Destruction of SO_3 in Claus thermal reactors

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Abstract

Haldor Topsoe and Comprimo has developed the TopClaus® process, which combines the well-known Claus and WSA technologies into a process, ensuring very low emissions, high energy efficiency and elemental sulfur as the only product. The WSA process treat the Claus tail gas by converting all sulfur species into concentrated sulfuric acid, which is then recycled to the thermal stage of the Claus plant.

This paper examines the faith of the sulfuric acid in the Claus thermal stage, both theoretically and experimentally, and answers the questions on how fast sulfuric acid is destroyed in the thermal stage and if the sulfuric acid somehow interacts with the commonly present Claus feed gas "contaminants" such as CH_4, BTX and NH_3.

The theoretical work was carried out in collaboration with the CHEC group at the Technical University of Denmark and the experimental work was carried out in collaboration with Alberta Sulfur Research Ltd., Canada.

Introduction

The Claus technology has for decades been the most widely used sulfur abatement technology in refineries and natural gas treatment plants. Concentrated H_2S containing waste stream from amine scrubbing units are combusted in an O_2 deficient atmosphere in the Claus thermal reactor to produce a process gas containing both SO_2 and H_2S, typically with a H_2S/SO_2 ratio of around 2. Elemental sulfur is formed, both in the thermal reactor and in downstream catalytic Claus reactors, and is condensed and withdrawn as a liquid product, which can be solidified, before shipped to an off taker, typically a sulfuric acid plant.

The overall Claus reaction can be described as

$$2\ H_2S + SO_2 \leftrightarrow 3/x\ S_x + 2\ H_2O$$

The extent of the Claus reaction is typically limited to 95-98% sulfur formation due to chemical equilibrium constraints. To comply with ever stricter environmental legislation, so-called TGTU's (Tail Gas Treatment Units) are installed downstream the Claus plant. Numerous TGTU technologies have been developed, ranging from simple, but less efficient, addons to very efficient and more complicated plants. The cost of the most efficient TGTU's are comparable with the cost of the Claus plant.

Haldor Topsoe's TGTU is the so-called WSA process, in which all sulfur compounds (H_2S, SO_2, S_X, COS and CS_2) are thermally and/or catalytically oxidized to SO_2, further catalytically oxidized to SO_3 and condensed as concentrated sulfuric acid, H_2SO_4. H_2 and CO are completely oxidized to H_2O and CO_2. The advantages of the WSA process is low cost, high thermal efficiency, high conversion, simple layout and robust operation.

A sketch of a typical layout of the WSA process is shown in Figure 1; the exact layout is optimized for the actual feed streams and requirements for emissions and sulfuric acid concentration. The combustor can be purely thermal or a combination of thermal and catalytic, the steam system pressure is typically in the range 40-60 barg, 1-3 catalytic beds are used for the oxidation of SO_2 to SO_3 and liquid sulfuric acid is recovered in a proprietary vertical glass tube condenser, using atmospheric air as cooling media. The hot cooling air can be used as preheated air to the combustor, thus increasing heat efficiency of the plant.

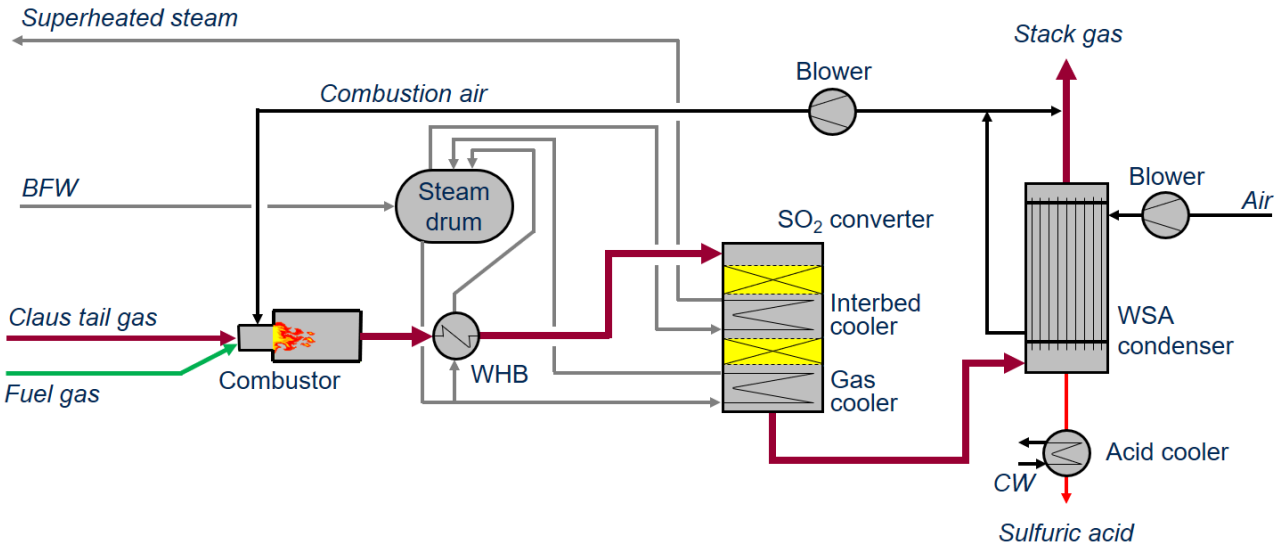

Figure 1 Example of layout of a WSA plant for conversion of sulfur compounds in e.g. Claus tail gases into concentrated sulfuric acid. In the combustor all sulfur compounds, CO and H_2 are converted into SO_2, H_2O and CO_2, SO_2 is oxidized to SO_3 in the SO_2 converter and sulfuric acid vapor in condensed in the WSA condenser. WHB = Waste Heat Boiler, CW = Cooling water, BFW = Boiler Feed Water.

Concentrated sulfuric acid is a very commonly traded chemical. However, there may be certain cases where a local use or easy access market is not available.

To mitigate that situation and make use of the existing infrastructure for molten sulfur, Haldor Topsoe, together with Comprimo, has developed the so-called TopClaus® process in which the sulfuric acid product from the WSA plant is returned to the thermal reactor of the Claus plant to become decomposed and reformed as elemental sulfur. A sketch of the TopClaus® principle is shown in Figure 2.

