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Innovative process for multi-point sequential SO2 injection in Claus Sulfur Recovery Unit

JACK D. ALLENBERG, P.E.
STROM SMITH, ANDY MOORE, P.E.
Sulfur Operations Support, Inc
Ocean Springs, Mississippi, USA

Abstract: This paper describes a newly patented process utilizing distributed SO_2 injection to increase the capacity of existing Claus units. It also reduces the equipment requirement for new plant sulfur recovery unit applications by eliminating the requirement for traditional thermal reactors, large waste heat boilers, and traditional re-heaters. The SO_2 is produced by a unique processing unit that also provides high quality nitrogen for use onsite as a by-product.

1. Introduction and Background

The use of sulfur dioxide (SO_2) to increase capacity in Claus units was most recently proposed in the early 1990's by Ron Schendel, P.E. at Brown and Root Braun [(1)]. To date, there have been very few practical commercial applications of the process for Claus units. The most probable reason is that most Claus unit operators did not want to be the first to utilize SO_2 technology.

Following is a brief explanation of the rationale for developing a process to add SO_2 to multiple stages in typical Claus units:

The familiar Claus reaction is:

$$2H_2S+SO_2 \rightarrow 3S+2H_2O \quad \text{Equation 1.}$$

Amine units treat hydrocarbon streams to, among other things, remove H_2S. Recovered H_2S ends up in the amine unit off gas stream as amine acid gas (AAG). The typical Claus operation is to feed (AAG) to the SRU burner to produce SO_2 by combustion to enable the Claus reaction.

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O \quad \text{Equation 2.}$$

The overall desired reaction is then:

$$3H_2S + 3/2O_2 \rightarrow 3S + 3H_2O \quad \text{Equation 3.}$$

The O_2 is normally supplied by air, so for every mole of O_2 there is about 4 moles of N_2 and a little H_2O (Assuming air composition: 19.6% O_2, 78.4% N_2, and 2% H_2O)

The reaction with air as the oxidant (and including some humidity) is then approximately:

$$3H_2S + 3/2O_2 + 6\ N_2 + 0.15\ H_2O \rightarrow 3S + 3.15\ H_2O + 6\ N_2 \quad \text{Equation 4.}$$

2 SRU Capacity Limiting Factors

The SRU equipment and piping sizing is primarily based on mass flow rate. The pressure drop through the SRU is usually the limiting factor for overall capacity. The SRU pressure drop approximates that of a fixed orifice and is proportional to the mass flow through the SRU squared.

$$\Delta\text{Pressure} = f\ (\text{Mass Flow rate})^2 \quad \text{Equation 5.}$$

A large portion of this pressure drop usually occurs in the thermal section of the Claus unit. (burner, thermal reactor, waste heat boiler, and the first sulfur condenser) This area is where the mass flow rate is the greatest. After mass flow rate, re-heat duty is also a limiting factor.

3 Gaining Additional Capacity

Capacity increases can be gained by:

- Eliminating non-reactive mass flow
- Minimizing H_2O in the process stream

A comparison of the products of Equation 4. above with those of Equation 3, shows that on a molar basis there are 12.2 moles (321 lb/hr) of product from Equation 4. and only 6 moles (150 lb/hr) from Equation 3. Using air as the oxidant results in at least 321/150 or a 114% increase in the mass flow rate to the SRU to produce the same amount of sulfur.
In addition, burning H_2S to generate the SO_2 for the Claus reaction also increases the water concentration in the process stream which promotes the reverse reaction in Equation 3. (Each mole of SO_2 generated using H_2S and air is accompanied by 1 mole of H_2O, and 0.15 moles H_2O(humidity). Thus, using oxygen instead of air as the source of O_2 Equation 3, will yield a capacity increase, but:

3.1 Adding oxygen to the airstream will reduce the mass flow rate and add capacity. The oxygen greatly increases the thermal reactor temperature usually requiring replacement of the refractory system. If the air stream oxygen content exceeds about 28%, the air piping material must be upgraded to an appropriate alloy. Many follow the guidelines of the industrial gas supplier organizations such as IHC, CGA, EIGA, or JIMGA. Above 28%, the oxygen must be injected directly into the burner area.

3.2 If SO_2 is added to the air stream, the capacity can be increased but is limited to about a 15% increase in AAG feed to the SRU to yield the same mass flow to the waste heat boiler in a typical refinery compared to the traditional operation. (See Case Studies below)

4 An Innovative approach for Capacity Gains by Distributed or Multipoint SO_2 Injection

The SO_2 can be added at multiple stages of the SRU instead of injecting it into the airstream. Combustion air flow will be limited to the amount required to destroy the ammonia and hydrocarbons in the sour water acid gas (SWAG) if present, and a small amount of AAG to provide a stable flame in the SRU burner. This will greatly reduce the mass flow rate to the front end of the SRU and allow for increasing the capacity by about 40% for the same mass flow rate to the waste heat boiler. The SRU recovery can be optimized by varying the SO_2 flow to each injection point.

