

## THE TROUBLE WITH AMMONIA HOW PROCESSING BIOFUELS CHANGES THE APPROACH

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Marco van Son, Comprimo, [marco.vanson@worley.com](mailto:marco.vanson@worley.com)  
Frank Bela, Comprimo, [frank.bela@worley.com](mailto:frank.bela@worley.com)

### **ABSTRACT**

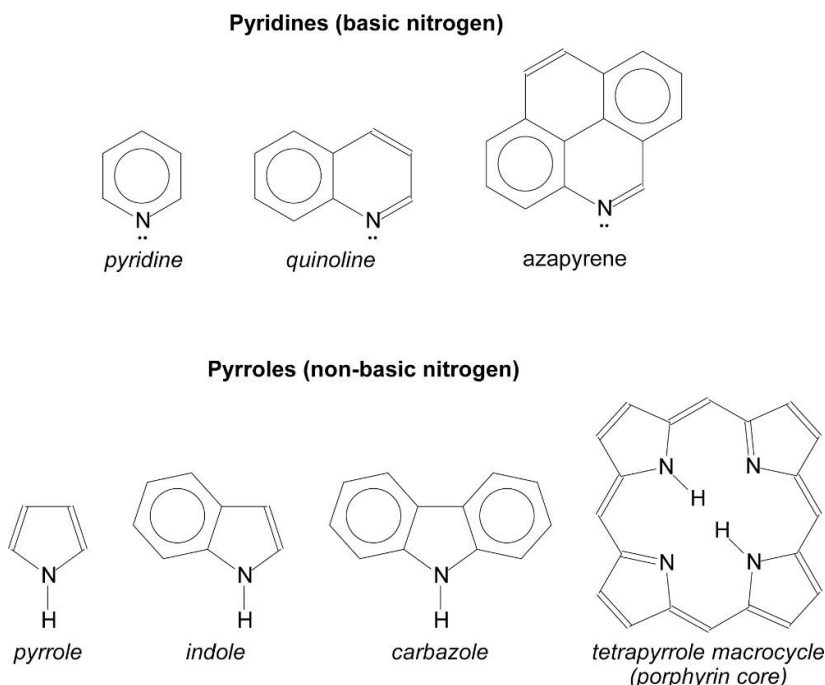
The processing of ammonia has been a very contentious subject in Sulfur Recovery Units for a very long time. From initial philosophies of having to operate oxidizing in the thermal reactor to properly destroy ammonia in SRUs to the work that was done by ASRL in the nineties to prove that sulfur dioxide (SO<sub>2</sub>) is the key component in the ammonia destruction process in the thermal reactors.

More recently, through the introduction of biofeeds to refineries, the ability to use sulfur recovery units to deal with ammonia produced in refineries may no longer always be available. As the amount of sulfur produced as well as the ratio of ammonia to H<sub>2</sub>S in the sour water acid gas produced is dramatically changing, alternative sulfur removal technologies may need to be considered instead of conventional SRUs and TGTUs. These technologies typically do not have the ability to deal or destroy ammonia by themselves and require other means to manage the presence of ammonia in the acid gas streams.

This paper will discuss how between co-processing and 100% processing of biofeeds, the ammonia processing path may need to be evaluated on a case-by-case basis.

### **1.0 INTRODUCTION**

Nitrogen is a natural component found in all feedstocks supplied to refineries, be it in the form of Crude Oil, Bitumen, bio feedstocks or condensates from gas plants. The nitrogen is predominantly present in crude oil in the form of pyridine derivatives (basic) and pyrrole derivatives (non basic)<sup>1</sup>. Figure 1 shows the predominant forms of nitrogen that can be found in crude oils.



**Figure 1. Predominant nitrogen-containing classes in crude oil.**

The nitrogen content of crude oils is usually less than 1 wt% and in 90% of the crude oils the nitrogen content is less than 0.25 wt%. The industry has classified oils with nitrogen contents greater than 0.25 wt% as high-nitrogen. Key high nitrogen containing feed stocks supplied to refineries can be found in bitumen from Alberta and a number of crudes from California, Utah and Brazil.

Nitrogen-containing compounds can lead to limitations in the ability to upgrade or refine to final products. Some key issues with nitrogen-containing compounds are:

- Poor thermal stability of products
- Poisoning of catalysts used in hydrocracking and fluid catalytic cracking units
- Formation of corrosive salts

Two classes of hydrocarbon conversion techniques are used to remove the nitrogen from the complex molecules. In thermal conversion units such as cokers, visbreakers and fluid catalytic crackers, the amide groups in the hydrocarbon molecules are converted to ammonia (NH<sub>3</sub>) and/or cyanide (HCN), where at the same time the sulfur groups are converted to H<sub>2</sub>S and mercaptans and any chloride in the oil may become hydrochloric acid.

In hydroconversion units such as Hydrocrackers and Hydrotreaters, the hydrogen is added to the process to convert the sulfur species in the oil products to H<sub>2</sub>S and the nitrogen species to NH<sub>3</sub> and no HCN is formed. In these units the concentrations of NH<sub>3</sub> and H<sub>2</sub>S are typically much higher than in the thermal conversion units.

In addition, NH<sub>3</sub> – either anhydrous or aqueous – may be injected in certain portions of the refinery for pH control, although it is becoming less common due to safety / environmental concerns.

NH<sub>3</sub> has a high affinity for water and as such water washes are required to remove it from the gas streams produced in the units indicated above. When H<sub>2</sub>S is present in the process gas together with NH<sub>3</sub>, the produced water will contain ammonium bisulfide in solution with varying concentration depending on the amount of water used for the water wash. The water wash is also advisable to prevent NH<sub>3</sub> from entering the amine absorbers used to remove H<sub>2</sub>S from the system. NH<sub>3</sub> in rich amine will concentrate in the Regenerator reflux, co-absorbing proportional H<sub>2</sub>S and CO<sub>2</sub>. Reflux NH<sub>3</sub> is typically limited to 1 wt% by purging the reflux to the sour water system to avoid breakthrough with the acid gas and limit increased regeneration heat duty, sulfide corrosion and elevated pH conducive to emulsion of surface-active contaminants likely to cause foaming.

The produced sour water is then processed in a sour water stripper where, through the introduction of heat, the ammonium bisulfide is removed from the water with a typical specification of 20 ppm NH<sub>3</sub> and 5 ppm H<sub>2</sub>S in the stripped water. In typical refineries, there is very little CO<sub>2</sub> present in the sour water and hence there is no expectation of high concentrations of CO<sub>2</sub> in the acid gas produced that is processed in the sulfur recovery units.

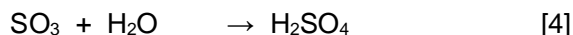
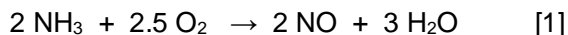
Sour water stripping can be done in either a single stage to produce a sour water acid gas stream that contains both NH<sub>3</sub> and H<sub>2</sub>S, or in a two-stage sour water stripper, like the WWT process, where separate H<sub>2</sub>S and NH<sub>3</sub> streams are produced, with the ammonia typically sold as either an anhydrous or aqueous product after purification. Discussion of sour water stripping technologies can be found in reference 9.

