Design and Optimization of Integrated Amine Sweetening, Claus Sulfur and Tail Gas Cleanup Units by Computer Simulation

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ABSTRACT

Integrated gas sweetening, sulfur and tail gas cleanup units (TGCU) were analyzed by a process simulation program, called TSWEET, to determine the sensitivity of the operating conditions and parameters on the performance of the system. The parameters investigated included the H2S/CO2 ratio in the acid gas from the main absorber, the hydrocarbon content of the acid gas, the reaction model for H2 and CO in the furnace, the formation and reaction of COS as well as CS2 and the CO2 slippage in the TGCU absorber. For the assortment of cases considered, the results showed that while some parts of the system were not overly sensitive to many of the operating conditions others were quite sensitive. Due to the complexity of the integrated system, a parameteric analysis is necessary to fully optimize the system.

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INTRODUCTION

A large portion of the natural gas and crude oil used in this country contains sulfur which must be removed before consumption. Current and anticipated legislation are commonly requiring sulfur recovery levels of 99.9% in many applications. The workhorses of the industry for sulfur recovery and processing continue to be conventional amine sweetening units followed by Claus plants. Since the Claus plants are capable of recoveries of about 93 to 96%, at best, for typical, three bed units, tail gas cleanup units (TGCU) are required to meet the stringent emission regulations.

The oldest and most common type of TGCU converts the sulfur in the tail gas back to hydrogen sulfide (H_2S) and then passes the tail gas to a low pressure amine sweetening unit which recycles the sulfur along with some carbon dioxide to the Claus unit for reprocessing. Only this type of TGCU is considered in the present work. This technique is usually capable of meeting the required recovery if the units are optimized to function together.

Because of the complexities of the calculations in designing and analyzing these units, process simulation programs have become a necessity to optimize the units in any reasonable length of time. Heretofore, simulation programs have only been available for amine sweetening units and Claus sulfur plants as separate, distinct programs. Thus, the historical practice was to use the sweetening simulator first, then to feed the acid gas to the Claus simulator.

However, if a TGCU is involved, this becomes a complex iterative process because of the recycle stream. The iterative process is further complicated if the rich amine from the tail gas absorber is fed to a common stripper with the amine from the main absorber. Due to the above complexities and the higher required sulfur recoveries, Bryan Research & Engineering has incorporated all features of its Claus sulfur program into its amine sweetening program, TSWEET. Using the new TSWEET, the recycle can be closed and the amine sweetening, Claus sulfur and TGCU can all be simulated in a single run permitting convenient optimization of the entire complex.

The new TSWEET performs rigorous tray by tray calculations for the contactor and stripper columns by the Ishii-Otto (1973) or Boston and Sullivan (1974) methods. The program contains a kinetic model to properly simulate acid gas selectivity due to the slow CO_2 amine reactions. An ionic species model is used to calculate the acid gas amine vapor-liquid equilibrium. The program has the ability to simulate gas and/or liquid absorbers feeding to a common stripper. The Claus and TGCU reaction operations in the furnace and beds are performed using minimization of free energy methods, literature correlations, and/or user specificed quench temperatures and amounts of key components formed.

In the present work, the new TSWEET program is used to examine the influence of various operating conditions and parameters on the design and operation of integrated amine sweetening, Claus sulfur and TGCU's.

OPERATING CONDITIONS AND PARAMETERS AFFECTING PERFORMANCE OF SYSTEM

Several operating conditions and parameters have a significant impact on the size, costs and performance of the sweetening unit, sulfur plant and TGCU. These will be discussed on a unit by unit basis:

Primary Sweetening Unit

The two major factors in the primary sweetening unit affecting the performance of the integrated system are the CO_2 and hydrocarbon pickup.

CO_2 Pickup:

The CO_2 in the acid gas from the sweetening unit affects the system in two ways. Obviously, the size of the sweetening unit varies directly with the CO_2 pickup. In addition, since it is a diluent in the sulfur plant, it reduces the sulfur conversion. This influence is magnified by the fact that the TGCU absorber picks up part of the CO_2 in the tail gas and recycles it back through the system. Thus, the CO_2 pickup also leads to a larger sulfur plant and TGCU. The only possible relief to this problem, if specifications permit, is to reject more CO_2 in the overheads of the main absorber by switching to a more selective amine or by changing the operating conditions in the absorber to achieve greater selectivity.

Hydrocarbon Pickup:

Higher absorber pressures and heavier hydrocarbons tend to increase the net amount of hydrocarbon in the rich amine. Due to the combined effects, these hydrocarbons influence the system performance dramatically. In the furnace, the hydrocarbons are converted to mostly CO_2 with its attendant problems previously discussed, and to H_2O which drives the sulfur reaction in the wrong direction. In addition, the hydrocarbons are known to affect the amount of COS and CS_2 formed in the furnace (Fischer, 1975, Parnell, 1975, Parnell, 1985, and Luinstra and d'Haene, 1989).

The only convenient means to reduce the hydrocarbon problem is to add a low pressure flash tank on the rich amine system.

