Using a Process Simulator to Improve Sulphur Recovery

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ABSTRACT

Increasingly stringent sulphur emissions regulations often require renovation of older sulphur recovery units (SRUs) to improve overall recovery. Optimization or modification of an existing Claus SRU or the design of a new unit can be simplified by use of a process simulator. In this paper, Karl W. Mattsson-Bozé and Lili G. Lyddon of Bryan Research & Engineering present examples to show how TSWEET® can be used to model a Claus SRU and then to simulate modifications to aid in evaluating the best design.

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INTRODUCTION

Exploring plant modifications to improve sulphur recovery in an existing unit can be a very difficult process due to the large number of possible design variations and an even greater number of feed compositions. A process simulator simplifies the task of evaluating Claus sulphur recovery unit operations such that a wide variety of modifications can be investigated. Almost any design option for a new Claus unit can be modelled based on feed composition. The most feasible options which should be considered for the final design can be determined quickly with the aid of a process simulator.

Two examples are presented to illustrate the use of the process simulator. The first example assumes that an existing four bed Claus sulphur recovery unit with lean feed and a sulphur recovery of 96.3% must be modified to achieve at least 99% recovery. Some of the options investigated include replacing the fourth bed with a cold (sub-dewpoint) bed or direct oxidation bed, oxygen enrichment of the combustion air, use of a catalytic burner, and the addition of a SCOT type tail gas cleanup unit. Combinations of these options are also considered.

The second example shows how current plant operations may be optimized by changing operating conditions without adding any new process equipment.

Example 1 – Matching plant data for an existing unit

The first example involves improving the sulphur recovery of an existing four bed Claus sulphur recovery unit currently operating at 96.3% sulphur recovery.[1] *Figure 1* shows the process flowsheet for the model. TSWEET uses three unit operations to model the burner/waste heat boiler. The burner unit operation simulates the combustion of the acid gas, with COS and CS_2 formation calculated by a correlation. COS and CS_2 concentrations can also be user set, as in this example.

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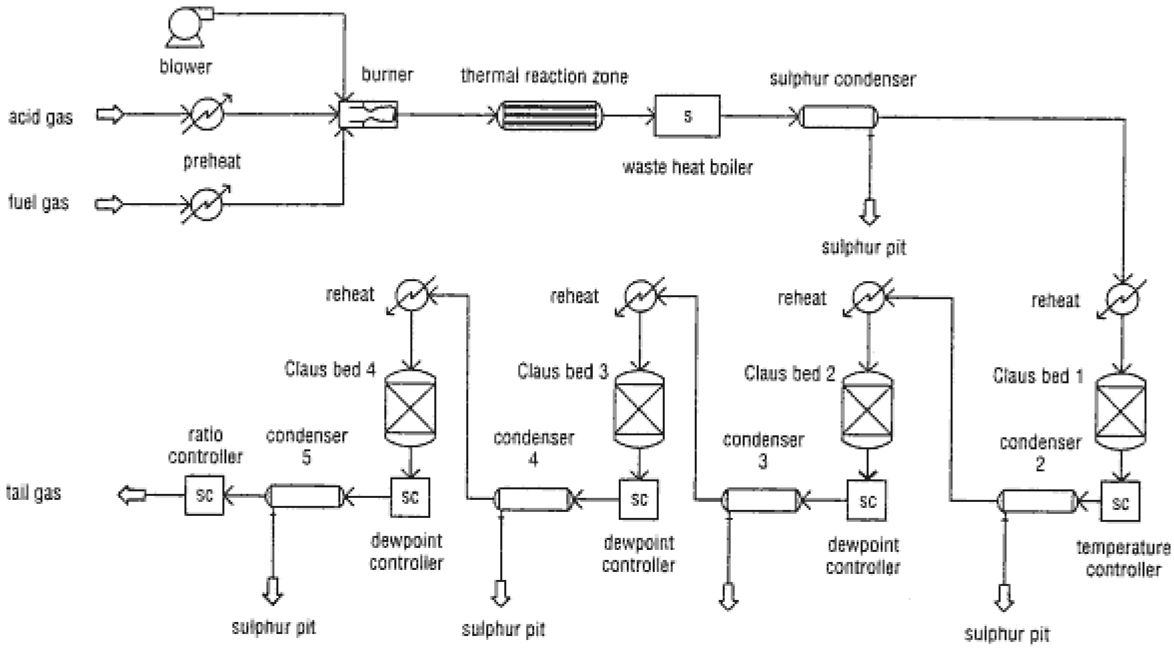