## **2.0 AMMONIA DESTRUCTION**

### **2.1 SULFUR RECOVERY UNIT THERMAL REACTORS**

In the 1950-60s it was generally assumed that complete NH<sub>3</sub> destruction required excess air ("oxidizing atmosphere"). This typically resulted in a two-zone Thermal Reactor where all sour water acid gas (SWAG) and combustion air was routed to zone 1, and at least some amine acid gas (AAG) could be bypassed to zone 2.

Processing SWAG in this manner typically results in downstream formation of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) which (1) deactivates alumina by forming aluminum sulfate, (2) deposits solid ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] and bisulfate (NH<sub>4</sub>HSO<sub>4</sub>) if NH<sub>3</sub> is present, and (3) corrodes steel upon condensation in the condensers. The fundamental mechanism appears to be initial formation of byproduct NO<sub>2</sub> which subsequently oxidizes SO<sub>2</sub> to SO<sub>3</sub>, thus forming sulfuric acid vapor:



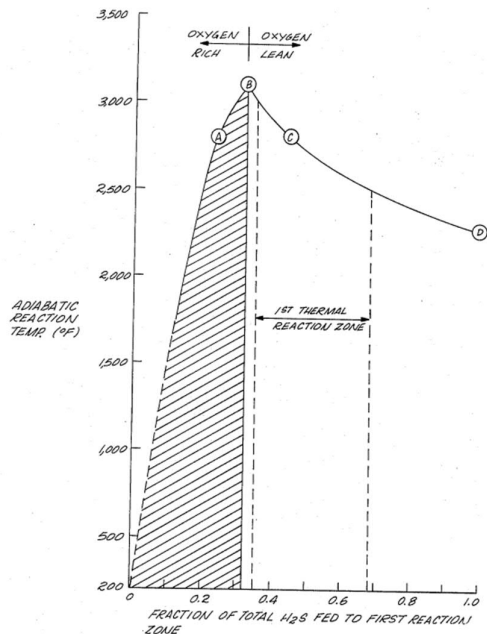
This was generally accepted as the price one had to pay until around 1970 when two developments revolutionized the industry:

- Comprimo demonstrated that efficient  $\text{NH}_3$  destruction could be achieved in a single-zone thermal reactor with proper temperature, sufficient residence time and a high intensity burner.
- The Ralph M. Parsons Company continued to favor the two-zone furnace concept while limiting the AAG bypass to ensure excess  $\text{H}_2\text{S}$  in zone 1.

In the two-zone case, the relative zone 1 temperature is determined by the fraction of total actual  $\text{H}_2\text{S}$  (not to be confused with “acid gas”) routed to zone 1. A graphical representation is provided in **Figure 2**. Since the Claus process only oxidizes one third of the  $\text{H}_2\text{S}$ , routing one third to zone 1 maximizes the temperature, where  $1300^\circ\text{C}$  is considered an optimum target. Arguably more important, however, is maintenance of reducing conditions (excess  $\text{H}_2\text{S}$ ) in zone 1 to avoid downstream formation of  $\text{H}_2\text{SO}_4$ .

Actual  $\text{H}_2\text{S}$  split will be approximate, given likely errors in flow measurement and assumed acid gas  $\text{H}_2\text{S}$  concentrations. To ensure excess  $\text{H}_2\text{S}$ , at least 40% of the total  $\text{H}_2\text{S}$  should be routed to zone 1. However, maximizing AAG to zone 1 is also desirable for better mixing and residence time, provided  $1250\text{--}1300^\circ\text{C}$  is maintained.

While most in the industry now recognize the importance of maintaining reducing conditions in zone 1, a notable minority still believe oxidizing is better. Original operating guidelines to that effect should thus be disregarded, which generally appears to be the case. That aside, reducing conditions are unavoidable once SWAG  $\text{H}_2\text{S}$  exceeds 35% of the total, when 40-60% appears to be common.



**Figure 2. Thermal Reactor zone 1 temperature as function of  $\text{H}_2\text{S}$  split**

The actual mechanism at work in the destruction of ammonia in the Claus Thermal stage was studied extensively by Alberta Sulphur Research Ltd. in both the nineties and 2010s. Prior to this research it

was assumed that ammonia would undergo rapid oxidation or dissociation to nitrogen and hydrogen<sup>[6]</sup>. It is now generally accepted that SO<sub>2</sub> is the key to ammonia destruction in the Claus Thermal Reactor:



In short, (1) H<sub>2</sub>S reacts faster with O<sub>2</sub> than does NH<sub>3</sub>, and (2) NH<sub>3</sub> reacts faster with SO<sub>2</sub> than with O<sub>2</sub>.

## 2.2 CONSEQUENCES OF INADEQUATE AMMONIA DESTRUCTION

The general guidelines for adequate ammonia have been typically as follows<sup>[3]</sup>:

- Maximum of 25-30 mol% ammonia in the feed (wet basis)
- Good destruction requires 2300°F (1260°C)
- Good destruction requires “long” residence time
- Industry consensus on destruction levels
  - <50 ppm – trouble free
  - <150 ppm – prevents plugging
  - >300 ppm – potentially problematic

If the right conditions exist in an SRU, plugging of areas of the sulphur recovery plant are definitely possible as shown in **Figure 3**, leading to unplanned outages of units as well as gradual reduction in processing capacity.



**Figure 3. Evidence of ammonium salt plugging on incinerator nozzle**

So, what salts are actually the main culprit for the plugging issues observed in sulfur recovery units? Ammonia is a base and there are a number of acidic components in the sulfur plant process gas, such as H<sub>2</sub>S, SO<sub>2</sub>, CO<sub>2</sub> and potentially SO<sub>3</sub>. There is no evidence in SRUs that ammonium bisulfide

(H<sub>2</sub>S) is a potential cause for any plugging issues. The sublimation temperature for ammonium bisulfide is much lower than the freezing point of sulfur and hence not expected to take place in an SRU before the unit would plug up with sulfur.

Ammonium carbonate salts are extremely volatile and are therefore not expected to be present in SRU tail gases.

Recent ASRL work<sup>[11]</sup> has shown trace quantities of (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> can be formed at temperatures up to 266°F (130°C), with further reaction to more stable thiosulfates. However, with typical ammonia residuals and the required formation temperature for thiosulfates (180-208°F or 83-98°C), it is again not expected that these salts will be present in the tail gas of an SRU, unless there are cold spots below about 201°F (94°C). At these cold conditions it is possible for ammonium thiosulfate to deposit if the tail gas piping and flanges are not properly heated.

Some plants reportedly avoid local salt deposition by operating the final condenser above 150°C, suggesting the culprit in that case is ammonium bisulfate which melts at 147°C.

The primary source of ammonium salts appears to be caused by the formation of SO<sub>3</sub> in the process resulting in deposits of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Barring oxidizing conditions in the front end of a 2-zone thermal reactor as discussed, this is likely due to O<sub>2</sub> slip from inline (aux) burners and/or NO<sub>x</sub> formation in a damaged main burner. It is very difficult though to prove the presence of SO<sub>3</sub> in a Claus plant by process gas analysis.

