

Modelling the Modified Claus Process Reaction Furnace and the Implications on Plant Design and Recovery

WAYNE D. MONNERY, WILLIAM Y. SVRCEK and LEO A. BEHIE*

Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada T2N 1N4

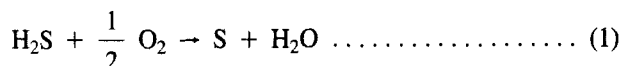
The calculation of product composition, flow rate and temperature of the modified Claus process reaction furnace is typically done by assuming either thermodynamic equilibrium or by empirical methods fitted to plant data. This paper extensively reviews the literature on the Claus reaction furnace and compares equilibrium and empirical results of the predicted concentrations of the key components: hydrogen (H_2), carbon monoxide (CO), carbonyl sulphide (COS) and carbon disulphide (CS_2). The implication of the reaction furnace model on the overall plant design and sulphur recovery is subsequently presented. It is well known that results of equilibrium calculations do not match plant data taken both before and after the waste heat boiler (WHB). Moreover, even though results of empirical methods do not match plant data taken before the WHB, one empirical method provides the best fit of highly scattered data taken after the WHB and provides a conservative plant design and estimates of sulphur recovery and emissions.

Le calcul de la composition des produits, du débit et de la température du four lors de la réaction du procédé Claus modifiée est effectué typiquement soit d'après l'hypothèse d'un équilibre thermodynamique soit par des méthodes empiriques adaptées aux données d'usine. Cet article présente une vaste étude bibliographique concernant le four de la réaction de Claus, et on compare les résultats d'équilibre et empiriques des concentrations prédites des composants clés: hydrogène (H_2), oxyde de carbone (CO), sulfure de carbone (COS) et bisulfure de carbone (CS_2). On expose par la suite les conséquences du choix du modèle de four sur la conception générale du procédé et la récupération de soufre. On sait que les résultats des calculs d'équilibre ne concordent pas avec les données d'usine recueillies avant et après la chaudière de récupération des chaleurs perdues. En outre, même si les résultats des méthodes empiriques ne concordent pas avec les données d'usine recueillies avant la chaudière, le meilleur calage des données hautement dispersées recueillies après la chaudière est obtenu avec une méthode empirique; cette méthode permet de concevoir l'usine de façon conservatrice tout en permettant l'estimation des émissions et de la récupération du soufre.

Keywords: Claus reaction furnace, equilibrium, empirical, key components, design, recovery and emissions.

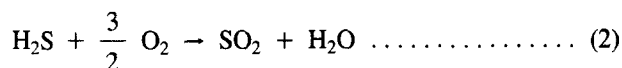
BASIC DESCRIPTION OF THE MODIFIED CLAUS PROCESS

The modified Claus process is the most popular process for recovering elemental sulphur from acid gas according to the following overall reaction:

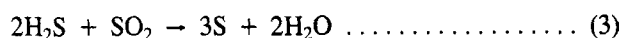


This oxidation of hydrogen sulphide is carried out in two steps:

1. The combustion or thermal oxidation of one-third of the feed H_2S to SO_2 .



2. The catalytic reaction of the remaining two-thirds of the feed H_2S with the SO_2 .



A simplified schematic diagram of the process is shown in Figure 1. The first step is carried out in a reaction furnace (RF) at the front end of the plant while the second step is carried out in two or three catalytic stages downstream (R1, R2, R3). Sulphur formed in each stage is condensed (C1, C2, C3, C4) and recovered to maximize conversion in the subsequent catalytic reactor. Prior to each catalytic reactor, the gas is reheated (RH1, RH2, RH3) such that it is sufficiently above the sulphur dew point at the exit of the reactor so that no sulphur condenses on the catalysts. After

the last stage, any remaining H_2S , unrecovered sulphur or other sulphur compounds such as COS and CS_2 are combusted to SO_2 in the tailgas incinerator and are then emitted into the atmosphere. Tailgas clean-up units (TGCU) are sometimes added prior to incineration to increase recovery.