Claus Sulfur Plant

Due to the high temperatures involved, the reactivity of the components and the associated sampling and analysis problems, the Claus sulfur process has evaded industry's considerable efforts to determine all of her secrets. Most of the remaining secrets involve the extent of formation or destruction of H_2, CO, COS, NH_3 and CS_2 in the furnace and their subsequent degree of reaction in the waste heat boiler and the catalyst beds. This topic has been widely discussed in the literature (Fischer, 1975, Parnell, 1985, and Luinstra and d'Haene, 1989). Based on observed data, several empirical equations which predict the concentration of these species at the exit of the waste heat boiler have been proposed (Wen, et al., 1986, Luinstra and d'Haene, 1989).

H_2 and CO Formation and Reaction:

Significant amounts of H_2 and CO are formed in the acid gas burner depending on the acid gas composition and flame temperature. Considerable disagreement exists in the industry over the degree to which the H_2 and CO participate in the reactions as the gases are cooled in the waste heat boiler and in the reactions in the catalyst beds. The most common beliefs range from no reaction at all once they are formed in the firebox, to a quench temperature (the temperature below which no further reaction occurs) of about 1800ºF for H_2 and 1500ºF for CO. Most experts believe that there is no reaction in the Claus beds by either of these species.

COS and CS_2 Formation and Reaction:

COS is believed to be formed in the furnace from the reaction of carbon monoxide with sulfur (Kerr and Paskall, 1976) while CS_2 is believed to be formed by the reaction of hydrocarbons directly with elemental sulfur (Luinstra and d'Haene, 1989). Due to the sampling and analysis problems, the amount of COS and CS_2 formed is most easily described in terms of the net formation in the furnace and waste heat boiler. The most convenient procedure is to assume that the net amount is formed in the furnace and that none of it reacts in the cooling process in the waste heat boiler.

COS and CS_2 are difficult to react in the catalyst beds and require a special catalyst with its associated operating conditions. These conditions (high temperatures) will reduce the effectiveness of the first bed in converting H_2S and SO_2, but if the COS and CS_2 are not converted in the sulfur plant, they will be reduced to H_2S in the TGCU, thus increasing the size of both the TGCU and sulfur plant.

Tail Gas Cleanup Unit

Some of the operating parameters of interest in the TGCU are the quantity of reducing gas required for the reactor and the CO_2 rejection in the TGCU absorber.

Reducing Gas:

The amount of the reducing gas required is directly affected by the quantity of unreacted H_2 and CO in the tail gas.

CO_2 Rejection in TGCU Absorber:

Obviously, the real key to TGCU performance is the ability to reject CO_2 in the tail gas absorber. In most cases, this feature has a moderate effect on the size and effectiveness of the sulfur plant and a profound effect on the TGCU absorber. All of the design considerations to increase selectivity must be fully optimized including amine selection, liquid residence times on the absorber trays, solution loading and absorber operating temperature.

ANALYSIS AND DISCUSSION OF RESULTS

The effect of the previously discussed operating conditions and parameters on the performance of an integrated amine sweetening, Claus sulfur and tail gas cleanup unit was examined using the TSWEET program. A wide range of operating conditions was to be explored to determine the sensitivity of the integrated system. In an effort to normalize the results, a base case with a fixed H_2S rate, as shown in Table l, was used for the study. This is a fairly common sample of a stream from a refinery application. The results obtained are thus somewhat specific to these base conditions. However, the general trends will follow for all Claus units, although their magnitudes may vary.

Table 1. Operating conditions for example sulfur recovery unit.

Composition of Inlet Gas:		
	Component	Mole %
	Hydrogen	12.32
	Nitrogen	9.11
	Hydrogen Sulfide	7.51
	Carbon Dioxide	1.81
	Water	0.55
	Methane	68.70
	TOTAL	*100.0*
	Temperature	100F
	Pressure	180 psia
Amine Unit Specifications:		
	MDEA Concentration	23 weight %
	Main Absorber Ideal Stages	7
	Stripper Ideal Stages	10
	Stripper Overhead Pressure	27.7 psia
	Stripper Reflux Ratio	2
	Lean Amine Cooler Temperature	100F
Claus Unit Specifications:		
	Beds	3
	Reheat	Indirect
	Condenser 1 Temperature	350F
	Condenser 2 Temperature	320F
	Condenser 3 Temperature	320F
	Condenser 4 Temperature	280F
	Bed 1 Inlet Temperature	450F
	Bed 2 Inlet Temperature	400F
	Bed 3 Inlet Temperature	375F
TGCU Specifications		
	TGCU Reactor Temperature	800F
	Spray Tower Temperature	100F
	TGCU Absorber Ideal Stages	4

The simulation was designed to obtain the maximum possible conversion. All beds are reheated indirectly, which is the most efficient method. The bed operating temperatures are as cool as practical without falling into either the sub dewpoint or below COS and CS_2 conversion temperature in the first bed. The condensers are operated as cool as practical. The conversion efficiencies for the beds were set to 100%, which apply only for a short time after the unit is first started up. These numbers, therefore, represent the absolute maximum conversions which may be obtained. As the catalysts in the beds degrade and sulfur condenser tubes foul, plant performance will decline by amounts which are determined by bed size and degree of fouling. The COS/CS_2 catalyst in particular can cause severe operating problems (Pearson, 1976,1980, Goodboy, 1985, Luinstra and d'Haene, 1989).