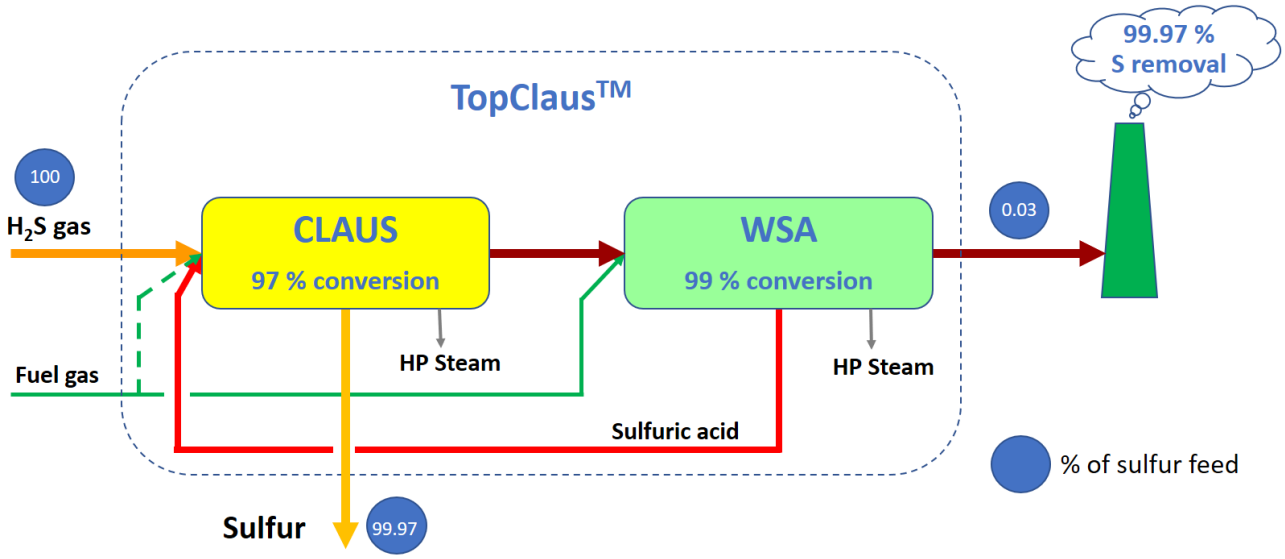

Figure 2. Schematic of TopClaus® layout, combining the well-proven Claus and WSA technologies for very high overall sulfur recovery.

In the high temperature reducing atmosphere in the Claus thermal reactor, the sulfuric acid from the WSA plant will decompose according to:

$$H_2SO_4 + \text{heat} \rightarrow SO_3 + H_2O \rightarrow SO_2 + 0.5\ O_2 + H_2O$$

The oxygen formed by the decomposition will react with H_2S from the acid gas feed to form SO_2. In addition to the O_2 formation, the direct SO_2 formation will further reduce the need for O_2 supplied to the thermal reactor. Using atmospheric air as O_2 source, the reduction in air flow result in a decrease in overall process gas flow as less N_2 diluent is introduced into the Claus plant. Process gas flow reductions up to 10-15 % are possible with the TopClaus® configuration, meaning lower size of the Claus plant for a given capacity, and making this configuration a good option not only for new plants but also for debottlenecking and capacity increase of existing units. As energy is required for evaporation and decomposition of the sulfuric acid, the temperature in the thermal reactor is decreased, which is often an advantage from material and revamping of existing Claus plants points of view. As a rough guideline for TopClaus®, the temperature decrease will be 50-80 °C compared to operation without acid injection. Oxygen enrichment, feed gas preheating and fuel co-firing can mitigate this temperature decrease, should the resulting thermal reactor temperature be too low for e.g. complete BTX or NH_3 destruction.

With the introduction of H_2SO_4 into the complicated chemical system of the thermal reactor, it is natural to consider if there will be any unexpected behavior in the thermal reactor and downstream equipment. Side reactions between H_2SO_4 and species such as CH_4, BTX (Benzene, Toluene and Xylene) and NH_3 may either be beneficial, i.e. accelerating the destruction, or hamper some reactions and/or form new species. Unconverted H_2SO_4 could also be an issue regarding sulfur product quality and Claus catalyst lifetime.

The open literature had not any useful information about the destruction of sulfuric acid in a high temperature reducing atmosphere and thus it became necessary to produce new knowledge on this topic.

Both a theoretical and an experimental investigation was conducted to increase the understanding of the destruction of H_2SO_4 and SO_3. The terms H_2SO_4 and SO_3 should be considered the same, i.e. a sulfur specie with sulfur in oxidation step +6. H_2SO_4, SO_3 and H_2O will always be found in equilibrium; at low temperature H_2SO_4 is dominant and at high temperature SO_3 is dominant.

The investigation focused on the gas phase chemistry in the Claus thermal reactor, i.e. the injection of the liquid sulfuric acid was not included. Haldor Topsoe has much experience in injection, atomization and evaporation of sulfuric acid from e.g. spent acid regeneration plants. The acid is injected via so-called twin fluid nozzles using pressurized air to form a cloud of fine droplets, which quickly evaporate at the high temperature present in the combustion chamber and now thermal reactor in the Claus plant.

Theoretical investigation

Thermodynamically, H_2SO_4 and SO_3 cannot exist in the high temperature reducing atmosphere of the thermal reactor of the Claus plant, as there will be both H_2S and H_2 present to reduce the highly oxidized state of SO_3 (+6 oxidation step) to the more stable SO_2 (+4 oxidation step).

This means that, given sufficient time, all H_2SO_4 and SO_3 will be reduced to SO_2. For practical purposes, it is of high importance to know the time it takes to reach this state, i.e. the kinetics of the reactions are needed.

The process gas residence time in the thermal reactor of the Claus plant will typically be 1-2 seconds, which set the upper limit for how slow the reactions are allowed to be without needing to e.g. increase the residence time in the thermal reactor.

The theoretical approach was to use a kinetic gas phase model, where so-called elementary reactions are combined in a large system, covering all possible chemical species (both stable molecules and radicals) and all possible chemical reactions. The work was carried out as a M.Sc. project in close collaboration with the CHEC group at the Department of Chemical Engineering at the Technical University of Denmark.

An elementary reaction is defined as a reaction including 1 or 2 (in some special cases 3) chemical species, in which the order of reaction for each specie is 1 and the rate constant, A_i, is given by the Arrhenius expression

$$A_i = k_i \cdot T^{ei} \cdot \exp(-E_{ai}/(R \cdot T)).$$

k_i is the pre-exponential factor of reaction i, E_{ai} is the energy of activation for reaction i, R is the universal gas constant and T is the absolute temperature. For some reactions, there is an additional temperature correction term given by T^{ei}, but for most elementary reactions, ei is 0.

Each elementary reaction and associated reaction parameters have been compiled from many different laboratory experiments, where focus has been to isolate as few elementary reactions as possible to determine the parameters with as high certainty as possible. All these reaction parameters are then collected in databases, which can be accessed by the scientific community worldwide.

Based on an initial composition of the process gas to be modelled, the chosen set of elementary reactions was calculated, and the concentration of all species were integrated over time. The temperature was typically kept constant during the calculations. The modelling software used was CHEMKIN.