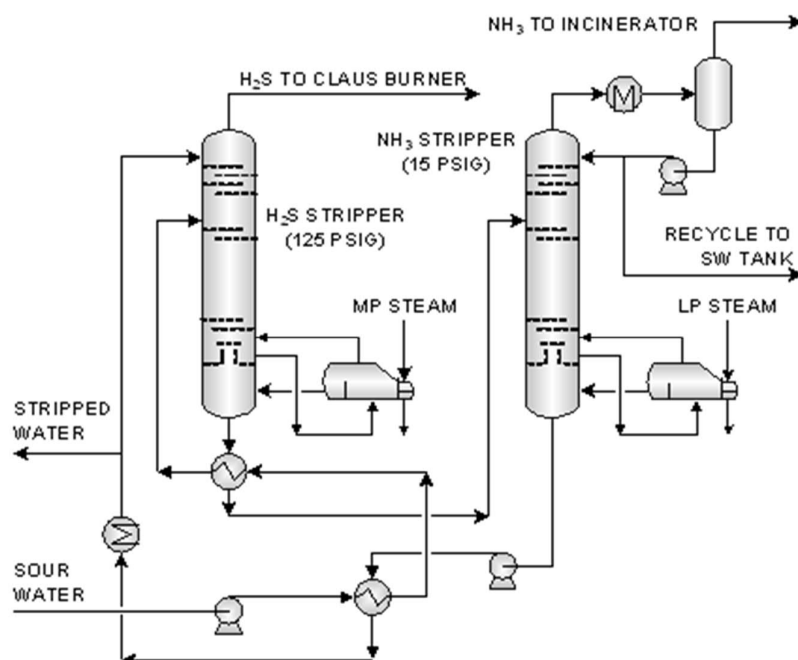
In general, it is difficult to remove salts that have deposited in a Claus plant as the decomposition temperature for sulfates are higher than the available temperatures in the unit.

### 2.3 AMMONIA INCINERATION

While the SRU fouling, corrosion and catalyst deactivation problems originally associated with ammonia processing are avoided by proper destruction under reducing conditions, ammonia destruction still takes up Claus capacity. Typical SWAG containing one-third H<sub>2</sub>S will have a molar air demand similar to AAG containing 80-90% H<sub>2</sub>S. At 25% NH<sub>3</sub> (wet basis), for example, sulfur production capacity is reduced by 50%, and Claus recovery efficiency is nominally reduced from 96.6% to 92.9% by virtue of tail gas dilution with N<sub>2</sub>.

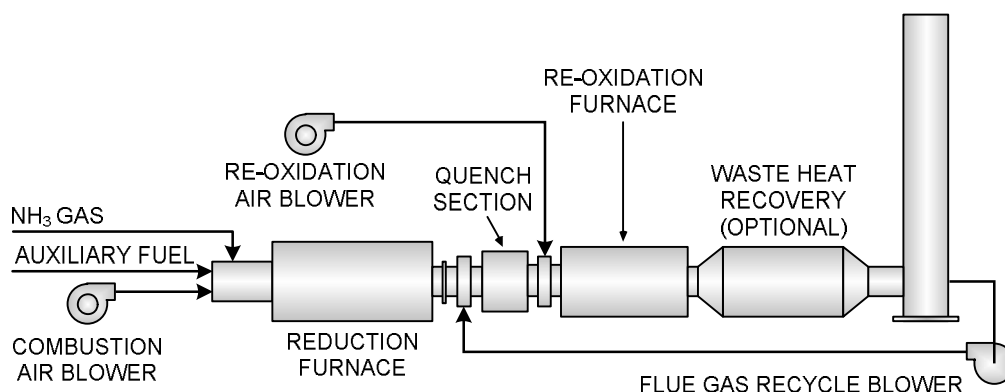
Within the past 30 years, FCCU-feed hydrotreating in particular has significantly increased NH<sub>3</sub> / H<sub>2</sub>S ratios.

In the 1960s, Chevron developed the two-stage Waste Water Treatment (WWT) process to process highly sour hydroprocessing unit wash water, whereby H<sub>2</sub>S is selectively stripped at 125 psig in the first stage, followed by NH<sub>3</sub> stripping at normal SWS pressures. (**Figure 4**). Bechtel now licenses the technology.



**Figure 4. Chevron WWT 2-Stage SWS**

While the original intent was to market anhydrous ammonia, increasingly stringent regulations governing handling / transportation has resulted in a trend toward incineration. The John Zink NOxIDIZER® is an example of how this is accomplished while minimizing NOx. In **Figure 5**, it is shown that ammonia is thermally oxidized under reducing conditions, quenched to 1000-1500°F with recycled flue gas, followed by addition of secondary air for oxidation of residual CO and H<sub>2</sub>.



**Figure 5. John Zink NOxIDIZER® for low-NOx NH<sub>3</sub> incineration**

Similar systems that can be used for ammonia destruction in Thermal Oxidizers while limiting NOx formation are the Duiker Stoichiometry Controlled Oxidation (SCO) system and Zeeco® Nitrogen Bearing Waste Thermal Oxidizer.

Improper destruction of ammonia in the Thermal Oxidizer can lead to ammonia emissions from the stack as well as problems with salt formation in cooler areas downstream of the waste heat boiler. An



example of the consequences of insufficient ammonia destruction upstream of a caustic scrubber are provided in **Figure 6**.



**Figure 6. Evidence of Fouling due to insufficient ammonia destruction in a thermal oxidizer**

### **3.0 IMPACT OF PROCESSING BIOFUELS ON AMMONIA DESTRUCTION**

Processing of bio feedstocks such as tallow, rapeseed oil and waste cooking oils can be broken down into two distinct options. In the first option, called co-processing, part of the feedstock to an existing oil refinery is converted to bio feedstock. In the second option, either a full conversion of an existing oil refinery or a new grassroots installation independent of an oil refinery can be considered where the full feed to the facility will be provided from bio feedstocks.

#### **3.1 CO-PROCESSING**

In co-processing, a portion of the feedstock to an existing hydrotreater or FCC unit is converted to a biofuel feedstock. Typical values of 10-20% of the total feed are chosen to minimize the required modifications to the existing units. The co-processing of bio feedstock in an existing unit means that the unit still produces similar products containing  $H_2S$  and  $NH_3$ , however due to the higher oxygen content of the bio feed stock and lower content in nitrogen and sulfur, the concentrations of these components to be processed in the existing amine and sour water strippers can be substantially different. In addition, due to the presence of oxygen in bio feed stocks, which is not present in conventional hydrocarbon feedstocks, there will be more  $CO_2$  and potentially more sour water to handle.

Alternatively, plants can also consider handling the “co-processing” of bio feedstock through the conversion of a single unit in the refinery while maintaining conventional hydrocarbons on the rest of the units. Similar conclusions can typically be taken in that scenario.



### 3.1.1 Typical Configuration

A typical refinery will have a number of amine regenerators stripping the rich amine supplied from the absorbers in the hydrotreating, coker, FCC and fuel gas system. Depending on the configuration of the refinery, the CO<sub>2</sub> content in the acid gas may range from very low concentrations to perhaps values of 10-15% with conventional crudes.