For most cases, the volumetric flow rate from the beds, condenser duties and overall sulfur recovery were used as indicators of plant size and performance. The volumetric flow rate of gas through the beds determines the size of the bed and the catalyst load required to achieve the required conversion, and the condenser duties determine the areas of these critical pieces of equipment.

To examine the effect of CO_2 pickup in the main amine unit, the base case was used for the first run, then the CO_2 rate was increased holding the other component rates constant for subsequent runs. The amine circulation rate was increased to maintain the H_2S in the sweet gas essentially constant. Using this procedure, the gas flow rate through the beds starts to increase sharply at H_2S/CO_2 ratios below about 1.5 as shown in Figure 1. The duties for the condensers follow essentially the same trend. If the operating parameters in the sulfur plant and TGCU are maintained constant, the sulfur recovery drops below 99.9% at an H_2S/CO_2 ratio of about 1.25 as shown in Figure 2.

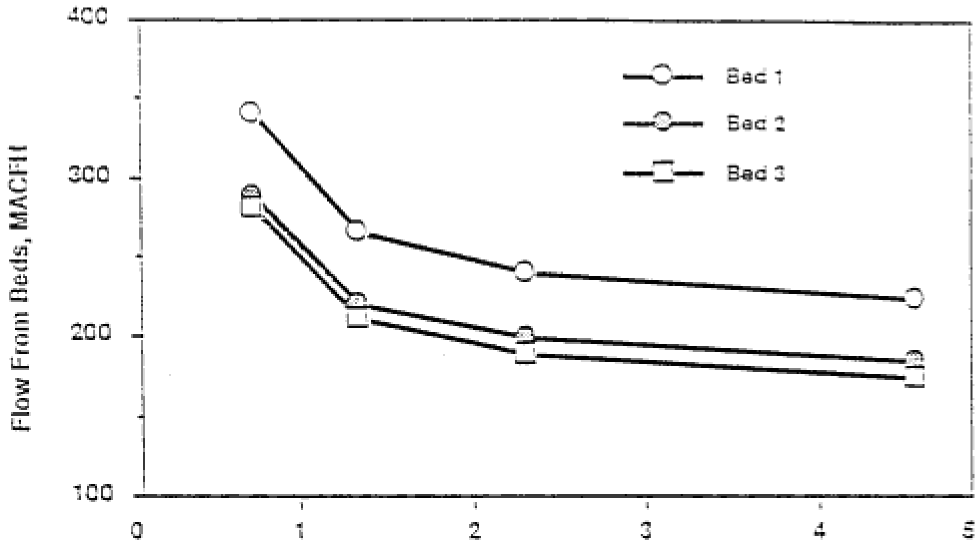

Figure 1. Effect of H2S/CO2 ratio from main absorber on flow from beds.

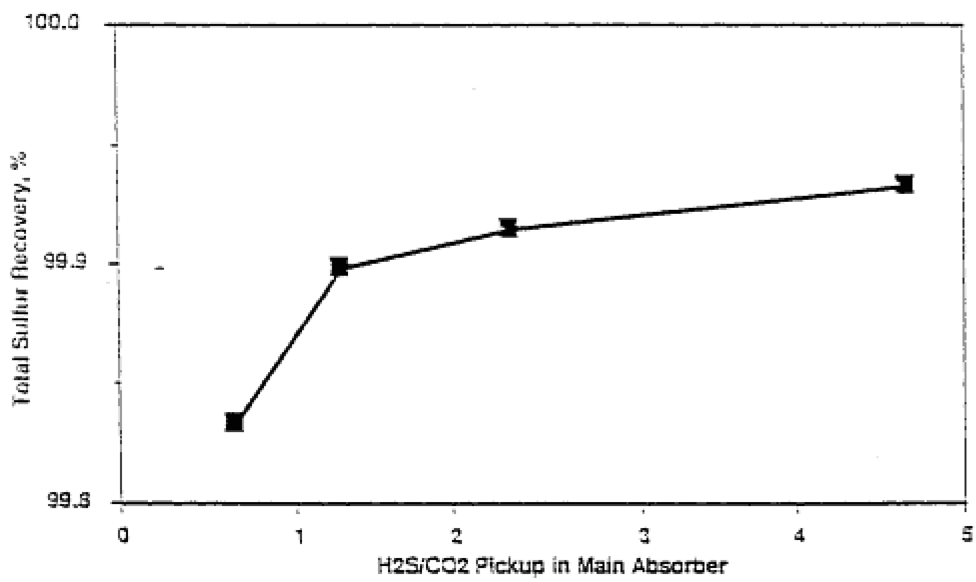

Figure 2. Effect of H2S/CO2 ratio from main absorber on sulfur recovery

The influence of the hydrocarbon content in the sulfur plant feed is shown in Figures 3 and 4. The hydrocarbons start to have significant effect on the flow rate through the beds at about 1.2% propane equivalent for the present base case. Again, the change in condenser duties responds very similarly to the flow rate though the beds. Because of the increased water and carbon dioxide, the sulfur recovery decreases as the hydrocarbons are increased.