The chosen reaction system investigated included the so-called H_2S, CH_4, H_2, CO subsystems, which were readily available in the database at the CHEC group. For the H_2SO_4 and SO_3 decompositions reactions, a literature study was conducted to find the relevant elementary reactions and their rate constants. For H_2SO_4, only the dissociation reaction into SO_3 and H_2O was found, apparently data on direct reaction between H_2S and H_2SO_4 at elevated temperature has never been investigated/published. The same picture was seen for SO_3, where only data for the direct dissociation to SO_2 and O_2 and a reaction with elemental sulfur was found in the literature, i.e. data on direct reaction with H_2S has not been published.

A total of 133 elementary reactions and 57 stable and intermediate species were included in the reaction system. The model was checked against published data on the Claus reactions (i.e. without H_2SO_4 addition) and reasonable good correspondence was found. Both with and without H_2SO_4 addition, the equilibrium composition calculated by the CHEMKIN model fitted very well to the equilibrium composition calculated by FactSage, a program which uses minimization of the Gibbs energy of the system to find the thermodynamical equilibrium composition.

Two Claus thermal reactor feed gas compositions were investigated, i.e. a refinery off gas with very high H_2S concentration and a natural gas processing plant off gas with medium H_2S concentration. To these feed

gases, a stream of atmospheric air and sulfuric acid was added, such that the H_2S / SO_2 ratio at the outlet of the thermal reactor would become close to 2.

Due to the endothermal evaporation and dissociation reactions, the addition of sulfuric acid will decrease the overall process gas temperature and thus slow down the chemical reactions. A thermodynamical balance calculation was carried out to find the "steady state" process gas temperature as the constant operating temperature for the detailed modelling with the CHEMKIN software.

The relative amount of sulfuric acid feed to the acid gas feed will in practice depend on the sulfur formation efficiency of the Claus plant, which for a plant layout with two catalytic Claus reactors is in the 94-96% range and for a layout with three catalytic Claus reactors 97-98 %. For a green field Claus plant, the most cost-effective option is to use a two-bed solution as addition of a third bed will only have minimal effect on the cost of the tail gas WSA plant. The calculations were thus made with around 5% of the total sulfur production being sulfuric acid recycled from the WSA tail gas plant. To test the system, a calculation was carried out with 10% of the sulfur production coming from the sulfuric acid feed. The sulfuric acid concentration used was 93 %w/w H_2SO_4 /7%w/w H_2O.

The feed gas compositions used are shown in Table 1.

		Natural gas sweetening	Refinery off gas
H_2S	vol%	66	91.4
CO_2	vol%	20	2.1
H_2O	vol%	8.6	3.3
N_2	vol%	2.6	-
CH_4	vol%	1.7	1.4
O_2	vol%	0 7	-
H_2	vol%	-	1.9

Table 1. Acid gas compositions for calculation the effect of adding sulfuric acid to the thermal reactor of the Claus plant

The results of the calculations are shown in Figure 4, Figure 3, Figure 5 and Figure 6.

In Figure 3, the gas composition comprising the major Claus species in the thermal reactor is shown as the reactions proceed. The calculations assume complete feed stream mixing at time = 0 seconds and a constant temperature of 1080 °C. It is seen that H_2S is almost instantaneously converted to H_2 (+S_2) and oxidized to SO_2 and then the slower Claus reaction will form elemental sulfur and water by reacting H_2S with SO_2. It is also seen that the peak of H_2 formed will decrease to a steady state level.

The change in H_2SO_4 and SO_3 concentration is shown in Figure 4. It is seen that both H_2SO_4 and SO_3 are almost instantaneously converted – they are no longer present after 0.002 seconds. From the figure, it is seen that it is the decomposition of H_2SO_4 to H_2O and SO_3, which is the time determining step. The SO_3 react as fast as it is formed and analysis of the reaction rates of the individual elementary reactions reveal that SO_3 mainly react with S_2 to form SO_2 and S_2O, the latter can react with other intermediate species to end up as SO_2. The direct SO_3 decomposition into SO_2 and ½ O_2 does not seem to be an important pathway in this system.

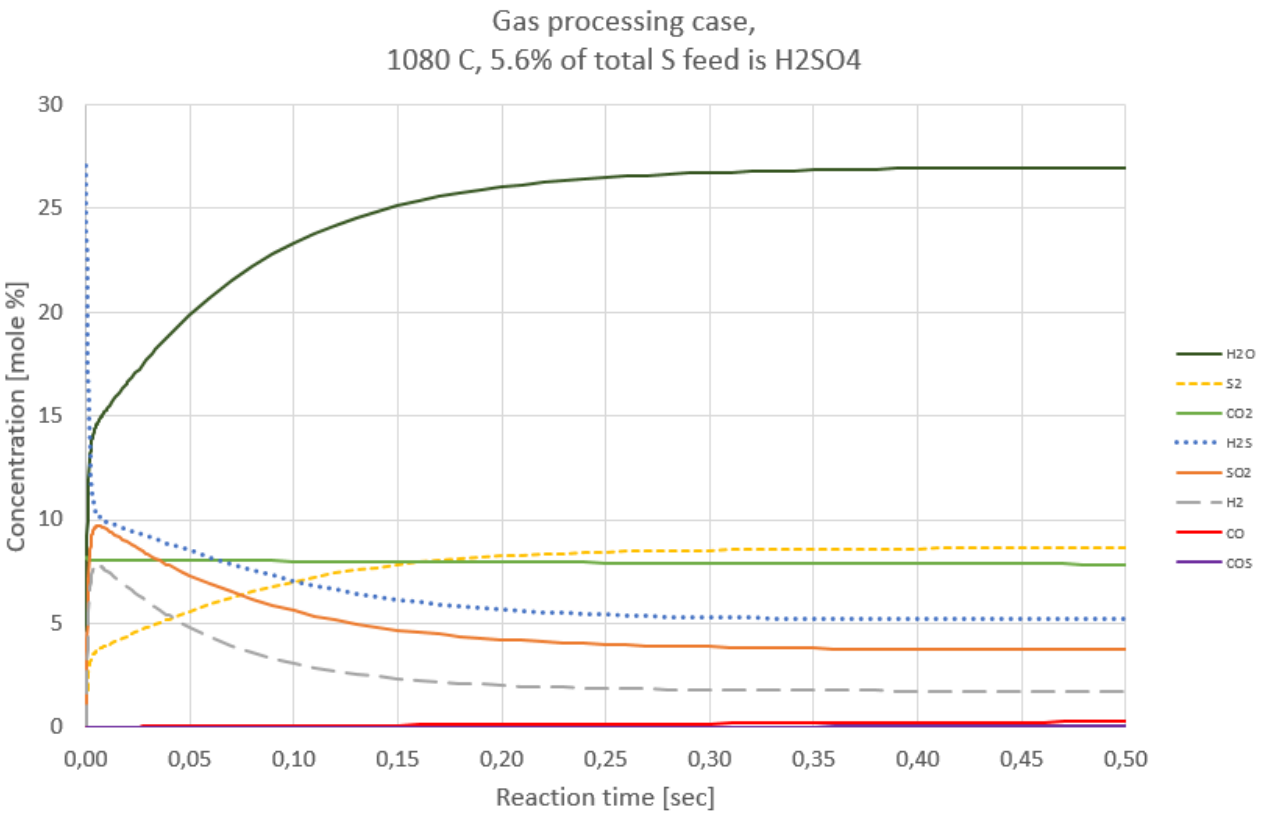

Figure 4 Gas composition in thermal reactor operating at 1080 °C and 1.5 bar pressure with acid gas from a natural gas treatment plant. 5.6% of the Sulphur production is sulphuric acid recycled from the tail gas WSA plant.