5 SO_2 Supply

There are several possible sources of SO_2. It can be purchased commercially in liquid form and then vaporized onsite. A SO_2 generation unit can be added to the site. There are two basic variations. Both burn liquid sulfur to form SO_2. One utilizes pure oxygen, and the other uses air. The advantage of the air based unit is that it also provides a source of high quality nitrogen for onsite usage at no extra cost

6 Case Studies of Typical Refinery and Gas Plant Sulfur Recovery Units

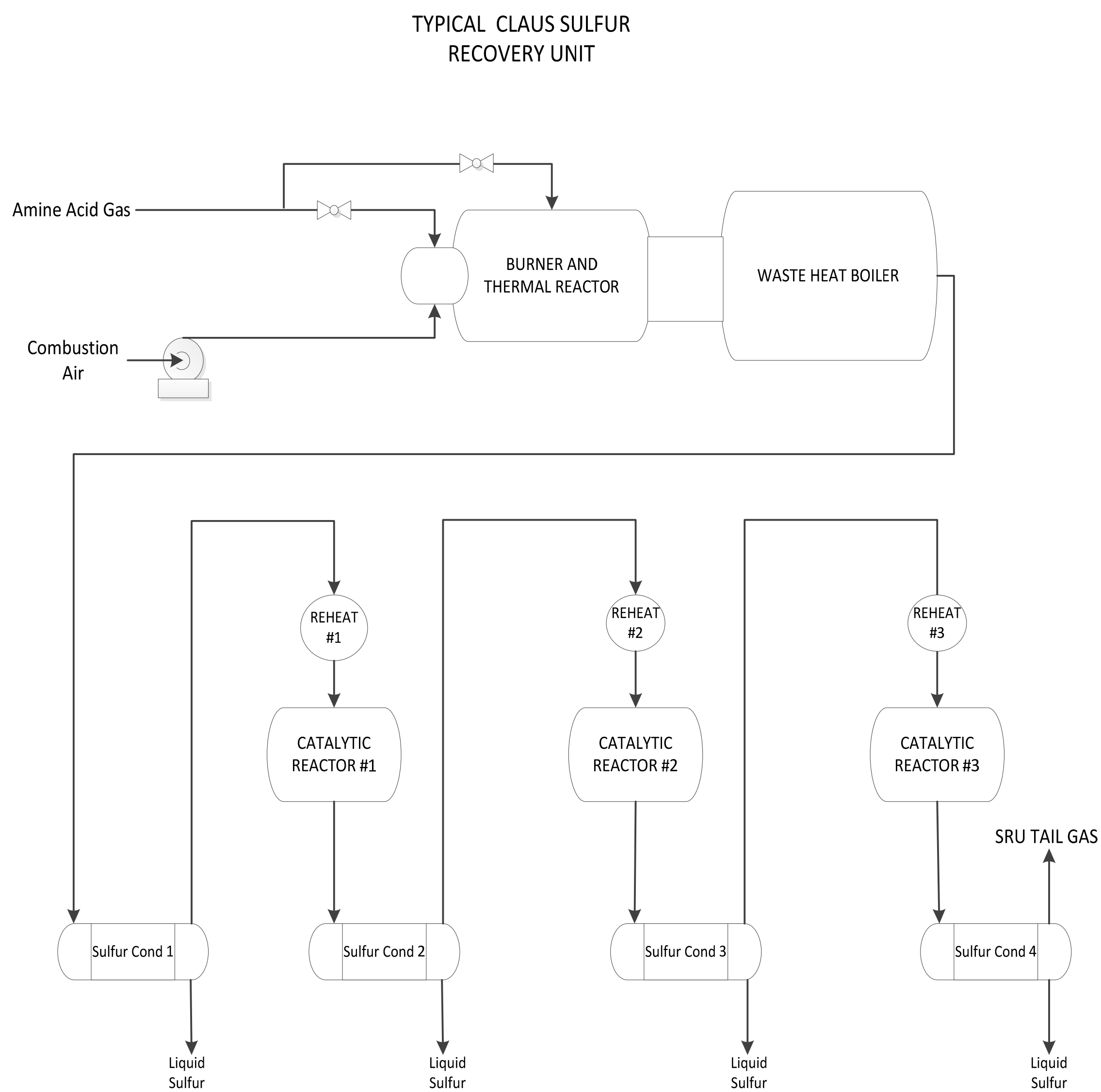
These studies were developed by modeling typical Claus sulfur recovery units with Bryan Research and Engineering ProMax software. Real world constraints were applied to match the simulated results to observed results from similar operating units that we have designed and operated. These results were also checked against identical models using Virtual Materials Group VMGSim™ simulation software. We found good agreement between the simulation model results.