THE REACTION FURNACE

The reaction furnace is simply a burner followed by a low pressure, refractory lined combustion chamber. From a design point of view, it is extremely important simply because it provides substantial sulphur conversion and is the source of key components which affect the entire plant material-balance and heat-balance and hence, the plant design and sulphur recovery and emissions. A simple schematic diagram is shown as Figure 2. Acid gas feed(s) and air enter the furnace and are ignited in a burner specially designed to promote maximum mixing and combustion efficiency. These designs, however, are highly proprietary and specific design criteria are unknown. The reaction furnace is followed by the waste heat boiler (WHB) where the furnace products are cooled from the flame temperature (926–1327°C) to about 230–370°C in one or two tube passes producing steam on the shell side.

The primary functions of the reaction furnace are to combust one-third of the feed H_2S (with air) to sulphur dioxide (SO_2) for subsequent catalytic reactions and to combust any contaminants such as hydrocarbons (i.e. producing $CO_2 + H_2O$) or ammonia (i.e. producing $N_2 + H_2O$). A benefit that occurs is the production of significant quantities of elemental sulphur as S_2 . According to Younger (1987), the sulphur produced in the furnace is 50–65% of the total production for "straight through" type plants. The term "straight through" implies that none of the acid gas feed

*Author to whom correspondence should be addressed.

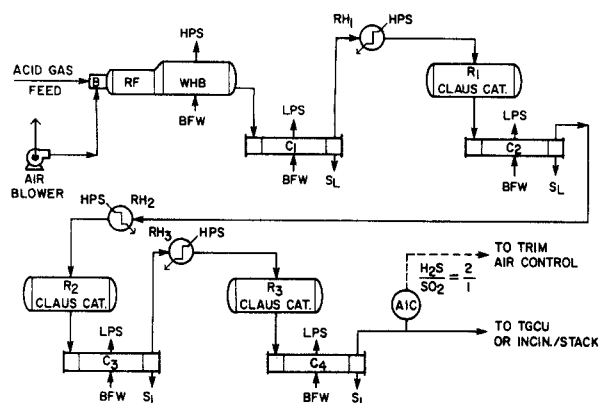


Figure 1 — Simplified flow diagram of a typical Claus sulphur recovery unit.

BFW = Boiler feed water
LPS = Low pressure steam
HPS = High pressure steam

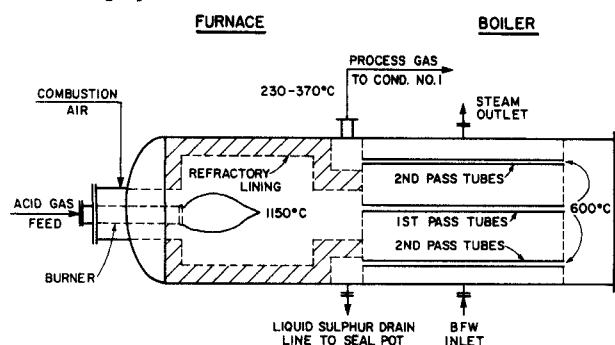


Figure 2 — Typical reaction furnace with waste heat boiler for Claus sulphur recovery unit.

BFW = Boiler feed water

is bypassed around the furnace. A bypass is required when the H_2S content of the feed gas reaches about 50%, in order to keep the flame temperature from falling to an unstable value ($< 926^\circ\text{C}$). Well known equilibrium curves, such as those published in the Gas Processors Suppliers Association (GPSA) Engineering Data Book (1987) or by Western Research (Paskall, 1979) show that sulphur conversion increases with flame temperature from about 68% at 926°C to about 75% at 1260°C . The flame temperature attained in the furnace primarily depends on the composition of the feed gas(es). Higher concentrations of combustibles such as H_2S , hydrocarbons and ammonia tend to increase the flame temperature while inerts such as N_2 and H_2O tend to decrease it. It should be noted here that N_2 and H_2O are considered inert because thermodynamic calculations show that very low concentrations of NO (typically 10^{-5} mol %) will be found in the furnace effluent and insignificant dissociation of H_2O will occur (typically 0.01 mol %) at furnace temperatures and oxygen levels. Typically, flame temperatures range from about 926 to 1327°C . At temperatures lower than 926°C , the flame is unstable and temperatures higher than 1327°C up to about 1627°C are only normally attained if oxygen enriched air is used. This upper limit is usually governed by the temperature limit of the refractory lining in the furnace.