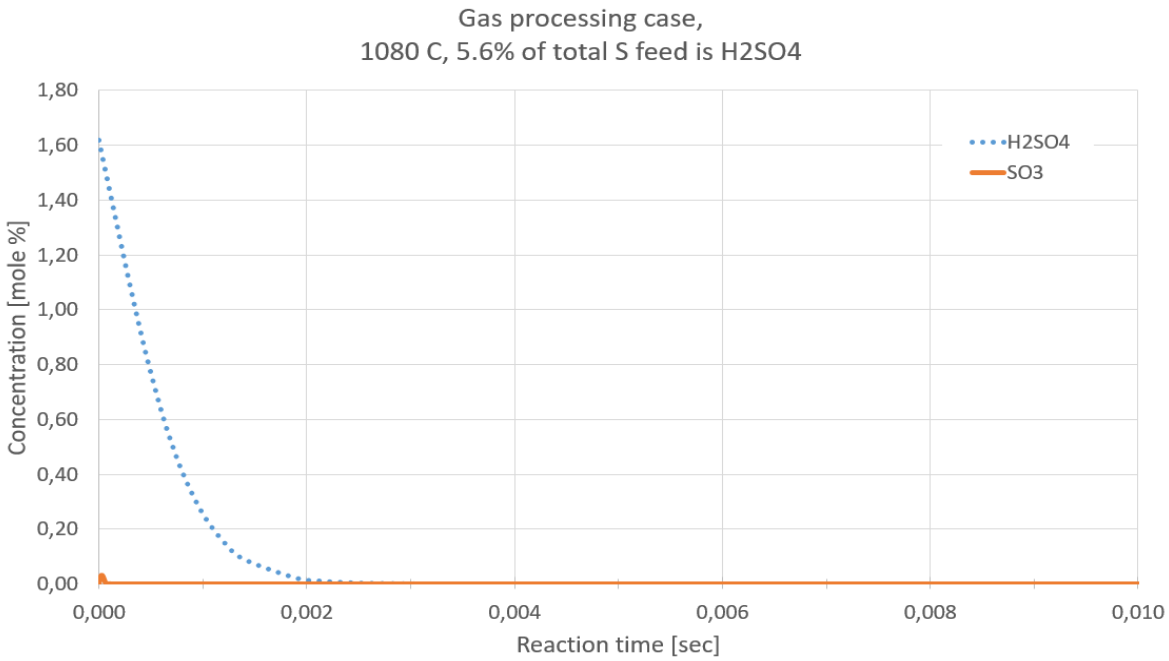

Figure 3. Evaluation of the H_2SO_4 and SO_3 concentration in the Claus thermal reactor, treating an acid gas from a natural gas treatment plant. Reaction temperature was 1080 °C and the pressure 1.5 bar. The sulfuric acid flow corresponded to 5.6 % of the total Sulphur production of the Claus plant.

The calculations showed that H_2SO_4 and SO_3 were practically instantaneously converted and the only effect they would have in the thermal reactor would be slowing down the kinetics of the Claus reaction due to the endothermal evaporation and decomposition reactions. At the given temperature, the Claus kinetics were fast enough to ensure chemical equilibrium within 0.3 seconds, i.e. well within the normal residence time of the thermal reactor.

The same qualitative behavior was calculated for the refinery off gas treatment, the evolution in gas compositions are shown in Figure 5 and Figure 6. Due to the slightly higher temperature, the reactions proceed faster and the limiting Claus reaction is now in chemical equilibrium after around 0.15 seconds. H_2SO_4 and SO_3 are still completely converted within the first 0.002 seconds and will thus only influence the reactions by slowing down the kinetics due to a lower reaction temperature.

For the refinery off gas, the calculations were also carried out in an off-design situation in which the sulfuric acid additions accounted for around 10% of the sulfur production of the Claus plant. The temperature was decreased from 1150 °C to 1050 °C, but otherwise the conclusions were the same: the sulfuric acid was quickly converted and was not present in the gas after 0.002 seconds.

In Table 2, an overall comparison of the kinetic simulations of the H_2SO_4 destruction in the thermal reactor is shown. Due to the sulfuric acid addition and duty needed for evaporation and decomposition, the reaction temperature decrease as the amount of H_2SO_4 is increased. This, together with a higher H_2O concentration, result in a slightly lower fractional formation of sulfur in the thermal reactor, but not more than can be recovered in the downstream catalytic converters. However, the S_2 concentration is as high as 11.4 vol% for the 9.8% H_2SO_4 case and 10.8 vol% for the 5.2 % case.

Due to the oxygen carrier effect of the sulfuric acid, the combustion air flow and associated N_2 diluent flow can be decreased by 16% and 32% and the total process gas flow can be decreased by 6% and 12% compared to the base case, where no H_2SO_4 is injected. This lower process gas flow result in a higher efficiency of the sulfur condensers as the fractional amount of non-condensed sulfur decreases.

The decrease in process gas flow can either be converted into a lower operating cost and higher efficiency of the existing Claus plant or an increase in sulfur forming capacity while maintaining the same efficiency.

H_2SO_4 feed	**% of S production**	**5.2**	**9.8**
Temperature	°C	1150	1050
S_2 formation	%	70	66
S_2 concentration	vol%	10.8	11.4
H_2S/SO_2 outlet	-	1.8	2.0
Combustion air flow	%	84	68
Process gas flow	%	94	88

Table 2. Comparison of overall results from kinetic modelling of the Claus thermal reactor with H_2SO_4 injection into a refinery acid gas. S_2 formation is the fractional formation of sulfur in the thermal reactor, based on the total sulfur feed, i.e. H_2S + H_2SO_4. The percentages of combustion air flow and process gas flow are related to the base case in which no H_2SO_4 is injected.