To process the sour water produced, one to several sour water strippers may be installed with the option to have either single or two-stage sour water strippers. For the purpose of this paper, only the refineries with a single stage sour water stripper have been investigated as the impact on the handling of the ammonia component in the system will be more complicated.

In Table 1 below, the composition of the acid gases to a refinery sulfur recovery unit are provided prior to the addition of bio feedstock to one of the hydrotreating units.

Table 1: Typical acid gas composition to SRU prior to co-processing

Parameter	Units	AAG	SWAG
H <sub>2</sub> S	mol%	82.227	34.635
C <sub>1</sub>	mol%	0.345	0.012
C <sub>2</sub>	mol%	0.380	0.010
C <sub>3</sub>	mol%	0.224	0.002
C <sub>4</sub>	mol%	0.130	0.012
C <sub>5</sub>	mol%	0.194	0.003
C <sub>6</sub> H <sub>6</sub>	mol%	0.131	0.055
C <sub>6</sub>	mol%	0.026	0.008
CO <sub>2</sub>	mol%	9.812	0.088
H <sub>2</sub>	mol%	0.511	0.070
N <sub>2</sub>	mol%	0.070	0.094
H <sub>2</sub> O	mol%	5.951	30.0
NH <sub>3</sub>	mol%	0	35.01
Temperature	°F	115	185
Pressure	psig	10.0	10.0

After the introduction of bio feedstock, the flows and compositions for one particular refinery changed as shown in Table 2.

Table 2: Example of modified acid gas compositions after introduction of co-processing

Parameter	Units	AAG	SWAG
H <sub>2</sub> S	mol%	71.28	26.318
C <sub>1</sub>	mol%	0.28	0.088
C <sub>2</sub>	mol%	0.37	0.013
C <sub>3</sub>	mol%	0.62	0.014
C <sub>4</sub>	mol%	0.60	0.001
C <sub>5</sub>	mol%	0.90	0
C <sub>6</sub>	mol%	1.17	0
O <sub>2</sub>	mol%	0.0003	0
CO <sub>2</sub>	mol%	18.40	4.121
CO	mol%	0.002	0.001
H <sub>2</sub>	mol%	0.17	0
N <sub>2</sub>	mol%	0.002	0.001
H <sub>2</sub> O	mol%	5.92	31.276
NH <sub>3</sub>	mol%	0.29	37.962
Ar	mol%	0	0.205
Temperature	°F	115	205
Pressure	psig	10.0	21.0

It is obvious from Table 1 and Table 2 that the change in acid gas feed stock is not dramatic and one can assume that the impact on the operation of the SRU will be minimal. There will be more CO<sub>2</sub> in the amine acid gas and more ammonia in the sour water acid gas relative to the H<sub>2</sub>S, however overall, with lower sulfur load, the key difference will not result in a substantial impact to the processing capacity of the SRU.

One of the potential issues of co-processing though is caused by the higher dilution of the process gases out of the thermal reactor. In the case of the installation of a SUPERCLAUS or amine-based tail gas treatment unit as the tail gas technology for the SRU, the move to bio-fuels will result in a reduction in overall sulfur recovery efficiency, which will lead to higher emissions.

In Table 3 the comparison between the sulfur recovery efficiency before and after the implementation of bio feedstock co-processing are provided. From the results, it is clear that co-processing does result in increased emissions.

Table 3: Comparison of sulfur recovery efficiency before and after co-processing

Tail Gas Technology	SRE	Without co-processing	With co-processing
2+1 SUPERCLAUS	%	99.1	98.9
3+1 SUPERCLAUS	%	99.35	99.16
TGTU <sup>1)</sup>	ppmv H <sub>2</sub> S	15	24

Notes:

1. 35 wt% DIPA solution

In general, it has been Comprimo's observation that very often it does not matter what the local or country regulations are with respect to emissions. For instance, the EPA Subpart Ja mandates 250 ppm SO<sub>2</sub> dry and at 0% oxygen for plants over 20 tpd, however in practice the local environmental regulating agencies demand that any modifications to the design or operations of the facility will not result in additional emissions compared to current operations.

As a result, even though the SRU itself will most likely be able to handle the modified feed stock in the case of a co-processing scenario, some additional focus will be required to determine what needs to be done with the tail gas technology. For instance, in the case of a Claus unit, a SUPERCLAUS® stage may need to be added to the unit and in the case of a 2+1 existing SUPERCLAUS® unit, a conversion to a 3+1 SUPERCLAUS® or EUROCLAUS® may be necessary. In the case of an amine based TGTU, the performance of the solvent needs to be evaluated to determine whether the H<sub>2</sub>S concentration in the overhead of the absorber can be reduced by either additional reboiler duty or whether a solvent swap is required to a more selective amine.

It is essential though to work with the local regulating agencies to determine what their expectations with respect to emissions are when co-processing is added to the operation of the facility.

### **3.1.2 The Trouble with Ammonia**

In the case of co-processing or conversion of only part of the refinery to bio feedstock processing, the existing amine, sour water and sulfur recovery system will remain intact and can typically be reused with only minor modifications. In certain instances, the sour water strippers may require some debottlenecking due to the higher production of water in the processes.

The key issue with ammonia then becomes the ability of the SRUs to be able to destroy the ammonia to levels indicated in Section 2.2. This needs to be evaluated on a case-by-case basis. In general, in most scenarios that were reviewed by Comprimo, the required temperatures for ammonia destructions can still be met with the existing design under the new conditions. Options such as additional oxygen enrichment, higher split to the second thermal reactor zone are all available to bring the temperature back to values over 2280°F (1260°C).

Therefore, one can conclude that there is little to no trouble with ammonia in the case of co-processing of bio feedstock.

## **3.2 GRASSROOTS BIOFUELS FACILITIES OR FULL CONVERSION PROJECTS**

Common renewable diesel production processes include transesterification or the hydrotreating of vegetable oils and/or grease, which produces a diesel product that can be blended with conventional diesel products from crude oils. Hydrotreaters are operated with sulfided catalysts which limit the formation of Fatty Acid Methyl Ester (FAME), whereas in transesterification the formation of FAME cannot be prevented currently. The blending of the diesel pool with FAME can lead to problems with corrosion, as well as stability and decomposition issues. As a result, many car manufacturers have limited the amount of FAME that can be present in the diesel used in automobiles.

New options have been developed for the hydrotreating options to work with sulfided hydrotreating catalysts, which have proven to be able to produce higher quality diesel product that can be blended directly with the refining diesel pool. As typical green fuel feed stocks, such as rapeseed oil, soybean

oil, vegetable oils or tallow contain very low concentrations of sulfur, it is essential to keep the hydrotreating catalyst sulfided and activated by supplying the unit with a sulfiding agent. This results in the formation of  $H_2S$  as a product from the hydrotreating unit. Due to presence of nitrogen in the bio feed stock in small quantities, small amounts of ammonia will be present in the sour water produced in these units, which will contain quantities of  $CO_2$  as well. The sour water rates produced are typically higher than conventional hydrotreaters due to the presence of oxygen in the feed stock which is converted to water across the catalysts.

### 3.2.1 Possible Configurations

In the case of a grassroots biofuels facility, there is no existing sulfur complex infrastructure and the handling of the sour components needs to be determined using a blank slate. The options for the installation of a sour water stripper for the sour water produced in the facility and the facility to sweeten the sour gases and potentially sour LPG need to be evaluated on a case-by-case basis. This also means that ammonia will not be handled in a similar fashion compared to the co-processing scenarios mentioned above.