Figure 1. Process flowsheet for Example 1.

The thermal reaction zone simulates the reaction furnace area and also the first pass of the waste heat boiler with an exit temperature of 1200°F (650°C). In the thermal reaction zone, large amounts of free sulphur, hydrogen, and water recombine into H_2S and SO_2. The second pass of the waste heat boiler is simulated by the sulphur redistribution unit operation with an exit temperature of 600°F (315°C). The primary reaction in the sulphur redistribution unit operation is the redistribution of S_2 to S_8. Since the feed to this plant is very lean, containing only 21% H_2S, a special burner to burn the fuel gas separately from the acid gas is used in combination with acid gas preheat to achieve a stable combustion temperature. The low percentage of H_2S in the feed will make it difficult to achieve the required 99.0% recovery.

In order to match plant data, the "quench temperatures" in the thermal reaction zone unit operation in the TSWEET simulation are adjusted until a reasonable match with the reported plant data compositions out of the waste heat boiler are achieved. In addition, the acid gas and fuel gas preheat temperatures are adjusted to match the reported burner temperature. A controller ensures that the first Claus bed outlet temperature is 598 °F, as reported in the data. Claus bed parameters are also adjusted to match the predicted tail gas composition with the plant data (see *Table 1*). Once the model reasonably matches the data, options for improving sulphur recovery are explored. For all of the following simulations, it is assumed that the Claus beds operate at 95% of equilibrium conversion and 4 Ib sulphur/100 moles of gas are entrained in the sulphur condensers since no data are available for these parameters. The second and third Claus beds are assumed to operate at 30°F (17°C) above the sulphur dewpoint, and the fourth bed operates at 25°F (14°C) above the sulphur dewpoint.

Table 1. TSWEET match of plant data for Example 1.

Composition (mol %)	**Acid gas + fuel gas**	**Waste heat boiler outlet**		**Tail gas**	
	actual data	actual data	TSWEET	actual data	TSWEET
Argon	0	0.51	--	0.55	--
Hydrogen	0	1.22	0.58	1.21	0.6
Nitrogen	1.3	42.47	41.99	45.78	44.52
Carbon monoxide	0	0.85	0.84	0.81	0.89
Carbon dioxide	74.41	47.74	49.32	51.20	53.67
Hydrogen sulphide	21.13	3.37	3.38	0.15	0.10
Carbonyl sulphide	0	1.08	1.10	0.02	0.07
Carbon disulphide	0	0.26	0.25	0.08	0.01

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Sulphur dioxide	0	2.50	2.54	0.20	0.14
Cl+	3.16	0	0	0	0
Total	100.00	100.0	100.0	100.0	100.0
Inlet gas:		**Furnace Temperature:**		**Overall sulphur recovery:**	
100oF, 20psia		Data 1684^{o}F	TSWEET 1695^{o}F	Data 96.3%	TSWEET 96.3%

Example 1 – Exploring options to increase sulphur recovery

After matching the plant data, a number of modifications to the plant are simulated for evaluation. For an option to be considered feasible, it must meet the minimum requirement of 99% overall sulphur recovery. *Table 2* lists simulation results comparing the overall sulphur recoveries predicted by the simulator. Since the existing plant operates at an $H_2S:SO_2$ tail gas ratio of 0.73, the plant is first simulated with the tail gas ratio controller set at 2. This change results in an improvement of 0.2% in sulphur recovery. A tail gas ratio of 2 is used for the remainder of the simulations.