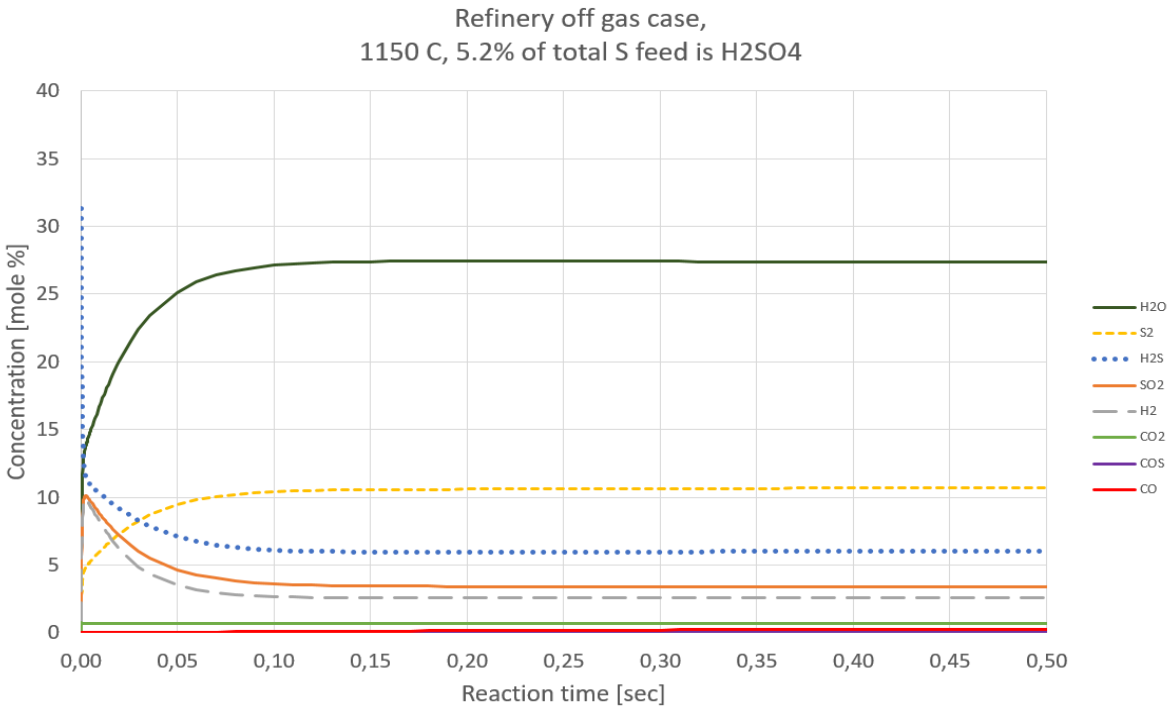

Figure 5. Gas composition of major Claus gas species in the thermal reactor of the Claus plant, treating an off gas from a refinery. The process gas temperature was 1150 °C and the pressure 1.65 bar. The flow of 93%w/w sulfuric acid corresponded to 5.2% of the total Sulphur production.

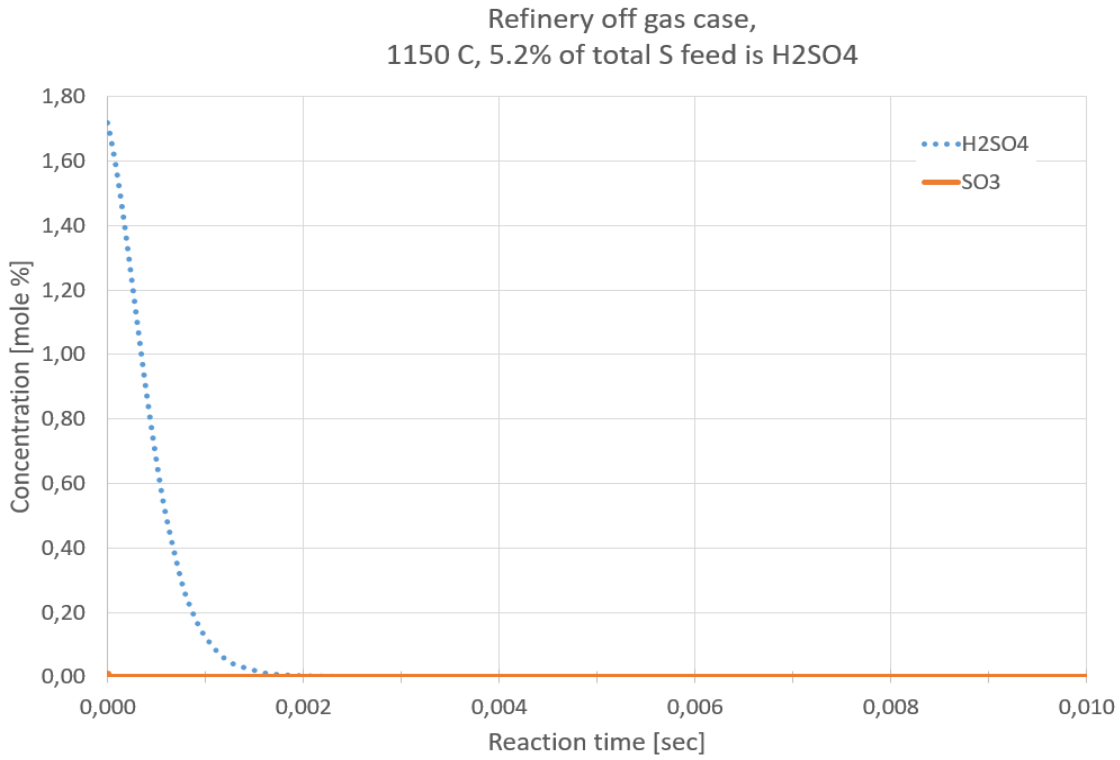

Figure 6. H_2SO_4 and SO_3 concentration in thermal reactor treating a refinery off gas. Temperature was 1150 °C and pressure was 1.65 bar. The flow of 93 %w/w H_2SO_4 corresponded to 5.2 % of the total Sulphur production of the Claus plant.

Simulation conclusions

Based on the kinetic calculations of the thermal reactor for different industrially relevant cases, there were strong indications supporting the conclusion that H_2SO_4 and SO_3 vapors were so quickly destroyed that they had no effect, besides lowering the temperature, on the chemistry proceeding in the thermal reactor.

The kinetic submodel for the H_2SO_4/ SO_3 chemistry was quite simple and may not have included all relevant elementary reactions. These non-included elementary reactions could both decrease or increase the overall reaction rates; a so-called radical termination reaction would combine very reactive species to less reactive species and thus slow down the overall reaction, whereas propagation or branching elementary reactions would increase the overall reaction rate.

Also, the lack of (unknown) important elementary reactions may overlook side reactions and e.g. formation or destruction of secondary species products such as COS, CS_2, H_2 and CO.

The addition of the well-known "contaminants" such as NH_3 and BTX will result in a many fold increase in the number of possible elementary reactions, possibly bringing the number of elementary reactions up well above 1,000.