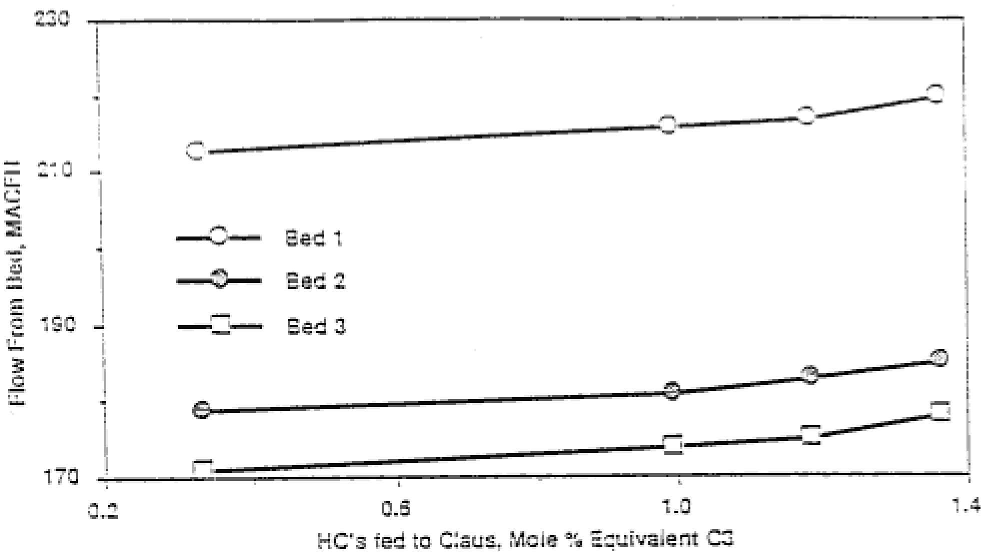

Figure 3. Effect of hydrocarbon pickup on flow from beds.

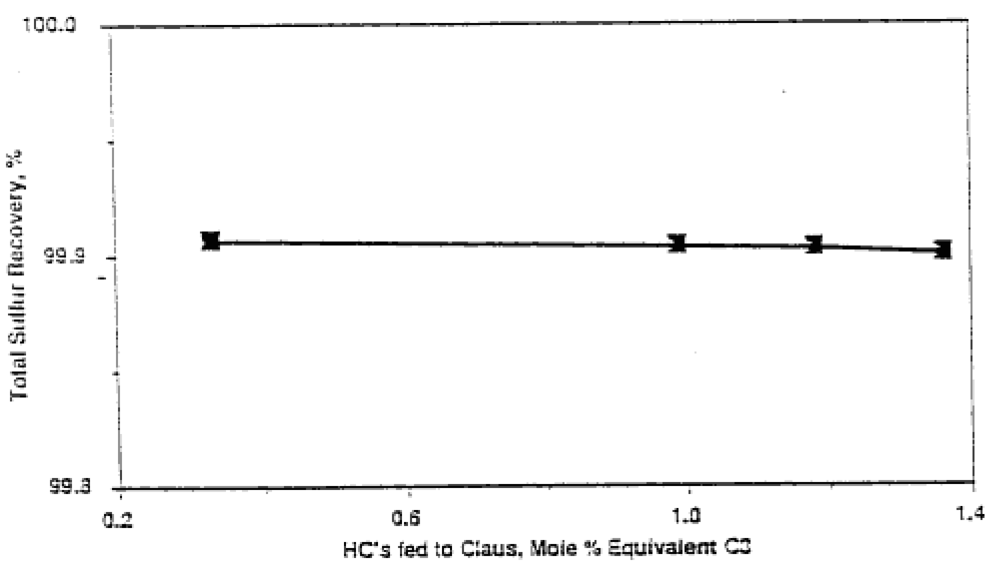

Figure 4. Effect of hydrocarbon pickup on sulfur recovery.

The effect of H_2 and CO formation and reaction were studied assuming that equilibrium amounts were formed in the burner and using three scenarios for subsequent reaction in the waste heat boiler: (1) no reaction (exclude H_2 and CO from reaction), (2) quench H_2 reaction at 1800º and CO at 1500ºF and (3) H_2 and CO react to equilibrium at 1200ºF. In all cases, no reaction of H_2 and CO was assumed to occur in the sulfur catalyst beds. As shown in Figure 5, the flow rate through the beds is reduced by less than 5% for the exclude H_2/CO and quench cases due to the lower combustion air requirements. This would also be reflected as an approximate 10% change in the horsepower requirements for the air blower as shown in Figure 6. As illustrated in Figure 7, the degree to which H_2 and CO react in the waste heat boiler will change the duty in the first pass of the waste heat boiler by as much as 30% for this case. However, the duties in the second pass and the condensers respond very similarly to the flow rate through the beds. Although the sulfur production is redistributed somewhat among the condensers, it has little affect on the condenser duties (Figure 7) and the per pass sulfur recovery (Figure 8). The additional required reducing gas for the TGCU reactor is highly dependent on the amount of H_2 and CO reacted in the sulfur plant and, for this case, varies from about 5 to 25 moles H_2 per hour as shown in Figure 9.