Table 2. Overall sulphur recoveries predicted by TSWEET for Example 1.

Configuration	**Simulation predicted recovery %**
4 Claus beds (original case)	96.3
4 Claus beds (tail gas H2S:SO2 ratio = 2)	96.5
3 Claus beds + 1 cold bed	98.0
3 Claus beds + 2 cold beds	98.0
3 Claus beds + 1 cold bed + oxygen enrichment (30%)	98.1
3 Claus beds + 1 cold bed + oxygen enrichment (100%)	98.3
3 Claus beds + 1 direct oxidation bed	97.5
3 Claus beds + hydrogenation reactor + 1 direct oxidation bed	97.8
3 Claus beds + hydrogenation reactor + 1 direct oxid'n bed + O2 enrich (30%)	98.1
3 Claus beds + hydrogenation reactor + 1 direct oxid'n bed + O2 enrich (40%)	98.3
3 Claus beds + hydrogenation reactor + 1 direct oxid'n bed + O2 enrich (50%)	98.4
3 Claus beds + hydrogenation reactor + 1 direct oxid'n bed + O2 enrich (75%)	98.5
3 Claus beds + hydrogenation reactor + 1 direct oxid'n bed + O2 enrich (100%)	98.6
Recycle Selectox + 4 Claus beds	97.8
Recycle Selectox + 3 Claus beds + 1 direct oxidation bed	98.6
Recycle Selectox + 3 Claus beds + 1 cold bed	98.8
3 Claus beds + SCOT tail gas cleanup unit	**99.9**

Use of a cold bed

The first modification to be simulated is replacing the fourth Claus bed with a cold bed.[2] The operation of the cold bed is similar to the Claus bed except that the bed operates below the sulphur dewpoint so that the sulphur formed in the bed condenses on the catalyst. Consequently, two beds are required. Sulphur is condensing on one bed while the other bed is being regenerated.

A cold bed increases sulphur recovery because the Claus reaction is exothermic, and the lower the reaction temperature the closer the reaction proceeds to completion. As shown in *Table 2*, the cold bed improved sulphur recovery to 98.0%, which is below the required 99% recovery. Adding a second cold bed makes no improvement in recovery and should not be considered further.

Oxygen enrichment of the combustion air[3,4] in combination with the cold bed is simulated next, although this

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modification can be expensive due to the cost of the oxygen and possible modification or replacement of the existing burner.

Two oxygen enrichment simulations were performed, one with 30% oxygen content in the combustion air and the other with 100% oxygen. The 30% oxygen case increases recovery to 98.1%, only a 0.1% improvement over the case with no oxygen enrichment. The 100% Oxygen case represents the best improvement in sulphur recovery which can be expected, although it is still well below 99%. (It should be noted that due to the very lean feed gas composition, excessive burner temperature caused by 100% oxygen is not an issue).

The simulation results indicate that replacing the fourth bed with a cold bed does not meet the required 99% recovery, even with oxygen enrichment of the air, and will not be considered as a feasible modification to this unit.

Use of a direct oxidation bed

The next option to be simulated is replacement of the fourth bed with a direct oxidation bed such as Superclaus[4] since this is also a relatively inexpensive modification to the existing unit. Direct oxidation requires a special catalyst which converts H_2S directly to sulphur. To simulate this type of catalyst bed in TSWEET, the bed is specified such that the only species included in the reactions are H_2S, water, oxygen, and sulphur. A direct oxidation bed eliminates the need to maintain an H_2S:SO_2 ratio of 2 since all non-H_2S sulphur species pass through the bed unreacted. A hydrogenation reactor, which converts all sulphur species to H_2S, is often used to increase sulphur recovery.