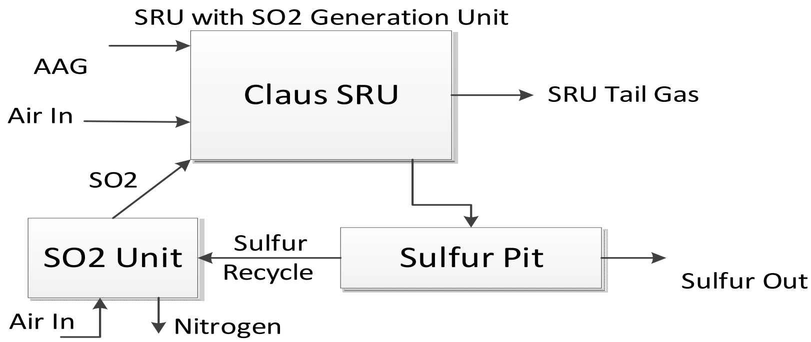
As mentioned above, the pressure drop across the Claus unit usually limits the ultimate processing capacity. This pressure drop is a function of the mass flow through the SRU squared. We have selected the mass flow rate (lb/hr) into the thermal stage (burner, thermal reactor, and waste heat boiler), and each of three catalytic stages as the comparison basis to estimate the maximum practical through-put for a given Claus unit with different feed rates.

The first study examines a typical three bed Claus unit with a rich (AAG) feed only. The AAG composition is:

81.4% H_2S, 15% CO_2, 3% H_2O, 0.5% CH_4, and 0.1% C_2H_6

The first has a normal combustion air feed, and the second has SO_2 added to the air stream only.





SRU Data

CASE #1 (No SO2)		Thermal Lb/Hr	Catalytic #1 Lb/Hr	Catalytic #2 Lb/Hr	Catalytic #3 Lb/Hr
Sulfur In (LTPD)	140	44817	35906	33169	32374
Sulfur Out(LTPD)	137	95.5	29.3	8.5	3.9
Recovery(%)	98	68	66	56	60

CASE #2 (SO2 in Air)		Thermal Lb/Hr	Catalytic #1 Lb/Hr	Catalytic #2 Lb/Hr	Catalytic #3 Lb/Hr
Sulfur In (LTPD)	161	45317	34490	29863	28447
Sulfur Out(LTPD)	158	116	49	15	6
Sulfur Recycle (LTPD)	28.7				
Recovery(%)	98	72	66.5	62.4	66

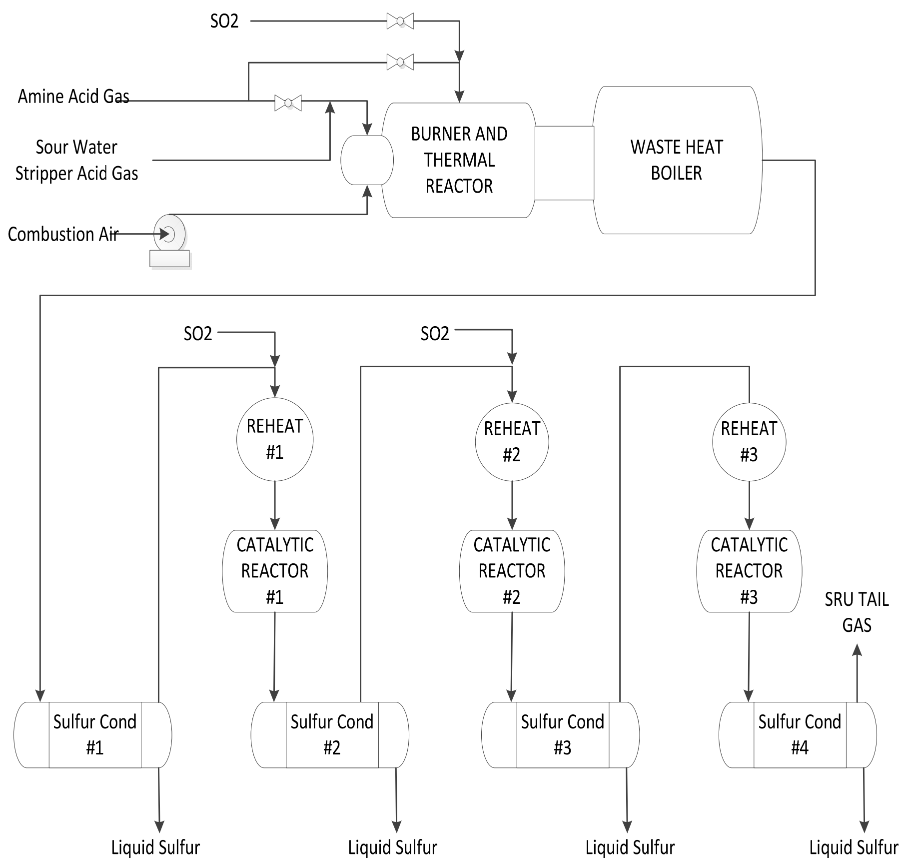
The tables above contain the pertinent data for the SRU with normal Combustion Air and the same SRU with SO_2 added to the Combustion Air stream.

The addition of SO_2 to the air stream allows the fresh sulfur feed to the unit to be increased 15% without any modification to the SRU. The overall sulfur recovery percentage is about the same for either case.