The main chemical reactions that occur in the furnace are summarized in Table 1 (Paskall, 1979). It has been reported (Hyne, 1972) that the complexity of the furnace reactions is much greater than these equations imply and very likely many free radical intermediates are involved. However, the

TABLE 1
Modified Claus Process Reaction Furnace Main Reactions (Paskall, 1979)

1. $3\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + 2\text{H}_2\text{S}$
2. $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow \frac{3}{2}\text{S}_2 + 2\text{H}_2\text{O}$
3. $3\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \frac{3}{2}\text{S}_2 + 3\text{H}_2\text{O}$
4. $\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}_1$
5. $\text{S}_1 + \text{O}_2 \rightarrow \text{SO}_2$
6. $2\text{S}_1 \rightarrow \text{S}_2$
7. $\text{S}_2 + 2\text{O}_2 \rightarrow 2\text{SO}_2$
8. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
9. $\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
10. $\text{C}_6\text{H}_6 \rightarrow 6\text{C} + 3\text{H}_2$
11. $\text{C}_7\text{H}_8 \rightarrow 7\text{C} + 4\text{H}_2$

net reactions listed in Table 1 are sufficient for most practical design applications. Note that in the furnace, the predominant sulphur species is S_2 .

Claus plant reaction furnaces are usually designed with a residence time of 0.5 – 1.5 seconds. This is considered to be adequate since the main reactions are considered to be fast. When ammonia is combusted, longer residence times and higher temperatures are required because the oxidation of ammonia is relatively slow. Hence, the design residence time is in the lower end of the range if ammonia is not being combusted, and in the upper end of the range if ammonia is being combusted.

In addition to the expected sulphur species (S_2 , H_2S , SO_2), combustion products (H_2O , CO_2) and inerts (N_2), four other species often appear, namely H_2 , CO , COS , and CS_2 . Reactions involving their components are summarized in Tables 2–4 (Paskall, 1979).

IMPORTANCE OF H_2 AND CO

Hydrogen and carbon monoxide do not contain sulphur and are often considered unimportant in sulphur plant modelling for design calculations. However, they can contain up to 10% and 20% of the inlet hydrogen and carbon (Paskall, 1981) and this affects both the air requirement and adiabatic flame temperature and the plant material-balance and heat-balances. Evidently, H_2 is formed from H_2S dissociation and O_2 (or air) would not be required for combusting this quantity of H_2S . Production of CO directly from CO_2 also produces O_2 . Hence, it is not possible to compute the correct air demand (air to acid gas ratio) based on acid gas analysis alone (Kerr and Berlie, 1977). According to Kerr and Berlie (1977), actual air demand falls between the limits of stoichiometric air required for combustion of 1/3 of the H_2S plus all hydrocarbons and ammonia in the acid gas feed (maximum) and air required to obtain a $\text{H}_2\text{S}/\text{SO}_2$ ratio of

TABLE 2
Modified Claus Process Reaction Furnace Possible CO
and H₂ Side Reactions (Paskall, 1979)

Forming:

1. $\text{CH}_4 + \frac{3}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$
2. $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2$
3. $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$
4. $\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
5. $\text{CO}_2 + \text{H}_2\text{S} \rightarrow \text{CO} + \text{H}_2\text{O} + \frac{1}{2}\text{S}_2$
6. $2\text{CO}_2 + \text{H}_2\text{S} \rightarrow 2\text{CO} + \text{H}_2 + \text{SO}_2$
7. $\text{H}_2\text{S} \rightarrow \frac{1}{2}\text{S}_2 + \text{H}_2$

Consuming:

8. $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$
9. $4\text{CO} + 2\text{SO}_2 \rightarrow 4\text{CO}_2 + \text{S}_2$
10. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$
11. $\text{H}_2 + \frac{1}{2}\text{S}_2 \rightarrow \text{H}_2\text{S}$

2/1 leaving the furnace, based on an equilibrium calculation (minimum). Additionally, the flame temperature is reduced because dissociation of H₂S reduces the amount of H₂S that must be burned to maintain the stoichiometric H₂S/SO₂ ratio of 2/1 as well as the fact that H₂ and CO producing reactions are endothermic. Kerr and Berlie (1977) further reported that the flame temperature falls between limits established by the above air demand limits.