Therefore, to increase the confidence in the fast destruction of H_2SO_4 and confirm the absence of undesired side reactions, it was decided to supplement the theoretical data with experimental data.

Experimental investigation

The purpose of the experimental investigation was to confirm the fast destruction of H_2SO_4 and absence of undesired side reactions under as industrially realistic conditions as possible.

The investigation required a high temperature laboratory setup (up to 1250 °C) and experience with handling and measuring Claus process related gases. Alberta Sulphur Research Ltd (ASRL, Home | University of Calgary (ucalgary.ca)) fulfilled both needs and together with Haldor Topsoe's experience in analyzing H_2SO_4 in process gases, a collaboration was agreed upon.

The experimental plan included both base line experiments and evaluation of the effect on individual Claus feed gas pollutants. The base line experiments included a standard acid gas with some CH_4 and the effect on temperature, residence time and H_2SO_4 concentration was analyzed. With that basis established, the effect on NH_3 and BTX was analyzed.

The experimental plan is shown schematically in Table 3.

Experiment #1 set the base line outlet composition when no H_2SO_4 is added to the system to confirm that the experimental setup did not have a positive bias with regard to determination and/or formation of H_2SO_4 in the high temperature reaction and low temperature analysis zones.

Experiment 2-3 were used to evaluate the H_2SO_4 destruction at both normal residence time and reduced residence time for to the Claus thermal reactor.

Experiments 4-5 tested if the H_2SO_4 had any effect on the destruction of BTX. Results from the normal operating temperature of 1050 °C would show whether BTX destruction was hindered by the H_2SO_4 and the results from the 950 °C temperature would show if BTX was destroyed faster than expected, for instance due to the presence of the reactive SO_3 molecule; SO_2 has been reported to have a positive effect on BTX destruction. The BTX was a 4:3:1 molar solution of the three compounds.

Experiments 6-7 tested whether NH_3 destruction was somehow influenced by the presence of H_2SO_4, following the same principles as described above.

Experiments 8-9 represented oxygen enrichment condition, under which the thermal reactor temperature would increase under adiabatic conditions. This temperature increase was then countered by an increase in addition of sulfuric acid, which require energy for evaporation and decomposition.

Experiment #	1	2	3	4	5	6	7	8	9
Gas	Natural	Natural	Natural	Natural	Natural	Refinery	Refinery	Natural	Natural
H_2SO_4	-	6 %	6 %	6 %	6 %	6 %	6 %	10 %	15 %
Temperature	1050°C	1050°C	1050°C	1050°C	950 °C	1250 °C	1100 °C	1050°C	1050 °C
Residence time	1 sec	1 sec	½ sec	1 sec	1 sec	1 sec	1 sec	1 sec	1 sec
BTX				Yes	Yes				
NH_3						Yes	Yes		

Table 3. Overview of experiments carried out to evaluate H_2SO_4 destruction under different operating conditions, i.e. temperature, residence time, H_2SO_4 amounts and presence of BTX (Benzene, Toluene, Xylene) and NH_3. Natural refers to an acid gas from a natural gas treatment plant with the composition 55 vol% H_2S, 36 vol% CO_2, 1.5 vol% CH_4, 7.5 vol% H_2O and Refinery refers to acid gas (~90 vol% H_2S) and sour water stripper gas (35 vol% H_2S, 40 vol% NH_3 and 25 vol% H_2O) from a hydrotreatment plant. Oxygen for experiment 1-7 correspond to atmospheric air to the Claus plant, oxygen enrichment was evaluated in experiment 8-9. H_2SO_4 refer to the relative amount of sulfur added as H_2SO_4 compared to the overall sulfur input.

The laboratory setup

The laboratory setup consisted of a process gas mixing and heating zone, a high temperature reaction zone and a downstream quench and analysis zone.

A sketch of the experimental setup is shown in Figure 7.

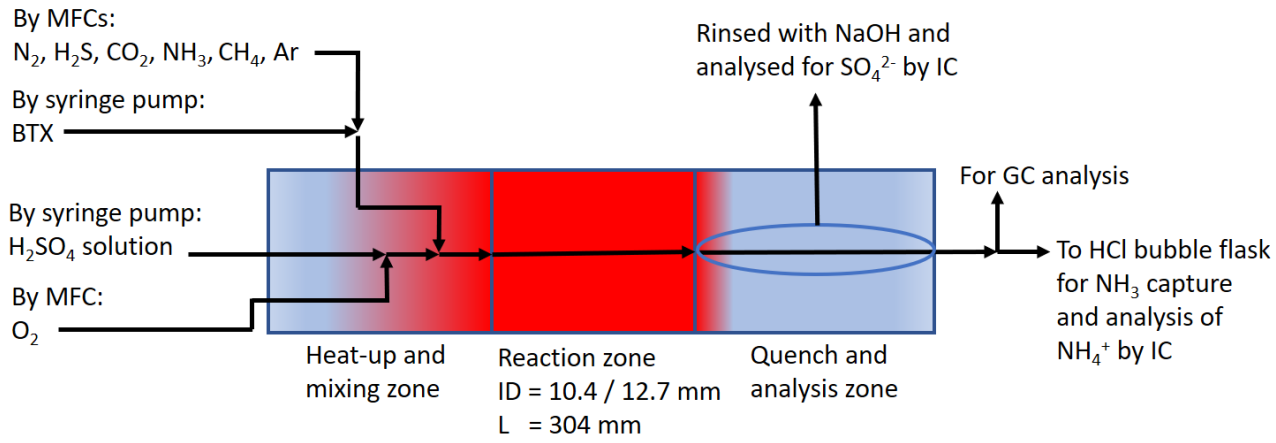

Figure 7. Schematic of the laboratory setup used for the H_2SO_4 destruction experiments at the laboratories of Alberta Sulfur Research Ltd. The color codes represent the process temperatures along the path of reaction, the light blue represent temperatures below 100 °C and the red represent temperatures above 900 °C. MFC = Mass Flow Controller, IC = Ion Chromatography, GC = Gas Chromatography.

Process gases such as H_2S, N_2, Ar, O_2, CH_4 and NH_3 were controlled by Mass Flow Controllers (MFC's) on the individual strings. BTX and sulfuric acid flows were controlled by syringe pumps, injecting the liquids into the heat up and mixing zone for evaporation. The addition of water was controlled by diluting concentrated sulfuric acid with water to a concentration which gave the correct H_2SO_4 and H_2O concentration in the process gas after evaporation and mixing.

To control the onset of the chemical reactions and fix reaction temperature and residence time, O_2 and H_2SO_4 were separated from the reduced gases until the gases had been heated up to the reaction temperature. O_2 has no effect on H_2SO_4 and thus the O_2 stream was used as carrier gas for the evaporated H_2SO_4. Just prior to entering the temperature controlled reaction zone, the O_2 and H_2SO_4 containing stream was mixed with the stream of reduced species and the reactions could proceed. The sulfuric acid stream, O_2 gas and gas mixture of reduced species were separated by concentric tubes in the heat-up zone: H_2SO_4 flowed in the inner tube, O_2 in the intermediate annulus and the reduced gases in the outer annulus.