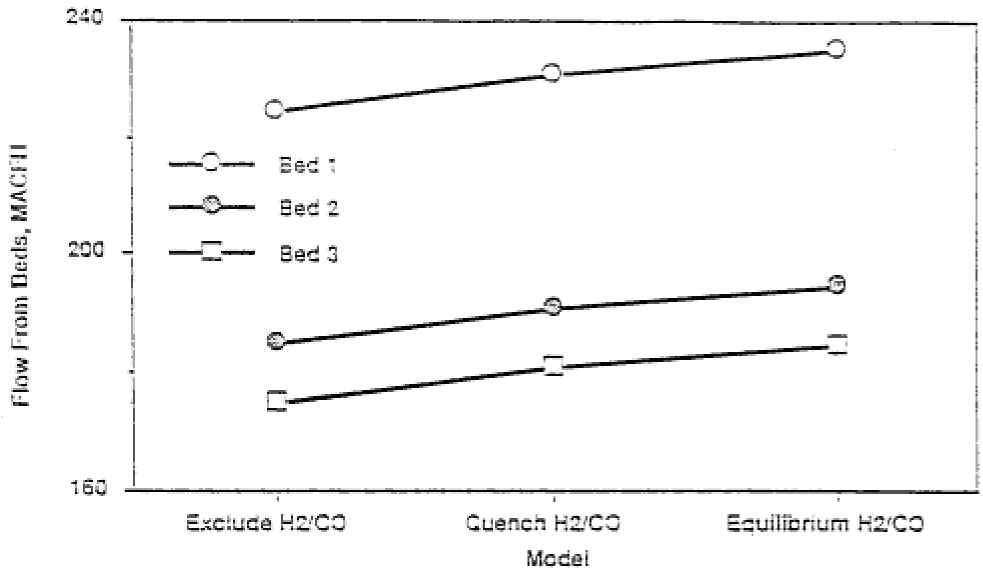

Figure 5. Impact of H2/CO model on flow from beds.

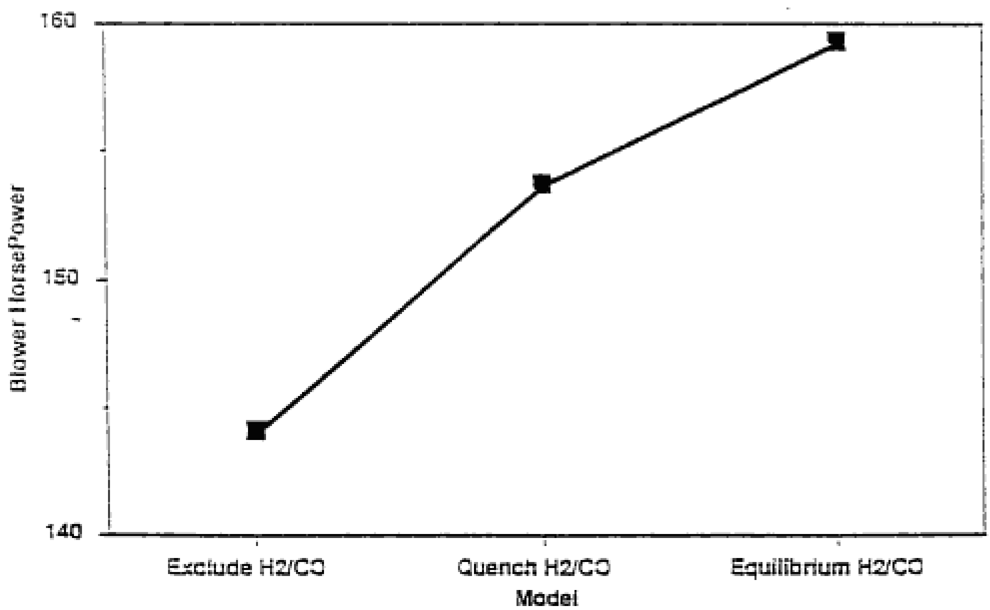

Figure 6. Impact of H2/CO model on blower horsepower.

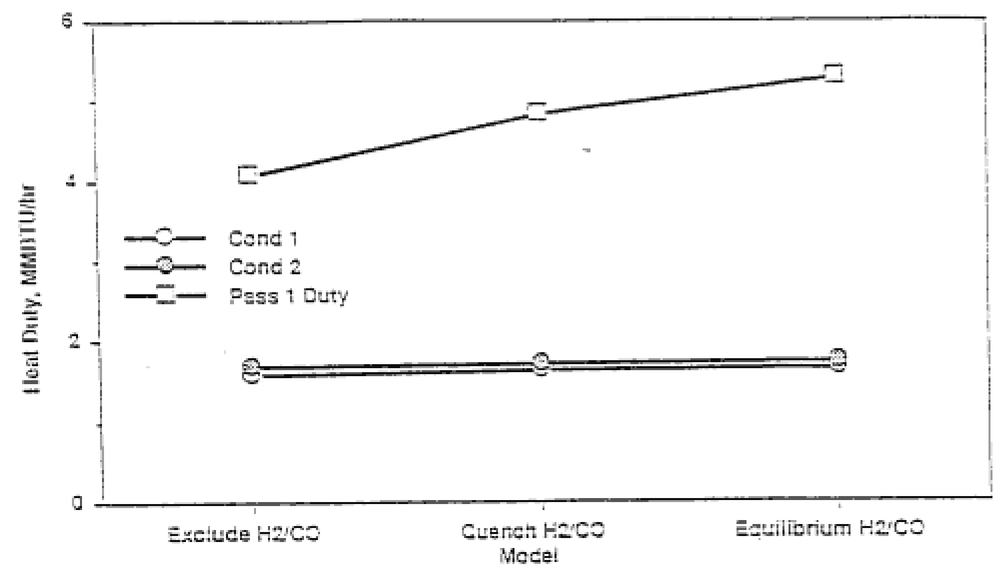

Figure 7. Impact of H2/CO model on boiler and condenser duties.