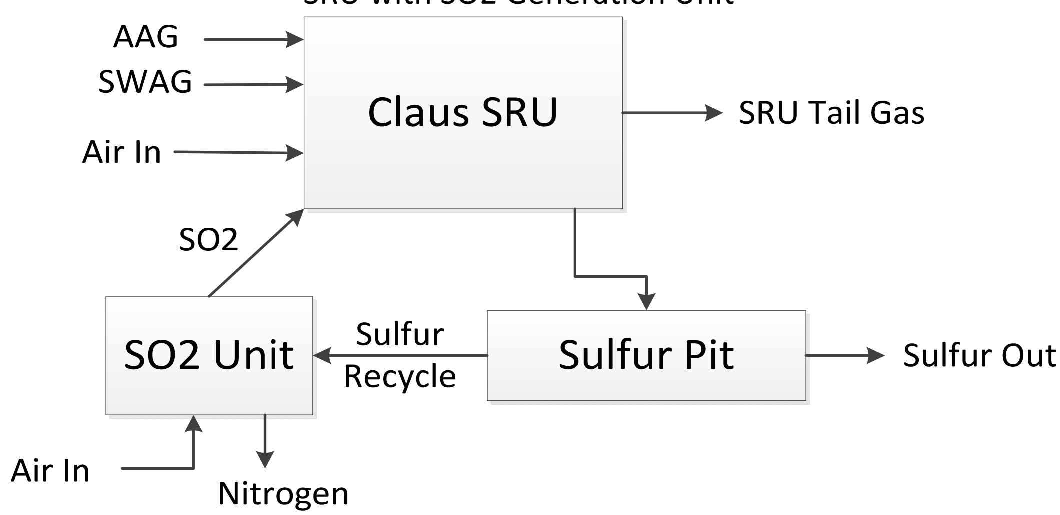
The next two studies utilize multi-point SO_2 injection to increase SRU capacity. The first studies a typical refinery SRU processing the same AAG feed as above plus a sour water stripper acid gas (SWAG) that is approximately 28% of the total acid gas fed to the units. The composition of the SWAG is:

30% H_2S, 35% NH_3, 33% H_2O, 1% CH_4, and 1% N_2

TYPICAL REFINERY CLAUS SULFUR RECOVERY UNIT WITH MULTI-POINT SO2 INJECTION



SRU with SO2 Generation Unit



SRU Data

CASE #3 (No SO2)		Thermal Lb/Hr	Catalytic #1 Lb/Hr	Catalytic #2 Lb/Hr	Catalytic #3 Lb/Hr
Sulfur In (LTPD)	160	60567	50725	47368	46423
Sulfur Out(LTPD)	157	105.5	36	10	5.2
Recovery(%)	98	66	65	53	58
Re-heat Duty			2 mmBtu/Hr	1.3 mmBtu/Hr	.92 mmBtu/Hr