For the simulations, the controller in the effluent of the third Claus bed is set to maintain 0.4% H_2S in the feed to the direct oxidation catalyst bed (0.4% H_2S was determined to be the optimum concentration for this case by simulation as described in the next section).

The direct oxidation bed conversion depends on the size of the bed and in these simulations, the bed is assumed to achieve 90% equilibrium conversion. A blower is added to the simulation upstream of the direct oxidation bed to provide air to promote the oxidation of H_2S to elemental sulphur. A controller maintains the oxygen content exiting the bed at 0.1% to ensure an excess of oxygen. As shown in Table 2, replacing the fourth Claus bed with a direct oxidation catalyst bed improved sulphur recovery to 97.5%, still below the required 99% recovery. Next, a hydrogenation reactor is added to the direct oxidation simulation to improve sulphur recovery. As shown, the predicted recovery is only 97.8%, a 0.3% improvement over the direct oxidation without hydrogenation. Finally, the direct oxidation simulation is modified to examine the improvement in recovery when the combustion air is oxygen-enriched. Simulations with 30-100% oxygen are performed with recoveries ranging from 98.1 to 98.6% overall sulphur recovery. Again, replacing the fourth bed with a direct oxidation catalyst bed does not meet the required 99% recovery, even with 100% oxygen as the combustion air, and should not be considered as a feasible modification to this unit.

Use of a Selectox catalytic burner

Another possible modification is replacing the existing burner with a Selectox[2,3,4] bed, which oxidizes the acid gas catalytically. Although the first Claus bed is maintained at 30^{o}F (17^{o}C) above the sulphur dewpoint due to no COS or CS_2 formation in the Selectox burner, the operation of the last three Claus beds remains unchanged from the original simulation. A straight through Selectox is typically used for acid gas containing less than 5% H_2S due to a temperature restriction in the catalyst bed. For this simulation, a recycle Selectox scheme is used to control temperature by recycling 80% of the first condenser effluent to maintain 5% H_2S in the Selectox catalyst bed feed to ensure that the bed temperature does not exceed 700^{o}F (370^{o}C).

As shown in Table 2, replacement of the burner by a Selectox bed increases the overall sulphur recovery to 97.8%.

Since this recovery does not meet the minimum 99% recovery requirement, the fourth Claus bed was replaced by a direct oxidation catalyst bed. This change boosted the recovery to 98.6%, still not high enough. Next the fourth bed was replaced by a cold bed, which increased sulphur recovery to 98.8%. Although closer to the 99% recovery

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requirement, the Selectox scheme probably should not receive further consideration.

Addition of a SCOT tail gas cleanup unit

Finally, addition of a SCOT[2,4] type tail gas cleanup unit is simulated to determine the improvement in overall recovery. This modification involves the use of a hydrogenation reactor to convert all non-H_2S sulphur species to H_2S, a quench tower to condense excess water, and an MDEA amine sweetening unit. All of this additional equipment can be relatively expensive to install. In the model, the SCOT unit replaces the original fourth bed.

As shown in Table 2, a recovery of 99.9% can be achieved. The only potential problem is reduced burner temperature due to recycling of the SCOT regenerator acid gas, which contains about 88 mole % CO_2. Increase of acid gas preheat temperature or oxygen enrichment of the combustion air to the burner may be required to achieve stable combustion.

Conclusions

These simulation results indicate that of the 16 modifications investigated, the only option which seems feasible is the three bed Claus with a SCOT tail gas cleanup unit since it achieves an overall sulphur recovery which exceeds 99%.

Example 2 -- Optimization of a Claus sulphur unit

The process simulator can be used to determine which operating parameters such as burner temperature, Claus bed temperatures, tail gas $H_2S:SO_2$ ratio, etc., have the greatest impact on overall sulphur recovery. In the following example, sulphur unit operating parameter settings which yield the highest overall sulphur recoveries are determined by performing a series of simulations.