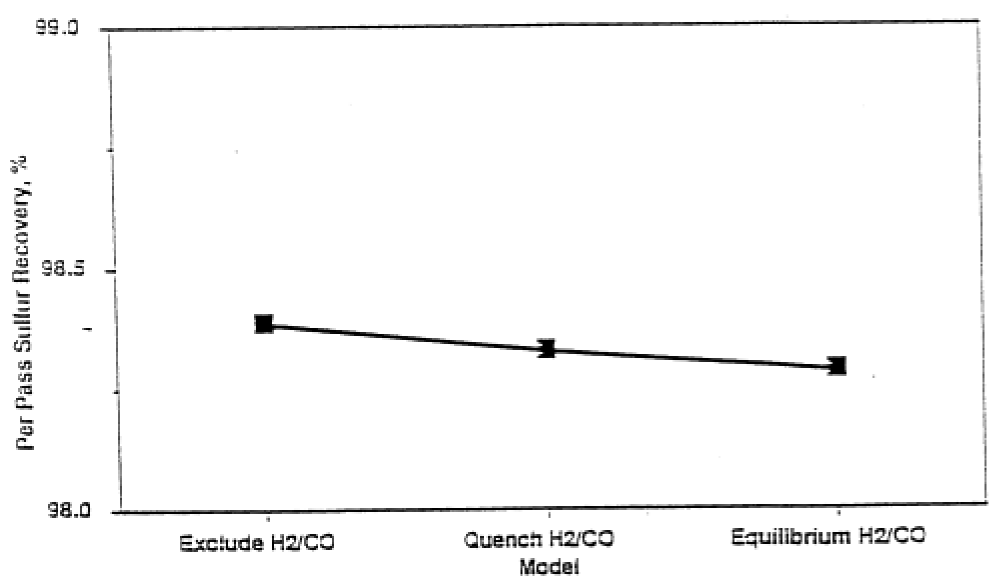

Figure 8. Impact of H2/CO model on sulfur recovery.

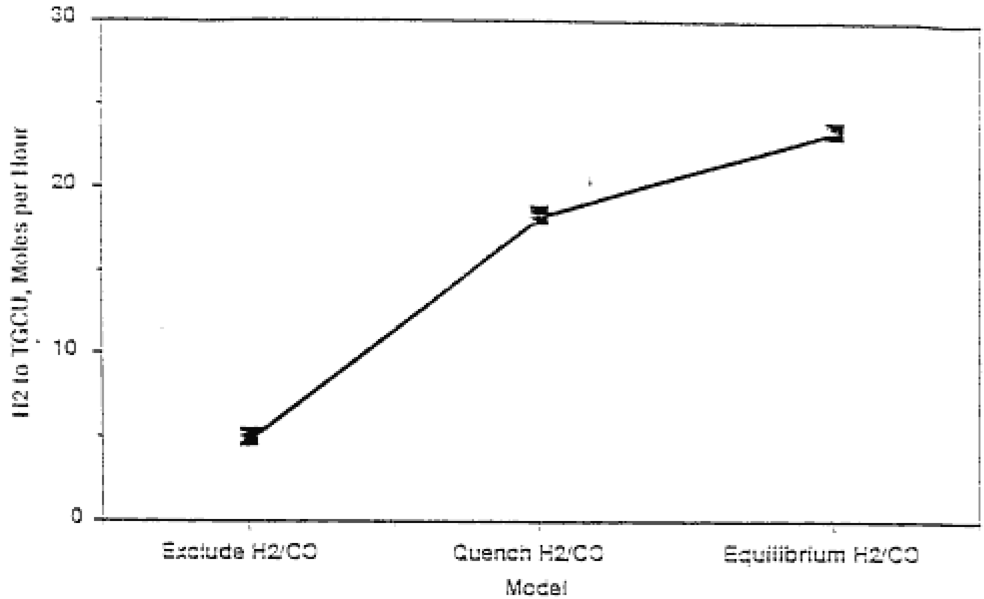

Figure 9. Impact of H2/CO model on TGCU hydrogen requirements.

The influence of COS and CS_2 formation and reaction is shown for four scenarios in Figure 10. The four scenarios are described in Table 2. Since the COS/CS_2 formation is usually described as the net amount from the furnace and waste heat boiler and relatively small, but significant, quantities of the total sulfur are tied up as COS/CS_2, and the amount of elemental sulfur produced in the furnace is reduced somewhat. This, in turn, places additional load on the catalytic beds as shown in Figure 10. Again, the change in condenser duties tracks the flow rate through the beds. As long as a COS/CS_2 catalyst is present in Bed 1 and it is functioning properly, the amount of COS/CS_2 formed has little impact on the overall sulfur recovery. However, as shown in Figure 11, if the catalyst fails, the per pass sulfur recovery decreases dramatically and the H_2S from the COS/CS_2 in the tail gas would likely overload the TGCU.