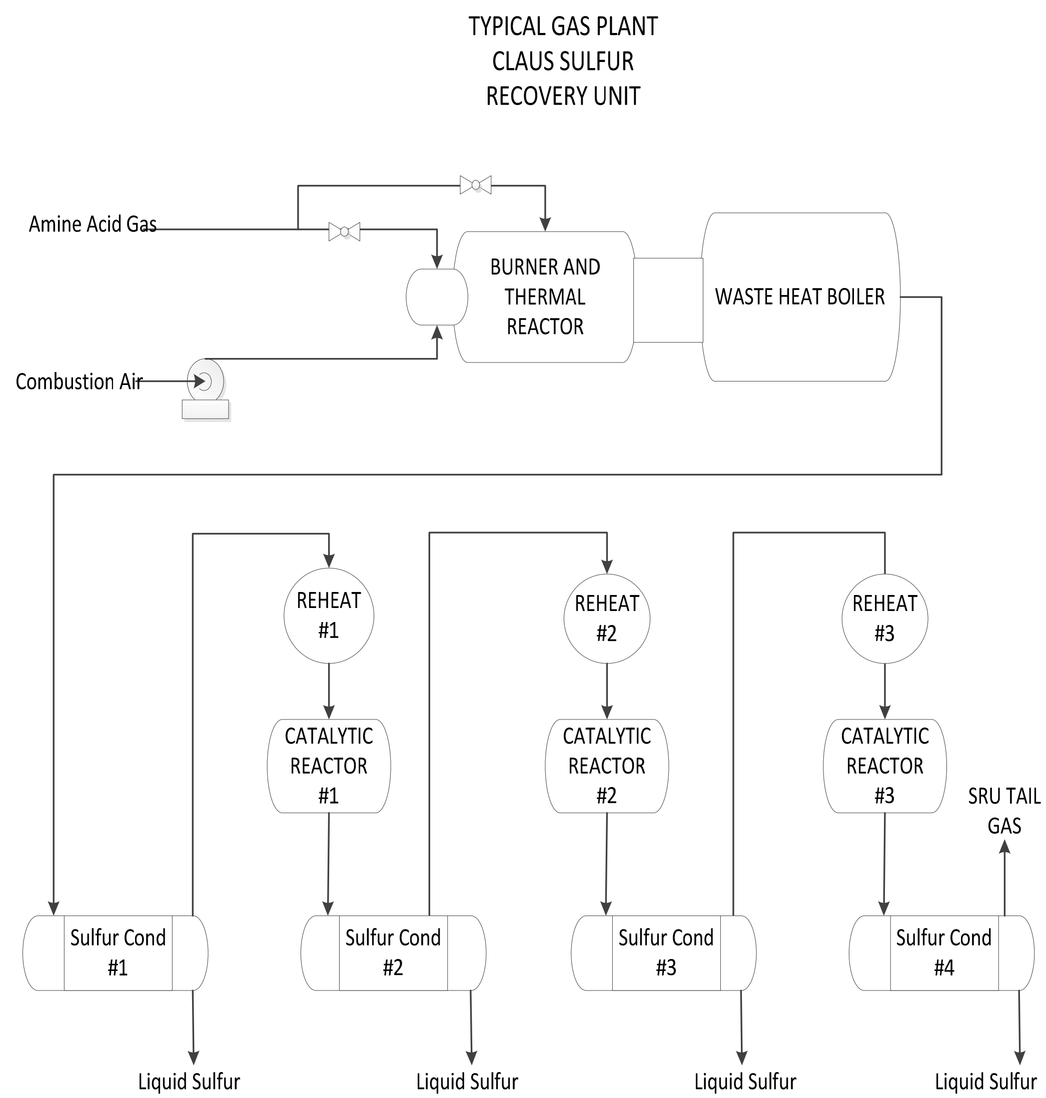
CASE #4 (SO2 MP Inj)		Thermal Lb/Hr	Catalytic #1 Lb/Hr	Catalytic #2 Lb/Hr	Catalytic #3 Lb/Hr
Sulfur In (LTPD)	225	60446	49732	47173	41942
Sulfur Out(LTPD) Sulfur Recycle (LTPD)	218 80	144	79	56	19.5
Recovery(%) Rec Fresh Feed	98 97	64	58.4	68	75
Re-heat Duty			None	.8 mmBtu/Hr	.71 mmBtu/Hr

Distributing the SO_2 injection allows minimization of the mass flow to the SRU thermal section. In case #4 above, the fresh sulfur feed to the unit has been increased by 41%, but the mass flow to the section is essentially the same. The mass flow to the catalytic stages is about the same as case #3 above. Most SRU thermal sections are designed conservatively to allow for feed composition variations. Further capacity increases are possible depending on the actual unit equipment design.

The re-heater available duty is usually the second most factor affecting SRU capacity. Note that the first catalytic stage requires no re-heat duty. The total duty for the other two catalytic stages is about 68% of that required for case #3 above.

The last two case studies a typical gas plant SRU. The gas plant cases are three bed units with a typical low quality AAG feed of:

46% H_2S, 1.5% CH_4, 9% H_2O, and 43.5% CO_2


TYPICAL GAS PLANT
CLAUS SULFUR
RECOVERY UNIT
Amine Acid Gas
Combustion Air
BURNER AND
THERMAL
REACTOR
WASTE HEAT BOILER
REHEAT
#1
REHEAT
#2
REHEAT
#3
CATALYTIC
REACTOR
#1
CATALYTIC
REACTOR
#2
CATALYTIC
REACTOR
#3
SRU TAIL
GAS
Sulfur Cond
#1
Sulfur Cond
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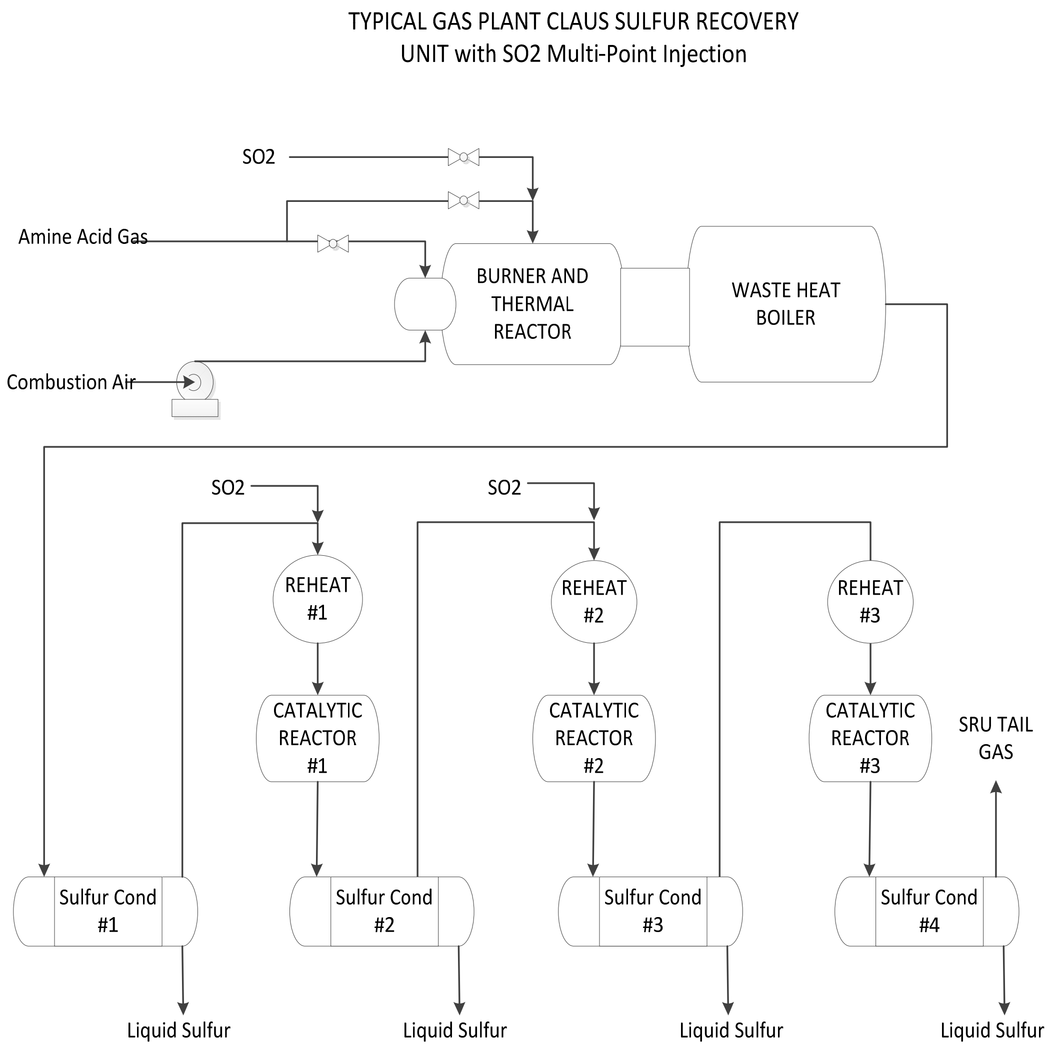
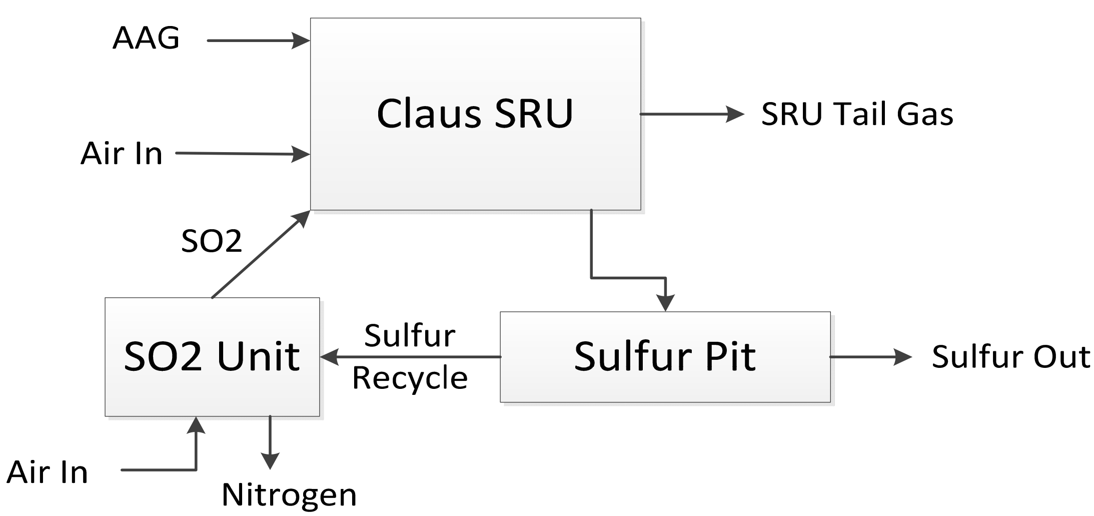


This unit is the same as the previous plus the addition of the SO_2 injection points.



SRU Data

CASE #6 (No SO2)		Thermal Lb/Hr	Catalytic #1 Lb/Hr	Catalytic #2 Lb/Hr	Catalytic #3 Lb/Hr
Sulfur In (LTPD)	100	42937	37155	34642	33909
Sulfur Out(LTPD)	98	62	27	8	1.3
Recovery(%)	98	62	71	70	49
Re-heat Duty			1.1mmBtu/Hr	.6 mmBtu/Hr	.8 mmBtu/Hr

CASE #7 (SO2 MP Inj)		Thermal Lb/Hr	Catalytic #1 Lb/Hr	Catalytic #2 Lb/Hr	Catalytic #3 Lb/Hr
Sulfur In (LTPD)	135	42412	40606	36754	33761
Sulfur Out(LTPD) Sulfur Recycle (LTPD)	130.5 56.4	59.2	69.7	43.5	14.5
Recovery(%) Rec Fresh Feed	98 97	44	62	76	76
Re-heat Duty			None	None	0.9 mmBtu/Hr

The feed to the unit was increased 35% while keeping the average mass flow to the thermal stage and the first catalytic stage about the same as the normal case. No reheat duty is required for the first two catalytic stages.