IMPORTANCE OF COS AND CS₂

According to Western Research (Paskall, 1981), as much as 8% of inlet sulphur has been measured as CS₂ and 4.5% as COS. If these components are not hydrolyzed in the first catalytic reactor, they represent substantial sulphur recovery losses. As much as 10% of inlet sulphur can be tied up in these compounds although the usual observed range is reported to be 0.5 to 2% of the inlet sulphur in the form of COS or CS₂ (Paskall, 1981; Sames et al., 1987). However, the seemingly low levels of COS and CS₂ in the reaction furnace effluent represent a significant portion of the total sulphur emission. Sames and Paskall (1984) showed that 17% of a tail gas sulphur emission was due to COS and CS₂. Luinstra and d'Haene (1989) reported that COS and CS₂ may comprise more than 50% of sulphur losses in the tail gas. Hence, the production of COS and CS₂ are a major environmental concern and represent an important design problem to be overcome.

NEED TO STUDY THE REACTION FURNACE

Of the equipment in a modified Claus plant, the reaction furnace is the most difficult to model and design as evident from the lack of agreement between equilibrium or empirical models and plant data. Unfortunately, the furnace is

at the front end of the plant and is the source of compounds which affect the material and heat balances and the sulphur recovery of the plant. The material and heat balances subsequently affect the size and design of the plant and the sulphur recovery ultimately affects the economics and plant emissions. Hence, the driving force to better understand the furnace is to optimize the plant design and operation in order to economically maximize sulphur recovery and minimize emissions. With the increased awareness and more stringent legislation of plant emissions, this is essential.

Of the methods available for modelling the reaction furnace, the question arises as to how these models compare to plant data for the furnace effluent composition and to one another. This would provide some insight to the design engineer of the applicability and reliability of these models. A subsequent question, to be addressed later, would be how the choice of the reaction furnace model affects the plant design and recovery.

Previous studies and furnace calculations

EQUILIBRIUM CALCULATIONS AND ACTUAL PLANT DATA

Bennett and Meisen (1973) calculated hydrogen sulphide-air equilibria under Claus furnace conditions (temperature ranging from 600–2000K) using a substantially higher number of compounds than in previous studies, including nitrogen compounds and free radicals. They also investigated the effect of oxygen to H₂S ratios other than 0.5. Equilibrium compositions were calculated by an iterative method based on partial pressures calculated from the equilibrium constant expression. It was assumed that gas mixtures were ideal, initial mixtures consisted only of air and pure H₂S and that air was made up of only 79% N₂ and 21% O₂. Results were given in the form of partial pressures as a function of temperature for the compounds present at equilibrium. They concluded that several compounds ignored in previous studies were present at equilibrium in sufficient quantities such that they should not be ignored. They also concluded that less than stoichiometric air maximized sulphur yield if the flame temperature could be maintained.

In a later study, Meisen and Bennett (1974) presented similar work except that initial mixtures consisted of H₂S, CO₂, H₂O and air. Again, results were presented in the form of partial pressures as a function of temperature for various compounds. In this work they concluded that the presence of CO₂ and/or H₂O in the acid gas feed reduced sulphur yield. They drew the same conclusions as their previous work with respect to compounds present at equilibrium, air supplied and sulphur yield.

Kerr and Berlie (1977) presented a graph which showed that generally, sulphur conversion in the reaction furnace from actual plant data was lower than equilibrium predictions. A graph was also presented which showed how individual product species varied with H₂S content of the acid gas feed, based on equilibrium calculations.

The results of equilibrium calculations in general indicate that significant amounts of H₂ and CO are produced in the reaction furnace. According to Western Research (Paskall, 1979, 1981) analysis of actual plant material balance data from samples taken downstream of the WHB show that H₂ is primarily formed from the thermal cracking of H₂S, which occurs at temperatures above 900°C (Dowling et al., 1990). These data also suggest that CO is produced predominately from CO₂ and most likely by a (CO₂ + H₂S)

reaction and/or by CO₂ dissociation. In all cases, the hydrogen and carbon contents of the acid gas constituents other than H₂S and CO₂ were insufficient to produce the observed quantities of H₂ and CO. However, these data also show considerably lower concentrations than the results of equilibrium calculations for these two compounds (Sames and Paskall, 1985). Sames et al. (1987) showed indirectly that CO production increased with temperature which they concluded tends to support the cracking of CO₂ as a CO forming reaction.