In the case of a full refinery conversion, there is typically already a number of absorbers, sour water strippers and sulfur recovery units available in the facility. The question in that case will be: is it possible to reuse any or part of it for the processing of the sour components and what will be the impact on the ability to deal with the ammonia produced?”

### 3.2.2 Acid gas composition in full biofuels facilities

In Table 4 a typical composition of the acid gas streams from a full biofuels facility are provided. As can be seen in this table, the amine acid gas is very lean and the sour water acid gas contains a very high concentration of  $CO_2$  to go with the  $NH_3$ . Also the total sulfur load from the facility is orders of magnitude lower than typical refineries.

Table 4: Acid gas compositions after conversion

Component	Amine Acid Gas		SW Acid Gas	
	Lbmol/h	Mol %	Lbmol/h	Mol %
$H_2$	0.69	1.30		
$CO_2$	40.33	76.12	2.34	18.80
$H_2S$	7.26	13.70	0.40	3.21
$NH_3$			4.36	35.02
$H_2O$	3.16	5.96	5.35	42.97
$C_1$	0.58	1.09		
$C_2$	0.17	0.32		
$C_3$	0.74	1.40		
$C_4$	0.05	0.09		
Total	52.98	100.00	12.45	100.00
Sulfur, LTPD	2.49		0.14	
$NH_3$ , TPD			0.89	

### **3.2.3 Options for Sour Product Processing**

#### **3.2.3.1 Grassroots facility**

In the case of a grassroots biofuels facility, there will be no sour gas, sour water or sulfur handling facilities available and with similar product specs as a conventional refinery, alternative paths need to be considered for the sweetening of the fuel gas, LPG, sour water and recycle gas streams from the biofuels facility. As can be seen in Table 4, the acid gases typically produced are not suitable for a sulfur recovery unit, which means that an SRU cannot be used to deal with the ammonia present in the sour water acid gas stream.

Processing the sour water is straight forward and for most facilities a conventional single stage sour water stripper can be considered. The sour water stripper will produce a sour water stripper acid gas stream that contains ammonia and CO<sub>2</sub> with low concentrations of H<sub>2</sub>S. Typical operating conditions are considered with overhead temperatures of 85°C (185°F) to prevent plugging of the acid gas piping and instrumentation with ammonium salts.

For the sour gases, the application can be considered to be more in the scavenging realm and therefore technologies

### **3.2.4 The trouble with Ammonia**

In a grassroots or conversion biofuels project, the amount of ammonia relative to the produced H<sub>2</sub>S is much higher than usual and add to it the fact that there is a lot of CO<sub>2</sub> in the sour gas streams as well as the sour water, there needs to be a different approach to how ammonia is handled. As there is still also the requirement to meet certain SO<sub>2</sub> emissions from the facility, the ammonia question cannot be looked at independently from the SO<sub>2</sub> emissions.

If there is a sulfur recovery unit available, for instance in a refinery conversion project or in the case of a biofuels plant near to or associated with an existing refinery that is still processing conventional hydrocarbon sources, there may be substantial benefits to evaluate the possibility to use the existing sulfur recovery unit in some fashion to deal with the ammonia. Due to the poor amine acid gas quality and the high relative concentration of ammonia as well as the substantially lower sulfur tonnage to be processed compared to conventional additional measures will need to be taken to ensure that the SRUs can operate properly.

Co-firing is one means to overcome the issues related to turndown. Typically, the acid gases produced in a biofuels facility are at least 1/10<sup>th</sup> of the typical acid gas loads of a conventional refinery and therefore the existing SRUs may have to be considered to operate at very high turndowns, sometimes as much as more than 50:1.

If there is no sulfur recovery unit available, the following options exist to manage the destruction of ammonia without a sulfur recovery unit:

- Remove the ammonia before the sulfur treatment
- Separate the ammonia from the H<sub>2</sub>S and process it in an incinerator
- Process the ammonia with H<sub>2</sub>S in an incinerator and scrub the off gas with caustic to reduce SO<sub>2</sub> emissions



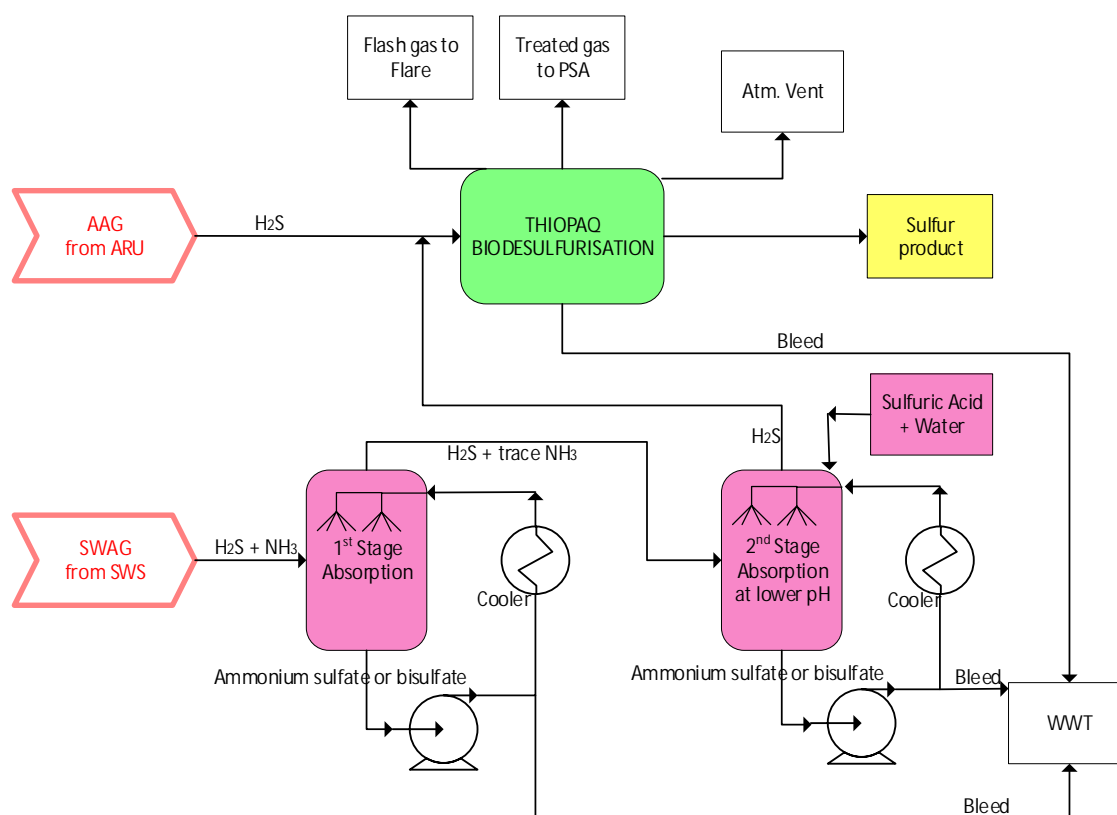
The key to an integral solution for the sour products from a biofuels facility, is how processing the  $\text{H}_2\text{S}$  and  $\text{NH}_3$  can be combined efficiently and effectively. As a sour water acid gas stream will pretty much always be produced in a biofuels facility, the key is really how to combine the processing of sour water stripper acid gas with the sweetening of all the sour streams. What are the options for sweetening for sour gas streams in a biofuels facility?