Figure 2 shows a plot of overall sulphur recovery percentage vs Claus bed 1 temperature at constant degrees over sulphur dewpoint in the second and third Claus beds of a three bed Claus unit with rich acid gas feed (H_2S concentration is 93.4 mole %). *Figure 2* was constructed from TSWEET simulation results by plotting Claus bed 1 temperature vs overall sulphur recovery at constant bed 2 and 3 temperatures. As expected, the closer to sulphur dewpoint all beds operate, the higher the overall recovery. The plot also shows how much additional sulphur recovery can be expected by changing operating conditions, specifically bed temperatures.

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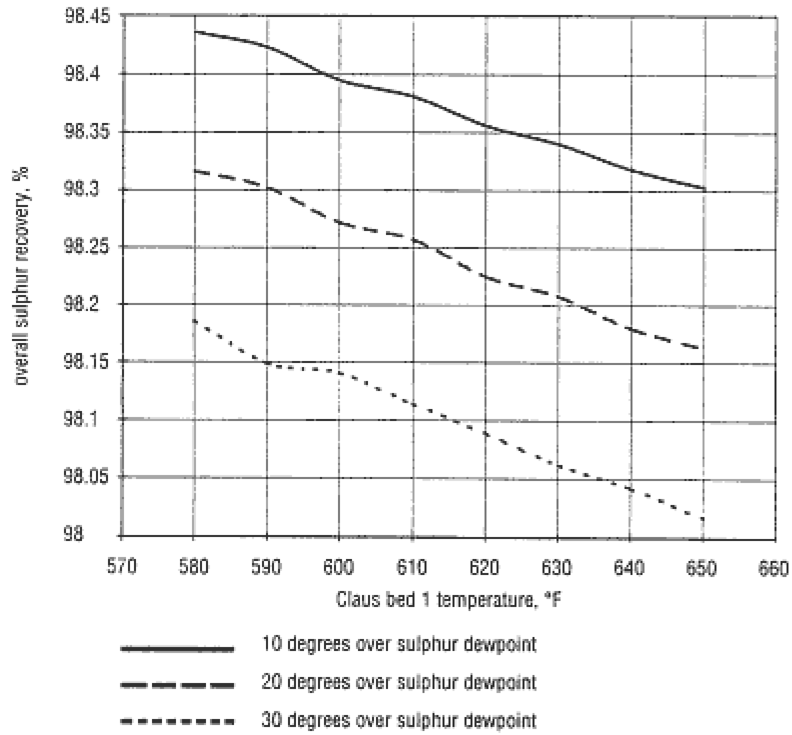

Figure 2. Overall sulphur recovery vs bed 1 temperature at constant bed 2 and 3 temperatures.

If the plant is currently operating at a Bed 1 temperature of 630°F (330°C) and subsequent beds at 30°F (17°C) over sulphur dewpoint, 98.07% recovery can be expected. By reducing the Bed 1 temperature to 600°F (315°C) and operating the other two beds at 10°F (5°C) over sulphur dewpoint, a 98.39% recovery can be expected, which is an improvement of 0.32%. Although this improvement may not seem significant, it represents a 16% reduction in emissions.

Another example of determining optimum operating conditions could be to perform simulations to determine overall sulphur recovery at various H_2S to SO_2 tail gas ratios. A plot of recovery percentage vs $H_2S:SO_2$ ratio at constant bed 1 temperatures indicates that a ratio of about 2 along with the lowest possible bed temperature is optimum, as expected.

Although it may seem obvious that colder bed temperatures and maintaining an $H_2S:SO_2$ tail gas ratio of 2 results in the highest overall sulphur recovery in a traditional Claus sulphur recovery unit, some other operating parameters, the importance of which may not be so apparent, can also be optimized.

As mentioned in Example 1, the concentration of H_2S in the feed to a direct oxidation catalyst bed can have a significant effect on overall sulphur recovery.