Recently, Western Research (Sames et al., 1990) was able to obtain samples of products leaving the furnace, before the waste heat boiler (WHB), as well as samples leaving the WHB. Previous to this, only data in the waste heat boiler effluent was reported which was assumed to be representative of the furnace effluent with any reactions rapidly quenched in the WHB. Based on the results of Dowling et al., (1990) and the fact that the WHB cools the hot (900–1600°C) furnace effluent down to 160 to 315°C in 0.3 to 1.5 seconds, it was stated that the probability that significant amounts of H₂ and S₂ would react to form H₂S in the WHB was high. The purpose of the Western Research work was to determine if the conclusions drawn by Dowling et al. (1990) were applicable to an operating Claus plant reaction furnace and WHB. Specifically, it was desired to determine the extent of H₂ produced in the furnace and then determine the degree of reassociation of H₂ and S₂ in the waste heat boiler. Sames et al. (1990) summarized the products of the reaction furnace effluent and waste heat boiler effluent for five tests and compared results of equilibrium calculations with measured, quenched values.

For every test, the data indicated that the H₂ concentration detected at the outlet of the waste heat boiler was significantly less than that detected at the outlet of the reaction furnace, which is consistent with H₂ re-associating with S₂ to form H₂S in the WHB (Sames et al., 1990). The fraction of H₂ that was consumed varied from 26–51% of the concentration at the WHB entrance. The concentration of H₂ leaving the furnace was, in all cases, less than 80% of that predicted by equilibrium calculations. The concentration of CO produced in the reaction furnace which was consumed in the WHB by reacting with S₂ to produce COS varied from about 29–37%. The fraction of CO leaving the furnace was, with the exception of one test, less than 85% of that predicted by equilibrium calculations. Since 93–98% of the furnace inlet carbon was in the form of CO₂, it was concluded that CO₂ was the major source of CO. These results were consistent with those reported by Dowling et al. (1990) at Alberta Sulphur Research at the University of Calgary which show that the recombination is favored at the lower temperatures in the WHB. Although not the main objective of their study, Western Research reported that the disappearance of CO across the WHB was counterbalanced by the appearance of COS and that the reaction between CO and S₂ appeared to be very rapid and not easily quenched. Hence, the consumption of CO was attributed to the formation of COS (via a CO + S₂ reaction), with the majority of the formation occurring in the WHB and not in the reaction furnace as is generally believed.

The results of equilibrium calculations in general indicate negligible amounts of COS and CS₂ are produced in the furnace. This is logical because if sufficient residence time was available to reach equilibrium, the hydrolysis reactions,

TABLE 3
Modified Claus Process Reaction Furnace Possible
COS Side Reactions (Paskall, 1979)

COS — Forming

1. $2\text{CH}_4 + 3\text{SO}_2 \rightarrow 2\text{COS} + \frac{1}{2}\text{S}_2 + 4\text{H}_2\text{O}$
2. $2\text{CO}_2 + 2\text{S}_1 \rightarrow 2\text{COS} + \text{SO}_2$
3. $\text{CS}_2 + \text{CO}_2 \rightarrow 2\text{COS}$
4. $2\text{S}_1 + 2\text{CO}_2 \rightarrow \text{COS} + \text{CO} + \text{SO}_2$
5. $\text{CO} + \text{S}_1 \rightarrow \text{COS}$
6. $\text{CH}_4 + \text{SO}_2 \rightarrow \text{COS} + \text{H}_2\text{O} + \text{H}_2$
7. $\text{CS}_2 + \text{H}_2\text{O} \rightarrow \text{COS} + \text{H}_2\text{S}$

COS — Consuming

8. $\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$
9. $2\text{COS} + \text{SO}_2 \rightarrow \frac{3}{2}\text{S}_2 + 2\text{CO}_2$
10. $\text{COS} + \text{CO} + \text{SO}_2 \rightarrow \text{S}_2 + 2\text{CO}_2$
11. $\text{COS} + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{S}$
12. $\text{COS} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + \text{SO}_2$
13. $\text{COS} \rightarrow \text{CO} + \frac{1}{2}\text{S}_2$

which are slower than the combustion reactions, would achieve high conversion of COS and CS₂ back to H₂S. However, there will be significant quantities of COS in the outlet of the WHB due to reaction in the boiler (Sames et al., 1990). These reactions are given as the first consuming reactions in Tables 3 and 4 (Paskall, 1979). Plant material balance data based on samples after the WHB indicate substantially higher concentrations of COS and CS₂ than what is predicted by equilibrium calculations for the furnace. In the same study referred to earlier (Sames et al., 1990), data based on samples of products leaving the furnace, before the WHB, indicated that even though the majority of COS is apparently formed in the WHB, the concentration of COS exiting the furnace is still an order of magnitude higher than what equilibrium calculations predict.