7 Process Testing and Results

A small test skid was fabricated and installed in a Claus Sulfur Recovery Unit to verify the viability of SO_2 Multi-point injection to increase the processing capacity of the Claus unit.

The only modification of the SRU for testing was to install tie-ins for the SO_2 injection as depicted on page 6. Above.

7.1 The test skid consiste of metering valves, flow transmitters, digital flow meters, and shutdown valves. The SRU was operating normally processing Amine Acid(AAG) gas and Sour Water Stripper Acid gas(SWAG). The SWAG flow was 61.5% of the total feed to the SRU and the AAG was 38.5% of the total flow. The composition of the AAG was approximately 95% H_2S, 3% H_2O, and 2% CO_2. The SWAG composition was approximately 33% H_2S, 33% NH_3, and 33% H_2O.

7.2 All of the SWAG was directed to the SRU burner, and all of the AAG was directed to the rear chamber of the thermal reactor.

7.3 The test procedure was as follows:

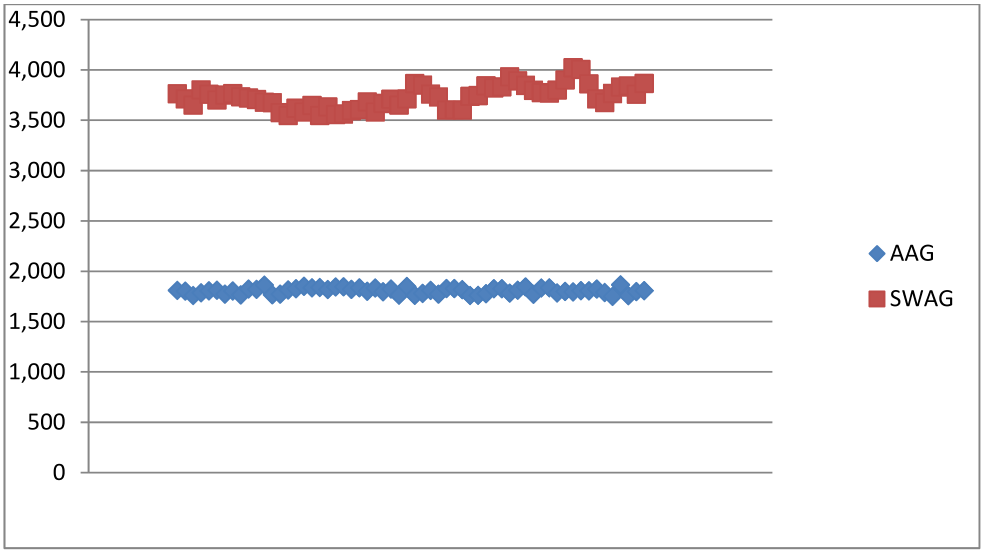
The Combustion Air to the burner was slowly reduced while SO_2 was slowly introduced to the injection points. 50% of the SO_2 was injected at the rear chamber of the thermal reactor, 25% of the SO_2 flow was injected into the first catalytic reactor, and the remainder of the SO_2 was injected into the second catalytic reactor. The SRU tailgas was monitored to maintain the ratio of H_2S to SO_2 at 2.0. The sufficient combustion air flow to the burner was maintained to destroy the NH_3 in the SWAG and maintain the temperature in the front chamber of the thermal reactor.