The reaction zone was a 12" (304 mm) long tube made of quartz (ID = 10.4 mm, used at <1100 °C) or alumina (ID = 12.7 mm, used at > 1100 °C) and positioned in an electrically heated oven. The process gas volume flow determined the residence time in the hot reaction zone.

At the outlet of the reaction zone the process gas was quenched and cooled to a temperature around 80-100 °C. At this temperature, elemental sulfur would condense and solidify, SO_3 would hydrolyze to H_2SO_4 and sulfuric acid would condense, while all other gases and especially H_2O would pass through this "condensation" zone and thus not influence the analysis of H_2SO_4. If water started to condense, there would be a risk that SO_2 and H_2S would become dissolved in the condensate and possibly influence the determination of H_2SO_4.

To collect all elemental sulfur and H_2SO_4, a quartz wool filter was placed in the glass tubing to provide surface for condensation and solidification. Downstream the quartz wool filter, glass tubing with glass beads ensured condensation of sulfuric acid which, for some reason, did not condense on the quartz wool.

The reactor off gas then passed through an absorber system and was released to the atmosphere via the ventilation system.

An important learning during the experimental work was that the sequence of turning on and off for the feed flows to the reactor was important. The "sampling" of H_2SO_4 started the second the H_2SO_4 flow was turned on and stopped the second the H_2SO_4 flow was stopped. The standard sampling time was 30 minutes. The inlet H_2SO_4 concentration was typically around 15,000 ppmv and an outlet concentration below 5 ppmv was expected, i.e. greater than 99.95 % destruction, leaving very little room for offset operation of the experiment. If just 3 seconds with H_2SO_4 flowing while no H_2S flowing to reduce the H_2SO_4, much of the H_2SO_4 would pass through the reactor and condense in the analysis zone and these 3 seconds out of 30 minutes would contribute with up to 25 ppmv bias on the analyzed H_2SO_4 concentration, i.e. 5 times higher than the expected concentration. Therefore, H_2SO_4 flow was always the last flow to start and the first to stop.

Chemical analyses

Gaseous species such as SO_2, H_2S, H_2 CO, CO_2, COS, CS_2, BTX, N_2, Ar, O_2, NH_3, CH_4 were analyzed by a Gas Chromatograph (GC) by withdrawing a small gas sample from the off gas and feed it to the GC column. 3-4 GC samples were made during each 30-minute experiment and the average value was used.

NH_3 could also be analyzed by passing the reactor off gas through a bubble flask with HCl to quantitatively capture the NH_3 and analyze the liquid for NH_4^+ by Ion Chromatography (IC). The agreement between the IC and GC methods was very good.

Elemental sulfur and water concentration was calculated based on inlet and outlet compositions of the process gas.

These analyses and methods were well known and well proven. Analyzing the slip of SO_3/ H_2SO_4 was somewhat more challenging. When cooling the reactor off gas to 80-100 °C, any SO_3 in the gas would react with water to form H_2SO_4 and the sulfuric acid vapor would condense on the surfaces of the available surfaces. At these temperatures, elemental sulfur would also condense and solidify on the same surfaces, i.e. the task was to analyze for H_2SO_4 in an elemental sulfur matrix, where the ratio of elemental sulfur to H_2SO_4 easily could be a factor of 1,000. This meant that just 0.1 % conversion or bias of elemental sulfur to sulfate would double the expected analytical result of sulfate.

Indeed, in the first attempts where H_2SO_4 was not added to the reactor, H_2SO_4 was detected in the sulfur matrix and attention was paid to elimination of this obvious bias. An important factor identified was oxygen ingress to the sulfur which had condensed and solidified but not completely cooled down; the oxygen could oxidize a very small fraction of the sulfur, but still enough to give a detectable H_2SO_4 concentration. After some testing, the procedure became to flush the reactor and analysis zone with N_2 until room temperature was reached and the risk of sulfur oxidation was minimized.

After N_2 purging and cooling down, the cold sampling lines were dismantled and thoroughly rinsed with a 0.1 M NaOH solution to wash out the H_2SO_4, while keeping the elemental sulfur undissolved. The solutions were then analyzed for SO_4^{2-} by Ion Chromatography. The amount of SO_4^{2-} could then be related to the amount of H_2SO_4 injected into the reactor during the course of the experiment.

It was tested whether elemental sulfur and NaOH would form sulfate and whether known amounts of sulfate added to elemental sulfur could be recovered by the Ion Chromatograph and luckily there was no positive bias from the NaOH rinsing and the added sulfate was quantitatively recovered in the NaOH and analyzed by the Ion Chromatograph.

Results and discussion

After the initial validation of the experimental procedure, H_2SO_4 rinsing procedure and sulfate analysis by Ion Chromatography, the experiments according to Table 3 were carried out.

The normal H_2SO_4 concentration at the inlet to the reaction zone was typically 13,000-15,000 ppmv, but in experiments 8-9 representing O_2 enrichment, the H_2SO_4 feed concentrations were 45,000 and 65,000 ppmv respectively. The target was to have less than 5 ppmv H_2SO_4 in the reactor off gas, i.e. minimum 99.96 % H_2SO_4 destruction.

The reactor off gas composition measured with the Gas Chromatograph was compared to the inlet gas composition based on MFC and syringe pump readings and adjusted for condensation of elemental sulfur to close the mass balance. Generally, the inlet-outlet mass balance deviation was typically below 5% for C, H, S and O. In a few occasions, the O mass balance deviation was up to 10%. Such low deviations were perfectly fine for the evaluation on the destruction of the H_2SO_4.

The results of the H_2SO_4 slip measurements are found in Table 4. As such they are very easy to interpret and conclude upon: H_2SO_4 and SO_3 have a very short life time in the hot reducing atmosphere in the Claus thermal reactor and will be quantitively destroyed under normal operating conditions. This is in very good agreement with the conclusions from the theoretical study.

The very low H_2SO_4/SO_3 emission concentrations make it difficult or even impossible to compare different experiments to evaluate whether one condition is better than the other. For instance, how does it make sense that there is a 9 ppm SO_3 slip in experiment 4, operating at 1050 °C while the slip is only 2 ppm for the same conditions when the temperature is decreased to 950 °C? And how does it make sense that there is an 8 ppm SO_3 slip in experiment 8 and none in experiment 9, where more acid is fed to the system? And is SO_3 really formed spontaneously in the reactor in experiment 1, when no acid is fed to the system?