Table 2. COS and CS2 concentration for alternative reaction models.

Model	Component, %*	Correlation
Luinstra	COS = 0.56 CS_2 = 1.2	Fischer (1975) Luinstra and d'Haene (1985)
Fischer	COS = 0.57 CS_2 = 0.07	Fischer (1975) Fischer (1975)
Equilibrium	COS = 0.09 CS_2 < 0.01	Minimization of free energy Minimization of free energy
Catalyst Failure**	COS = 0.57 CS_2 = 0.07	Fischer (1975) Fischer (1975)

* Dry molar concentration at entrance to first bed
** Fischer correlation used in boiler, but no reaction allowed in any beds

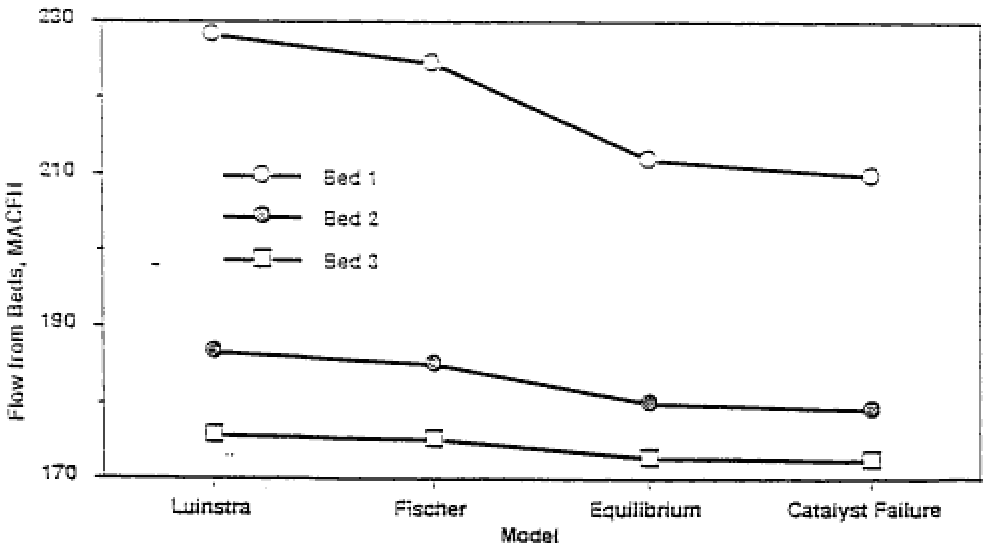

Figure 10. Influence of COS/CS2 model on flow through beds.

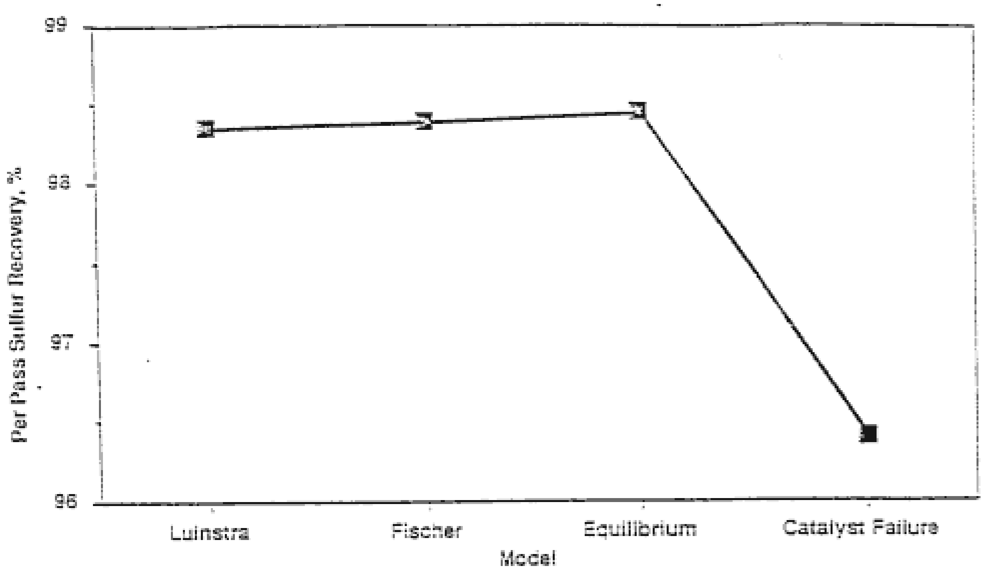

Figure 11. Influence of COS/CS2 model on sulfur recovery.

As expected for the base case of a 4.5 H_2S/CO_2 ratio in main acid gas feed to the sulfur plant, the overall operation is not very sensitive to the CO_2 slippage in the TGCU absorber. CO_2 slippage as low as 60% increases the flow through the beds and condenser duties by less than 5% and is still able to meet a 99.9% recovery specification. Even for reduced quality acid gas feeds such as about 0.6 H_2S/CO_2 ratio, the CO_2 slippage in the TGCU absorber does not have a large impact (less than 10%) on the sulfur plant as shown in Figure 12. However, if a 99.9% sulfur recovery is to be maintained, the amine solution circulation rate to the TGCU absorber more than doubles when the CO_2 slippage drops from about 83% to about 63% as shown in Figure 13.