High levels of COS appear in conjunction with high levels of CO (CO production, as previously stated, is predominantly produced from CO₂ in the feed gas). This lends support to the argument that the reaction involving CO and elemental sulphur is a principal COS forming reaction (Sames and Paskall, 1984). It is shown as reaction 5 in Table 3. Many other possible reactions are also shown in Table 3. The production of CS₂ is believed to be related to the quantity of hydrocarbons in the feed (Paskall 1979, 1981; Sames and Paskall, 1984). Support for this supposition is found from the observed production of CS₂ in plants from saturated hydrocarbons and elemental sulphur, given as reactions 3 and 4 in Table 4. Sames and Paskall (1984) also reported a marked increase in CS₂ in the WHB effluent during methane spiking of the acid gas feed.

TABLE 4
Modified Claus Process Reaction Furnace Possible
CS₂ Side Reactions (Paskall, 1979)

CS ₂ — Forming	
1.	C + 2S ₁ → CS ₂
2.	CH ₄ + 2H ₂ S → CS ₂ + 4H ₂
3.	CH ₄ + 4S ₁ → CS ₂ + 2H ₂ S
4.	CH ₄ + 2S ₂ → CS ₂ + 2H ₂ S
5.	CO ₂ + 3S ₁ → CS ₂ + SO ₂
6.	C ₂ H ₆ + $\frac{7}{2}$ S ₂ → 2CS ₂ + 3H ₂ S
7.	C ₃ H ₈ + 5S ₂ → 3CS ₂ + 4H ₂ S
CS ₂ — Consuming	
8.	CS ₂ + 2H ₂ O → CO ₂ + 2H ₂ S
9.	CS ₂ + 2H ₂ O → 2SO ₂ + CH ₄
10.	CS ₂ + SO ₂ → CO ₂ + $\frac{3}{2}$ S ₂
11.	CS ₂ + CO ₂ → 2CO + S ₂

Sames et al. (1987) have also shown indirectly that the formation of COS and CS₂ in the furnace is a function of the flame temperature. CS₂ concentration appeared to drop as temperature increased although it was not clear whether less CS₂ was just forming or whether it was forming and then rapidly hydrolyzing. COS concentration rose to a maximum level and then decreased as the temperature increased. Sames et al. concluded that COS might have a higher activation energy for formation than CS₂ and, once the maximum reached, there was enough energy for the hydrolysis reaction to take over. It was subsequently concluded that in the furnace, CS₂ was relatively easy to form and hydrolyze, whereas COS was slower to form and more difficult to hydrolyze once formed. Hence, COS and CS₂ formation levels were functions of feed composition, flame temperature and residence time.

For sulphur conversion, plant data shows that equilibrium sulphur conversion in the furnace is not attained for lean feed plants (low H₂S feed concentration) but is attained for rich feed plants (high H₂S feed concentration), although equilibrium concentrations of other components are not attained (Paskall, 1979). Above 926°C, there is negligible difference between sulphur conversions achievable in the furnace by rich and lean feed plants (Paskall, 1981).

EMPIRICAL CORRELATIONS

Fischer (1974) presented nomographs for calculating the volume percent of the major compounds in the product gas from a Claus reaction furnace. The nomographs are a function of H₂S, CO₂ and CH₄ composition in the acid gas feed, assuming an H₂O content of 5.6% (volume). Fischer assumed a particular formation reaction for each of H₂, CO, COS and CS₂. The nomographs were then generated based on ideal gas equilibrium constants (*K_p*) and ideal enthalpies of formation. Apparently, the results of the nomographs

coincided well with experimental data, although no comparisons or references were given.