A conventional amine system can be installed, which produces an amine acid gas stream indicated in Table 4, which will then need to be processed somewhere. It could be processed in technologies such as LOCAT or Thiopaq, however both these technologies do not deal with ammonia, which means that alternative solutions would have to be investigated for the ammonia itself. In addition, both these technologies may not be able to handle the ammonia all together which means that the sour water stripper acid gas needs a different destination.

In absence of a sulfur recovery unit, ammonia incineration, which was already discussed in Section 2.3, is a very well-established methodology to deal with the ammonia in Biofuels facilities. As the SWAG also contains  $\text{H}_2\text{S}$ , the produced  $\text{SO}_2$  from the thermal oxidizer will need to be recovered before venting the off gases from the thermal oxidizer to the stack. The most practical method for this is the use of a Scrubber, in which typically caustic is used to remove the  $\text{SO}_2$ . It is possible to consider a Wet Sulfuric Acid technology as well, however due to the low sulfur tonnage, the economics are typically not favourable.

A two-stage sour water stripper can be considered, however due to the presence of substantial amounts of  $\text{CO}_2$  in the sour water, the ability to separate the ammonia and  $\text{H}_2\text{S}$  is complicated and as there is no real use for the ammonia, the installation of an ammonia thermal oxidizer will still be necessary.

One option that can be considered, is the removal of ammonia via an Ammonia Acid Wash ( $\text{NH}_3$  Scrubber), which consists of a dual stage absorption system designed to remove 99.9% of the ammonia from the sour acid gas stream. The  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , which are not absorbed in the scrubber, can then be routed to be scrubbed in an  $\text{H}_2\text{S}$  scavenging system as shown in **Figure 7** with Thiopaq as the technology for the recovery of sulfur. This scheme can be used though with any  $\text{H}_2\text{S}$  scavenging system.



**Figure 7. Combining ammonia acid wash with Thiopaq.**

The benefit of this system is that there are no difficult to operate thermal oxidizers required where NOx and lack of ammonia destruction can potentially cause issues with both emissions as well as plugging of colder equipment with ammonium salts.

Furthermore, consideration can be given to eliminate amine systems all together by treating sour streams directly in contactors using a REDOX or biological solvent to remove H<sub>2</sub>S. Only in the case of LPG streams, amine systems need to be absolutely considered.

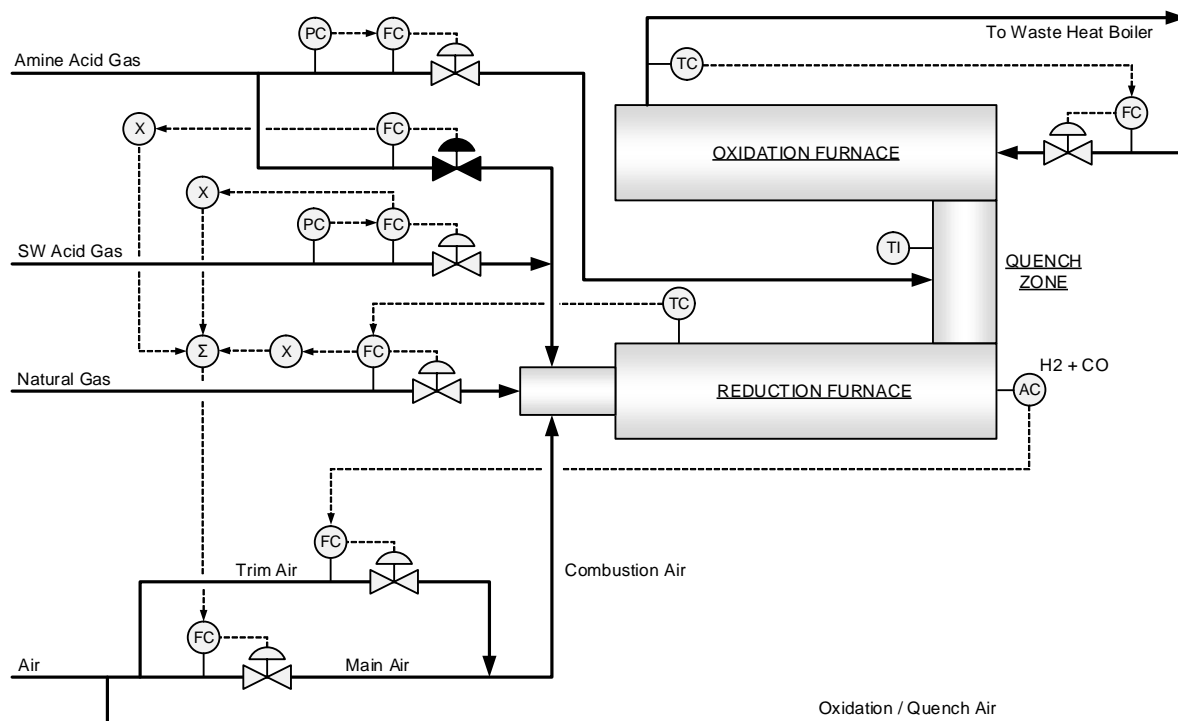
### 3.3 CASE STUDIES

#### 3.3.1 Case Study 1

A refinery biofuels conversion project included diesel hydrotreater feed capacity of 9,000 BPD and hydrocracking capacity of 45,000 BPD. Sulfur production of the facility was around 50 LTPD prior to the full conversion to bio feedstock.

Hydrotreater recycle hydrogen must contain 200 ppmv H<sub>2</sub>S to maintain catalyst metals in the sulfide state and thus prevent permanent over-reduction. The plant opted to do so by continuous injection of a sulfiding agent to avoid the CapEx and logistical complications of concentrated H<sub>2</sub>S recycle, which would have reduced net acid gas sulfur by 0.6 LTPD. While dimethyl disulfide (DMS) is typically employed for one-time conditioning of new / regenerated catalyst, safer alternatives more amenable to routine handling such as di-tertiary-butyl polysulfide (TBPS) – e.g.; SulfrZol 54® – are available (at a premium cost).





**Figure 9. Thermal Oxidizer**

Environmental regulations required a minimum Thermal Oxidizer temperature of 1500°F to ensure virtually complete CO destruction. In addition, temperatures greater than 1500°F would likely increase NO<sub>x</sub>, which the plant was under regulatory pressure to minimize. Excess quench air required to limit the Thermal Oxidizer temperatures to 1500°F resulted in almost 10 mol % residual O<sub>2</sub>. The silver lining in that cloud is that oxidation air is optimized by simple temperature control independent of potentially unreliable O<sub>2</sub> analyzers.