The SO_4^{2-} detection limit in the Ion Chromatograph was 1 ppmw and the quantification limit was 10 ppmw, which correspond to around 1 ppmv and 10 ppmv in the gas phase for the experiments presented in Table 4. This means that the answer to the questions above is that the results were within the uncertainty of the data and thus the values must be considered identical.

Experiment #	1	2	3	4	5	6	7	8	9
Gas	Natural	Natural	Natural	Natural	Natural	Refinery	Refinery	Natural	Natural
H_2SO_4	-	6 %	6 %	6 %	6 %	6 %	6 %	10 %	15 %
Temperature	1050°C	1050°C	1050°C	1050°C	950 °C	1250 °C	1100 °C	1050°C	1050 °C
Res time	1 sec	1 sec	½ sec	1 sec	1 sec	1 sec	1 sec	1 sec	1 sec
BTX				Yes	Yes				
NH_3						Yes	Yes		
SO_3 inlet [ppmv]	0	16,000	16,000	14,000	14,000	13,000	17,000	45,000	65,000
SO_3 outlet [ppmv]	1	3	3	9	2	3	109	8	0
SO_3 conversion [%]	N/A	99.98	99.98	99.94	99.99	99.97	99.36	99.98	100
SO_3 slip [%]	N/A	0.02	0.02	0.06	0.01	0.03	0.64	0.02	0

Table 4. Overview of H_2SO_4/ SO_3 values at the inlet and outlet of the hot reaction zone. Inlet SO_3 values were based on flow and concentration of sulfuric acid solution injected through the syringe pump. Outlet values were based on condensation of sulfuric acid vapor in the quench zone, rinsing with NaOH solution and analysis by Ion Chromatography.

The results shown in Table 4 are for experiments lasting 30 minutes. To test whether the duration had a marked effect on the results, experiment 1 and 2 were repeated with 240 minutes duration. The SO_3 outlet concentrations were 0.5-0.6 ppmv for both experiments, with detection and quantification limits of 0.15 and

1.5 ppmv, respectively. So, these results could only confirm that H_2SO_4 was quantitatively destroyed and that the emission values were below the quantification limits.

The only experiment which had a SO_3 slip above the quantification limit, was number 7, representing a case with NH_3 in the feed in which the operating temperature was 150 °C lower than the industrially accepted minimum operating temperature for complete NH_3 destruction. In this experiment, the NH_3 destruction was measured to around 95%, meaning that there was around 500 ppmv NH_3 in the reactor off gas. There can be many reasons for the relative high SO_3 outlet concentration, but due to limited resources and lack of practical relevance, the reason was not sought in this experimental campaign.

In experiment 4 and 5, the effect on adding BTX to the process gas was evaluated to see whether BTX and H_2SO_4 had any significant interaction. As seen in Table 4, the SO_3 slip was below the quantification limit for both experiments and thus no apparent effect on H_2SO_4 destruction could be concluded.

The inlet gas phase BTX concentration was 2,000 ppmv and the molar BTX distribution was 4:3:1 for Benzene, Toluene and Xylene. Benzene is considered the most difficult molecule to destroy as it lacks methyl site for easier "attack" by the oxidative species.

The BTX outlet concentrations were analyzed by Gas Chromatography. For experiment 4, operating at the recommended minimum temperature of 1050 °C, 10 ppmv Benzene was detected at the outlet of the reactor, no traces of Toluene or Xylene were found. At 950 °C, the Benzene outlet concentration was around 350 ppmv, indicating around 70% Benzene conversion. No traces of Toluene or Xylene were found, which result in an overall BTX destruction of 85%. These values were on par with what was expected for H_2SO_4 free conditions at the given temperature and residence time, i.e. it did not seem that H_2SO_4 either increased or decreased the BTX destruction rates.

The destruction of NH_3 was tested in experiment 6 and 7; the first experiment was carried out at standard operating temperature and the second experiment was carried out at a 150 °C lower temperature to see if there would be any benefits or disadvantages by having H_2SO_4 present in the gas. As seen in Table 4, under normal operating conditions, the SO_3 slip was below the quantification limit whereas a higher number was observed at the low temperature.

In both experiments, the inlet NH_3 concentration was around 13,000 ppmv and the outlet concentration was ~0 ppmv at 1250 °C and 470 ppmv at 1100 °C. The NH_3 conversions were in line with what would be expected in a H_2SO_4-free gas, operating at the same temperatures, i.e. H_2SO_4 did not seem to affect the NH_3 destruction.

Conclusion

The newly developed TopClaus® process utilizes Haldor Topsoe's sulfuric acid producing Claus tail gas treatment plant, where the formed sulfuric acid is returned to the thermal reactor of the Claus plant for destruction and reformation to elemental sulfur. In that way very low emissions to the atmosphere can be achieved while only producing elemental sulfur from the TopClaus® process.

No published literature on the H_2SO_4 destruction under Claus thermal reactor conditions was found and thus new knowledge was required to confirm the expected fast destruction; thermodynamics showed that H_2SO_4/ SO_3 are not thermodynamically stable at the high temperature and reducing conditions and their equilibrium concentrations would be 0.

A study comprising detailed mathematical modelling of elementary reactions in a simplified Claus process gas was carried out. The modelling system was ideal, i.e. comprising complete mixing and constant temperature. The modelling results showed very fast decomposition of H_2SO_4 to SO_3 and H_2O and fast

reaction of SO_3, i.e. in less than 0.002 seconds. The sulfur forming Claus reaction was the rate determining reaction path, reaching chemical equilibrium after 0.2-0.3 seconds.

The mathematical model was not able to simulate the effect of the well-known "contaminants" of BTX and NH_3, primarily due to a lack of a model of elementary reactions to describe all relevant reaction paths but also because the complexity of such a mathematical model would increase considerably.

Therefore, an experimental study was planned and executed in a collaboration between Alberta Sulfur Research Ltd and Haldor Topsoe. By combining complementary analytical knowledge, it was possible to measure the H_2SO_4 destruction in a laboratory scale thermal reactor, testing industrially relevant process gas compositions.

The results showed that H_2SO_4 and SO_3 concentrations at the outlet of the hot reaction zone were below the quantification limit, i.e. more than 99.95 % H_2SO_4 destruction was measured. The destruction of BTX and NH_3 seemed to be unaffected by the addition of H_2SO_4 to the process gas.

The conclusion of this work was that H_2SO_4 and SO_3 vapor is quickly and quantitively destroyed in the thermal reactor of the Claus plant, with no undesired side reactions with BTX or NH_3.

CV for Morten Thellefsen

Morten Thellefsen graduated from the Technical University of Denmark with a Master and Ph.D. degree in Chemical Engineering and has worked for Haldor Topsoe for 20 years now. Morten has worked most of the time in Clean Air R&D, in the field of cleaning process gases containing sulfur compounds. The work has included laboratory experiments, pilot plants, engineering, troubleshooting industrial plants, new developments and Intellectual Properties.