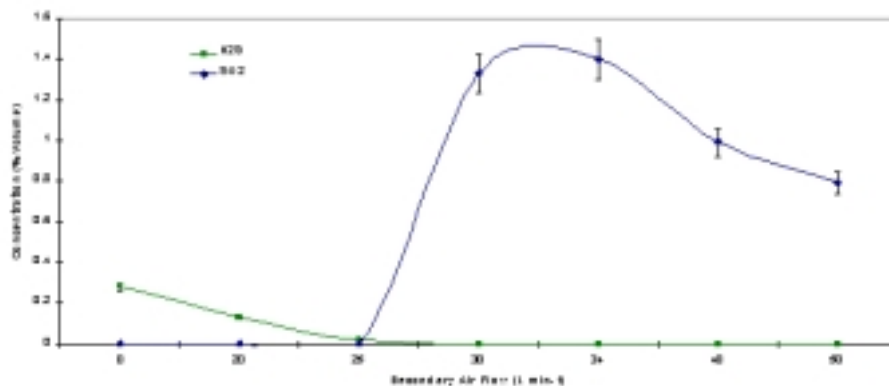


Figure 8. Measured SO₂ and H₂S concentrations obtained through ABS combustion in the two-stage combustor at varied secondary airflow.