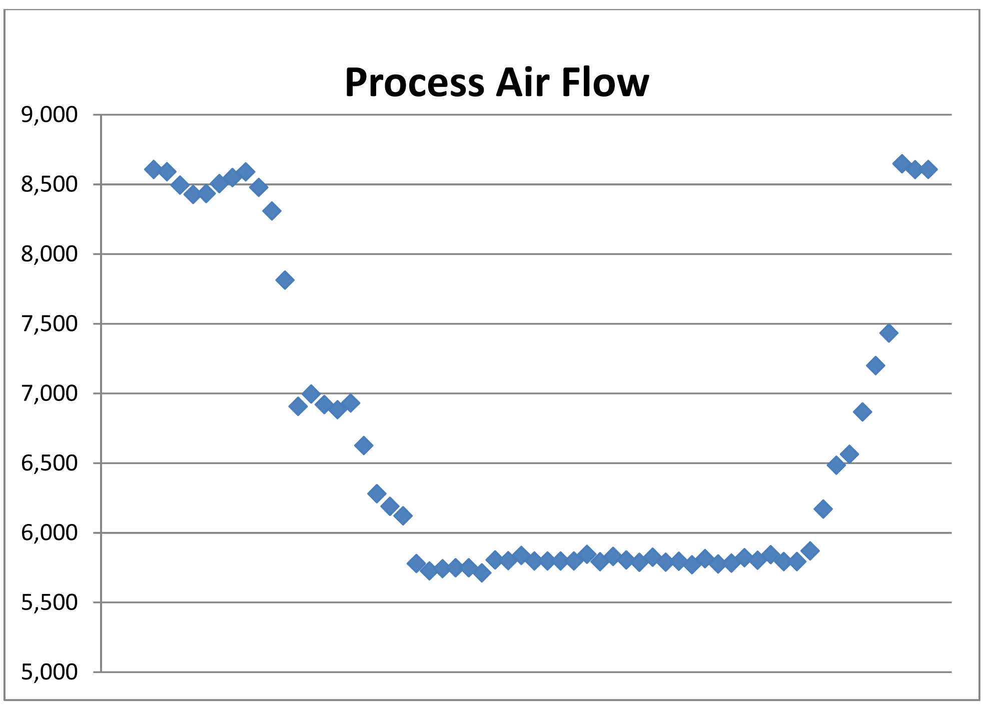
Below are graphs showing the Air Flow, the AAG flow, the SWAG flow, and the burner pressure. Note that although the acid gas feed to the unit was fairly constant, the front end pressure at the burner decreased dramatically as the air was reduced and partially replaced by SO_2.

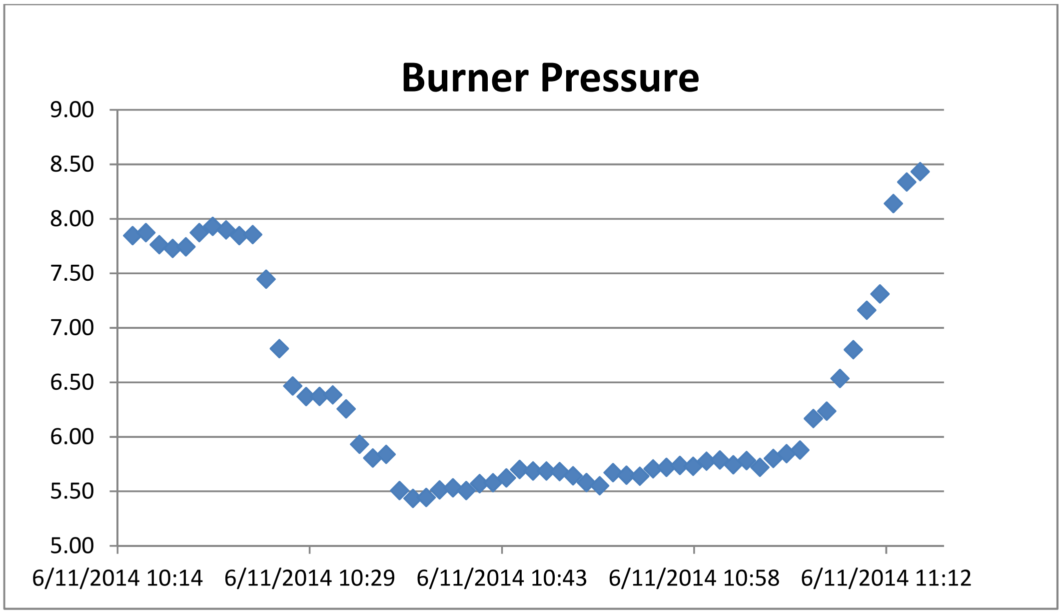
If more acid gas had been available, we could have increased the acid gas feed rate until the burner pressure increased to the 8.5 PSIG range for a considerable increase in the total sulfur throughput.

This SRU is rather unique in that it was operating well while processing 160% more SWAG than AAG. We typically design a Claus unit to process SWAG in the range of 15 to 20 % of the total acid gas fed to the unit.

The other effect noted was a decrease in the duty of the first and second rehaters. Conventional Claus units require more reheat duty as the acid gas feed is increased and become secondary bottlenecks limiting increased production.


4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
AAG
SWAG


Process Air Flow
9,000
8,500
8,000
7,500
7,000
6,500
6,000
5,500
5,000



8. Conclusions

These studies have shown the feasibility of multi-point SO_2 injection to increase the capacity of existing Claus based Sulfur Recovery Units. For most units, only minor modifications are required to achieve the capacity gains outlined above.

The multi-point injection of SO_2 provides a great amount of flexibility for SRU performance optimization.

The addition of a SO_2 generation unit based on proven existing technology is straightforward. An available option is to use air to oxidize the sulfur to produce SO_2. This process generates 4 Moles of high purity dry N_2 for every Mole of SO_2 produced. The cost of the SO_2 unit is much less than the cost of adding an additional Claus unit. The SO_2 unit may be shut down when not required and the SRU can then be operated normally.

This technology can greatly affect future SRU designs with regard to equipment sizing versus capacity.

REFERENCES

1. Technology, Oil and Gas Journal Sept 1993, pp. 33-66.