However, high % O<sub>2</sub> can have unintended punitive consequences in the likely event environmental regulations require correction of measured stack concentrations to X % O<sub>2</sub> according to the formula in **Table 5** where X will typically = 0 or 3:

**Table 5: Normal Stack Emission Correction for Excess O<sub>2</sub>**

			Concentration (dry basis)
Let	C	=	Component, corrected, ppmv
	R	=	Component, raw, ppmv
	X	=	Reference O <sub>2</sub> in stack, mol %
	A	=	Actual O <sub>2</sub> in stack, mol %
Where	21.0	=	O <sub>2</sub> in air, mol %
Then	C	=	$R * (21.0 - X) / (21.0 - A)$

Stack emission concentrations measured at O<sub>2</sub> concentrations greater than the reference value (0 or 3%) increase when corrected. At a reference value of 0% O<sub>2</sub>, for example, 100 ppmv measured at 10% O<sub>2</sub> equates to  $100 * (21 - 0) / (21 - 10) = 191$  ppmv corrected. In a typical Claus thermal oxidizer, high O<sub>2</sub> represents unnecessary dilution. In this case, however, it is a process requirement. That distinction should be made when negotiating environmental permit limits.

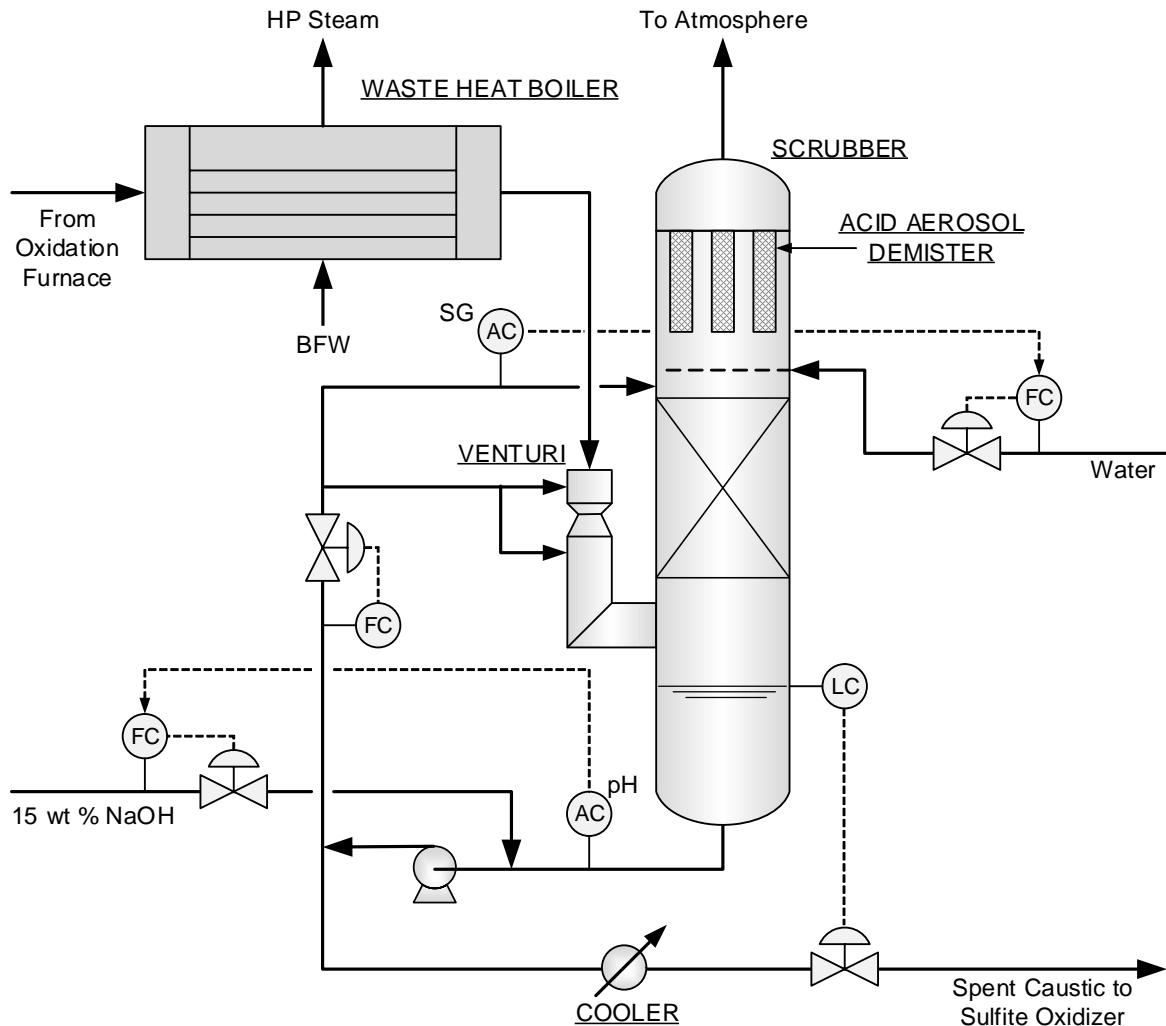
The Oxidation Furnace effluent is cooled from 1500°F to 530°F by generation of saturated 650-psig steam in a kettle waste heat boiler. The need for selective catalytic reduction (SCR) of NO<sub>x</sub> was deemed unnecessary. Had an SCR been employed, cooling to 450°F would have been considered in order to minimize potential catalyst fouling with ammonium bisulfate.

Potential cooling is limited by the sulfuric acid dew point. Above 1000°C (1832°F), 1-5% of the SO<sub>2</sub> will typically be oxidized by O<sub>2</sub> to SO<sub>3</sub>, forming sulfuric acid vapor (H<sub>2</sub>SO<sub>4</sub>). While lower temperatures favor SO<sub>3</sub> formation, the reaction does not readily occur below 1000°C because of the high activation energy required, and it is thus assumed that the SO<sub>3</sub> content is set by the equilibrium at 1000°C, for which equilibrium correlations exist. Four different methods predicted dew points of 222-293°F. Another literature source simply cites 350°F as a safe upper limit. [7]

Special design considerations to efficiently mix the Reduction Furnace effluent and oxidation air as quickly as possible would seem advisable, since most SO<sub>3</sub> / NO<sub>x</sub> is made during the transition. If so, the principle appears to have been generally overlooked by industry.

Hot gases are initially quenched with a recirculating caustic solution sidestream in a venturi scrubber at the inlet to the packed column to prevent localized high temperature corrosion of column internals despite SS construction. In this case both the venturi and scrubber were constructed of 316 SS. Fiberglass is a common alternative for the column shell, and brick-lined venturis are sometimes employed when there is greater incentive to minimize upstream cooling. Maximum recommended inlet temperature to a SS venturi is 650°F. (Figure 10)