Sames and Paskall (1985) presented empirical correlations which predict the fractions of CO, H₂, COS, CS₂, and sulphur (as S₁) in the effluent of a kinetically limited furnace. The correlations were based on fitting plant data from more than 300 tests on 100 different sulphur trains, including both straight through and split flow configurations processing acid gas feed streams containing from 8 to 98 mol percent H₂S with 0.1 to 5.0 mol percent hydrocarbons and ranging in size from 14 to 1700 tonnes/day of sulphur production. The rationale for the correlations was that plant data showed that, in general, equilibrium was not attained in the furnace, with the deviation increasing as H₂S content in the acid gas decreased. Also, kinetic modelling of the furnace was not possible due to the fact that a complete list of reactions that occur in the furnace had not been delineated and for the reactions known to occur, kinetic reaction rate expressions were not available. The Western Research (Sames and Paskall, 1985) correlations are given below:

$$R(\text{CO}) = \text{fraction of furnace inlet carbon that forms CO} \\ = 0.002A^{0.0345} \exp(4.53A) \dots\dots\dots (4)$$

$$R(\text{H}_2) = \text{fraction of furnace inlet H}_2\text{S that cracks to H}_2 \text{ and S} \\ = 0.056 (\pm 0.024)$$

$$R(\text{COS}) = \text{fraction of furnace inlet carbon that forms COS} \\ = 0.01 \tan(100A), \text{ for } 0 \leq A \leq 0.86 \\ = 0.143 A > 0.86$$

$$R(\text{CS}_2) = \text{fraction of furnace inlet hydrocarbon that forms CS}_2 \\ = 2.6A^{0.971} \exp(-0.965A)$$

$$R(\text{S}) = \text{fraction of furnace inlet H}_2\text{S that forms elemental S} \\ = 1.58A^{1.099} \exp(-0.73A)$$

where *A* = mole fraction of H₂S in the acid gas feed on a dry basis.

Wen et al. (1987) integrated the empirical prediction of H₂, CO, COS and CS₂ into a free energy minimization equilibrium calculation. They curve fitted the Fischer (1974) charts and forced the values of these components at equilibrium to be equal to the empirical values while the distribution of the rest of the components was determined by equilibrium. This was done in an attempt to account for kinetic limitations in the furnace. The authors reported that CO + COS production from the furnace was closer to field data, published by Kerr (1976), than equilibrium calculations alone. Sulphur conversion in the furnace *also matched* field data (Kerr and Berlie, 1977) somewhat better than equilibrium calculations.

Another common technique for modifying equilibrium results for kinetic limitations is allowing some reactions to continue on below the adiabatic flame temperature to a "cutoff temperature" which is determined by matching plant data.

In one of the only true kinetics studies published for the temperatures occurring in the reaction furnace, Dowling et al. (1990) from Alberta Sulphur Research at the University of Calgary studied the kinetics of only one reaction, the reversible reaction between H_2 and S_2 to form H_2S . They concluded that the reaction was very rapid and showed that lower temperatures favored the forward reaction while higher temperatures favored the reverse reaction, the thermal decomposition of H_2S to H_2 and S_2 . Hence, H_2 consumption becomes more significant than the H_2S decomposition at the temperatures existing in the WHB of a Claus plant. The authors also formulated a rate expression for the reversible reaction and evaluated the frequency factors and activation energies in the Arrhenius type expressions for the specific rate constant. The forward reaction was first order with respect to H_2 and S_2 (overall second order) while the reverse reaction was first order with respect to H_2S . It was also concluded that quenching the gases leaving the furnace could maximize the S_2 and H_2 production in the furnace and that a quench time in the order of 0.05 seconds would be required to preserve as much as 80% of the initial H_2 on quenching from a temperature of 1300°C down to 600°C.

Objectives

It is clear from reviewing the many studies on the Claus furnace that the results of equilibrium calculations to estimate the composition of the gas mixture exiting the furnace do not match plant data. This has been attributed to kinetic limitations in the furnace. Because complete kinetic studies have not been done, the nature of these limitations is not well understood. Further, some of the reactions, such as the main Claus reactions, are considered fast while other reactions, such as the hydrolysis reactions are considered relatively slow at average furnace temperatures. It is also believed that the effectiveness of the mixing of the acid gases and air in the furnace, which is more of a mass transfer limitation, is a dominant factor (Paskall 1979, 1981; Fischer, 1974). This has resulted in empirical models being proposed (Sames and Paskall, 1985; Fisher, 1974; Wen et al., 1987) which attempt to account for these effects.

The primary objective of this work is to provide a review and perspective on how the results of equilibrium and empirical calculations and actual plant data compare in terms of the concentrations of H_2 , CO, COS and CS_2 in the furnace effluent and sulphur conversion in the furnace. Subsequently, the effect of the model used in simulating a modified Claus plant on the equipment size and sulphur recovery is discussed.