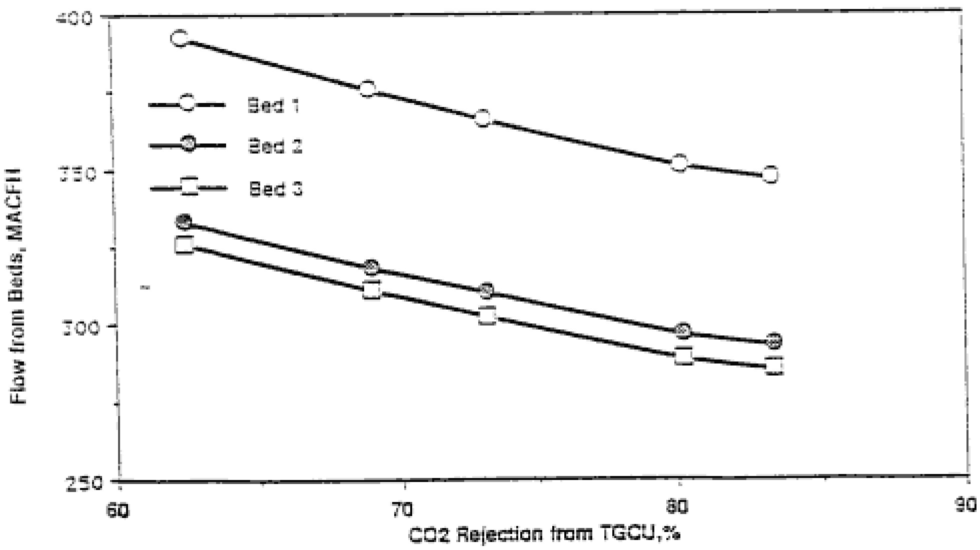

Figure 12. Impact of TGCU CO2 rejection on flow through beds.

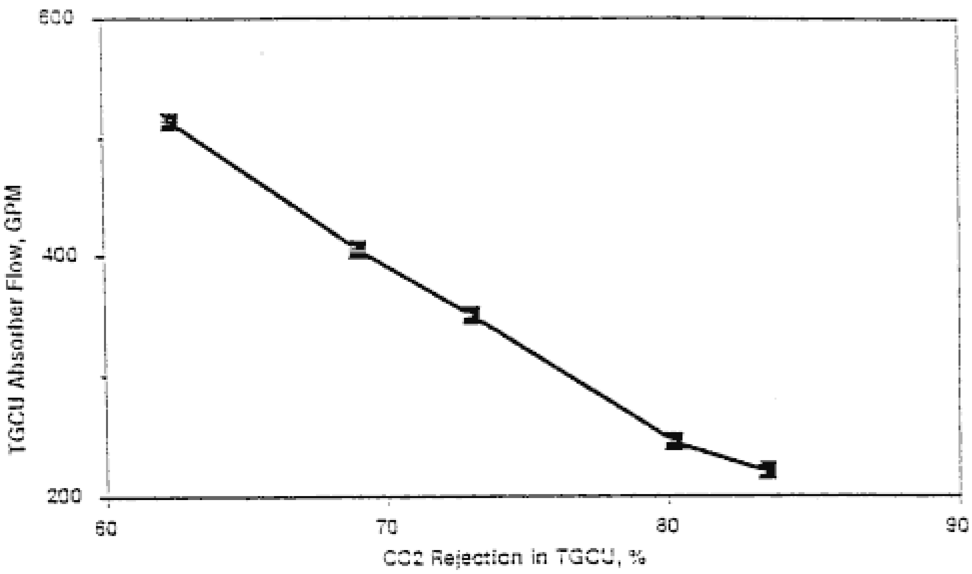

Figure 13. Impact of CO2 rejection from TGCU on TGCU amine circulation.

SUMMARY AND CONCLUSIONS

Integrated gas sweetening, sulfur and tail gas cleanup units (TGCU) were analyzed by a process simulation program, called TSWEET, to determine the sensitivity of the operating conditions and parameters on the performance of the system. For the assortment of cases considered, the results showed that while some parts of the system were not overly sensitive to many of the operating conditions others were quite sensitive. The H_2S/CO_2 ratio in the acid gas from the main absorber to the sulfur plant has little impact on the size of the sulfur plant and TGCU at values above about 1.5. The hydrocarbons in the sulfur plant feed have little influence up to about 1.2% propane equivalent.

The type of reaction model used for H_2 and CO in the sulfur plant affects the size of system by about 10% or less, except for as high as a 30% change in the duty for the first pass of the waste heat boiler and a very large change in the reducing H_2 required for the TGCU reactor. The net COs and CS_2 formation in the furnace was also found to affect the size of the system by less than 10% as long as a properly functioning COS/CS_2 catalyst was used in the first bed. While the CO_2 slippage in the TGCU absorber has little affect on the sulfur plant, it has a profound affect on the solution circulation rate to the TGCU absorber.

Due to the complexities of integrated amine sweetening, sulfur and TGCU systems, a parametric analysis is necessary in all cases to fully optimize the system.

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