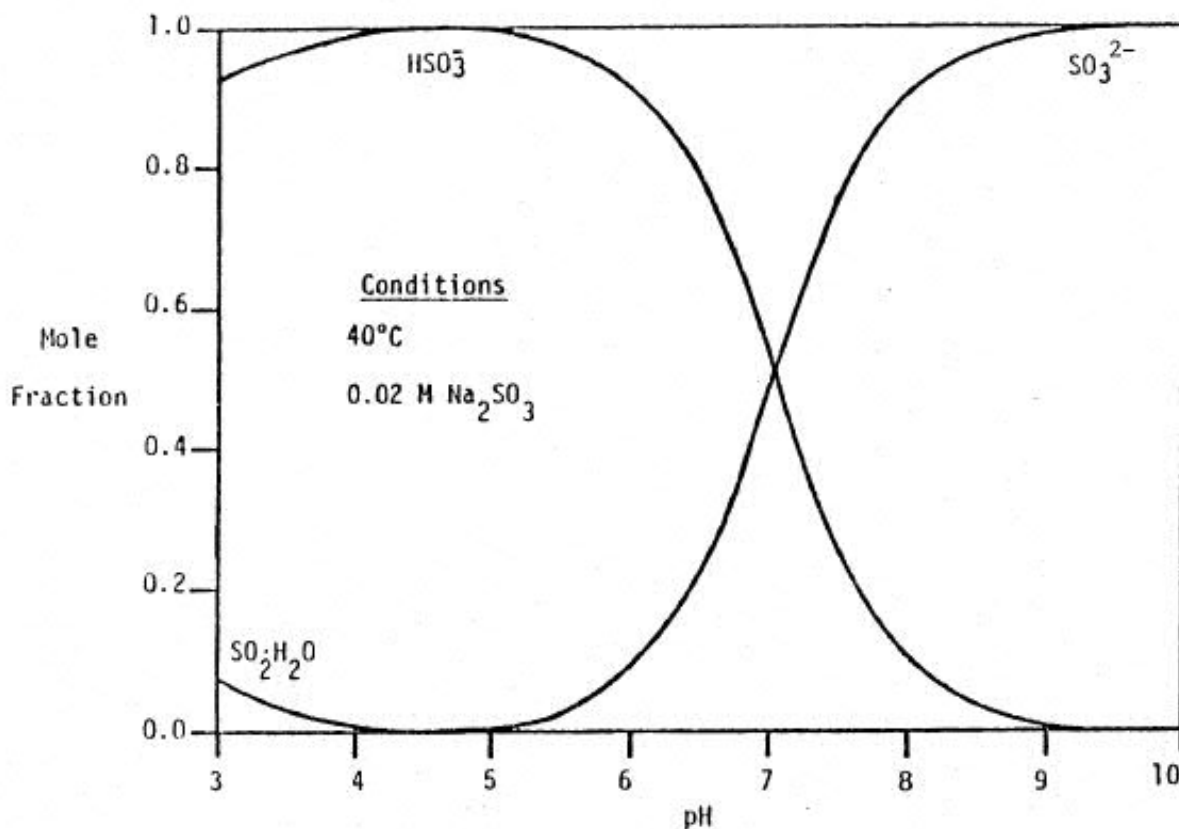
**Figure 10. Caustic Scrubber**

Some sulfuric acid vapor will be absorbed in the venturi but, once the gas is quenched below the dew point, resultant acid aerosol mist particles lack the momentum required for efficient scrubbing upon impingement with caustic solution droplets. Counterintuitively, many thus pass unabsorbed through the scrubber.

Condensed sulfuric acid mist (SAM) tends to form a white visible plume upon discharge to atmosphere. Perhaps for this reason, it is often treated quantitatively as 10+ micron particle (PM10) emissions, despite the fact that acid mist particles tend to be sub-micron. In this case the plant had separate annual PM10 and SAM mass limits, where allowable SAM emissions were 100 x allowable PM10 emissions.

Specialized “candle filters” designed to rely on Brownian diffusion are located at the scrubber outlet to coalesce sub-micron SAM. Vendors claim up to 99.9% particulate removal with pressure drops of 10-20 inches H<sub>2</sub>O. Fouling can be problematic if particulates tend to be sticky. Wet electrostatic precipitators (WESP) are considered a superior alternative if the additional cost can be justified.

The circulating liquor contains the equivalent of 5-6 wt-% sodium hydroxide (NaOH), with roughly 85% as sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and the balance split between sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and sodium bisulfite ( $\text{NaHSO}_3$ ). Bisulfite/sulfite equilibrium is highly buffered, making it relatively easy to maintain an optimum pH of 7-8 while absorbing negligible  $\text{CO}_2$ . (**Figure 11**)



**Figure 11. Effect of pH on the Relative Concentrations of Sulfur Species in Solution**

In this case 15 wt-% NaOH is added on pH control, and water added separately to maintain a specific gravity of 1.08. It was decided to add the makeup water via a wash tray above the packed bed on the premise that knocking down entrained liquor may tend to reduce fouling of the candle filters. This does not appear to be normal practice, so the value in doing so remains to be seen.

In addition to being corrosive to carbon steel, sulfite/bisulfite have a chemical oxygen demand (COD) and must be oxidized to sulfate before discharge to the environment.

### 3.3.2 Case Study 2

In the third case study, a grassroots renewable diesel facility was to be built near to a refinery with the ability to build interconnecting piping between the new facility and the existing sulfur complex of the refinery. This option included the potential to enrich the acid gas from the primary unit to be able to recycle a rich  $\text{H}_2\text{S}$  stream back to the hydrotreater for the continuous sulfiding of the hydrotreating catalyst to maintain activity.

In addition, ammonia from the sour water stripper needed to be considered in the different options to determine what the optimal possibility was to process it if not sulfur recovery unit was available at the new renewable diesel hydrotreater. The paper that was presented on this project is referred to in reference 10.

The conclusion of the study was that it was technically more prudent to integrate the sour water stripper operation into the existing refinery complex. Several different options were evaluated to bring the sour water associated with the new renewable diesel hydrotreater to the existing sulfur complex to eliminate the more complicated options to deal with the ammonia at the new hydrotreater location. These options included the installation of a new sour water stripper in the existing sulfur complex to replace the one that was too small to handle the existing loads as well as the installation of a sour water concentrator to allow the use of the existing sour water stripper.

By integrating the sour water stripping into the existing complex, the ammonia issue could be resolved in a more conventional methodology using the existing SRU. One item of note though was that due to the high concentration of CO<sub>2</sub> in the sour water, the bleed stream of the Sour Water Concentrator option still needed the installation of a caustic scrubber to reduce the emissions of SO<sub>2</sub>.

In the end due to complications with routing sour stream across public roads and the cost associated with long runs of piping, the customer decided to stay with the installation of a dedicated sulfur complex for the new renewable diesel hydrotreater.

## Conclusions

Ammonia is a crucial component to be considered in decisions regarding processing bio feedstocks. In the case of co-processing, the impact is typically minimal as the existing sulfur recovery units can still be maintained in operation at fairly similar conditions. Some additional oxygen or split flow to the second zone of the thermal reactor may need to be considered, however in practice there should be very limited impact on operation from an ammonia perspective.

In the case of a full conversion or grassroots biofuel facility, the ammonia can pose a substantial issue as in most scenarios there is no feasible way to either reuse an existing SRU or install a new SRU that can handle the low concentrations of H<sub>2</sub>S in the total acid gas. Therefore, alternative methods need to be found in the line up that ensure that the ammonia does not become a source of emissions. Options discussed include high turndown SRU operation with co-firing, ammonia scrubbing as part of the technology solution and ammonia incineration with caustic scrubbing to remove SO<sub>2</sub>. Each potential option needs to be evaluated from an OPEX and CAPEX perspective as well as how it impact the facility environmentally.

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