In a plant with a direct oxidation bed, $H_2S:SO_2$ ratio is unimportant, since maximizing the H_2S content while minimizing the content of other sulphur species in the feed to the direct oxidation bed improves the conversion in the bed.

Using the conditions of the lean acid gas feed plant in Example 1, 12 simulations were performed to determine the overall sulphur recovery for the plant at various H_2S concentrations in the direct oxidation bed feed. The results are plotted in *Figure 3*. This plot indicated that for this case, 0.4% H_2S yields the highest overall sulphur recovery for the unit.

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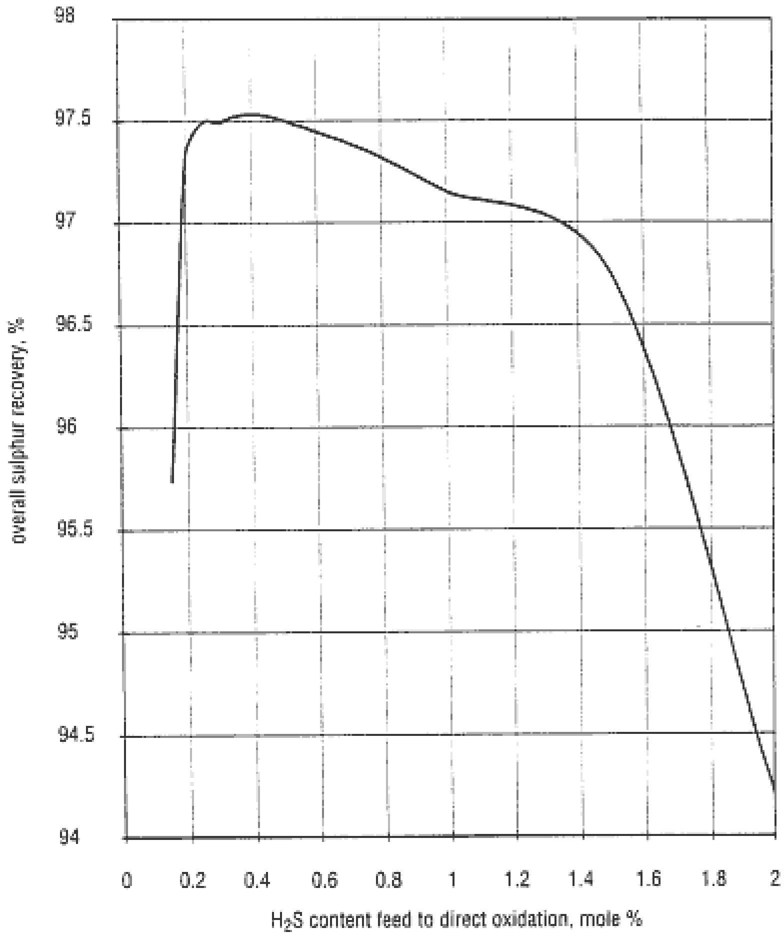

Figure 3. Overall sulphur recovery vs H_2S content in feed to direct oxidation.

Optimizing a new design

In the same manner that an existing plant is optimized, a process simulator can be used as a tool for optimizing a new design based on feed composition. The simulator can predict recoveries for almost any plant configuration. However, the engineer performing the simulations must be familiar with the Claus process and must also be aware of any limitations associated with the operation of a Claus unit such as maximum and minimum burner temperatures, special provisions for feed containing ammonia, etc.

Conclusions

Existing sulphur recovery facilities must often be modified to increase sulphur recovery due to increasingly stringent sulphur emissions regulations. A process simulator is a valuable tool to aid in the analysis of an existing Claus unit, either to evaluate necessary modifications to improve sulphur recovery, or to determine the optimum operating conditions to maximize sulphur recovery. The process simulator can also be used as a tool to aid in the design of a new Claus sulphur recovery unit by predicting recoveries for a variety of configurations.

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