In order to accomplish this an equilibrium model was required. Thus, a secondary objective was to develop an equilibrium model and verify it against an accepted equilibrium model.

Equilibrium model

Our model developed for this study of the modified Claus process reaction furnace is based on Gibbs free energy minimization using the method outlined by Walas (1985). The main advantage of free energy minimization is the fact that stoichiometry for all the possible reactions is not required, but simply a list of chemical species expected to be present at equilibrium and their Gibbs energies of

TABLE 5
Equilibrium Model Calculation Test (SULSIM® Comparison)
(Example taken from GPSA Engineering Data Book, 1987)

Component	Product (kmol/h)	
	This study	SULSIM®
H_2S	22.32	22.19
CO_2	62.68	63.13
H_2O	128.37	128.59
CH_4	0.00	0.00
NH_3	0.00	0.00
SO_2	20.43	20.11
S_2	44.28	44.63
N_2	264.27	264.22
O_2	0.00	0.00
H_2	9.06	8.99
CO	8.77	8.91
COS	0.22	0.12
CS_2	0.00	0.00
Total:	560.40	560.89
Adiabatic flame temperature (°C)	1096.6	1090.2
Sulphur conversion (%)	67.07	67.87

formation at equilibrium temperature and pressure, heat of formation at 298.15K and specific heat values from 298.15K to equilibrium conditions.

To perform the calculations, a computer program was written. The Gibbs free energies and heats of formation (at 298.15K) were obtained from the JANAF Thermochemical Tables (Chase et al., 1985). Constants for the specific heat equations were obtained from Reid et al. (1986). The Gibbs free energies were fit to a cubic polynomial in temperature through the range 1000 to 2000K, which covers the typical range of furnace adiabatic flame temperatures.

It should be noted here that S_2 was the only sulphur species considered in this work. This is because virtually all elemental sulphur is in the form of S_2 at temperatures ranging from 1000 – 2000K as can be seen by equilibrium results generated by Meisen et al. (1974), Wen et al. (1987) and Western Research (Paskall, 1979; Sames et al., 1990). Also, all simulations were for "straight through" configurations.

Results and discussion

The equilibrium model developed in this work was verified against the commercial simulator SULSIM®. In all cases, the results closely matched. For instance, one comparison which is an example problem from the Gas Processors Suppliers Association (GPSA) Engineering Data Book (1987) is shown in Table 5. The distribution of products, the adiabatic flame temperature and the sulphur conversion all agree well with SULSIM®.

After verifying the model, two sets of results were generated. The first set of results was based on hypothetical acid gas feeds, ranging from 50 mol % to 90 mol % H_2S (dry). For each case, the acid gas was assumed to have 1.0% (dry) hydrocarbons, as methane (CH_4), which is average for

TABLE 6
Composition of Hypothetical Acid Gas Feeds Given on a Dry and Wet Basis

H ₂ S mol % Dry	CO ₂ mol % Dry	CH ₄ mol % Dry	H ₂ S mol % Wet	CO ₂ mol % Wet	CH ₄ mol % Wet	H ₂ O mol %
50.00	49.00	1.00	46.70	45.76	0.93	6.61
60.00	39.00	1.00	56.03	36.42	0.93	6.61
70.00	29.00	1.00	65.37	27.08	0.93	6.61
80.00	19.00	1.00	74.71	17.74	0.93	6.61
90.00	9.00	1.00	84.05	8.41	0.93	6.61

TABLE 7
Feeds of Ultramar Refinery Tests

Test	Amine acid gas	Sour water stripper	Oxygen (enrichment)	Air
kmol/h				
1	81.44	35.26	9.86	168.89
2	68.71	31.52	0.00	189.37
3	59.77	0.00	0.00	112.06
4	83.32	0.00	6.96	123.59
5	92.94	51.39	25.66	139.14

Composition (mol %):

Test:	Amine Acid gas		Sour water stripper		Air
	1,2	3,4,5	1,2	3,4,5	
Component					
H ₂ S	88.80	89.16	58.71	54.48	0.00
CO ₂	10.57	10.55	2.31	1.76	0.00
NH ₃	0.00	0.00	37.97	43.22	0.00
C ₂ H ₆	0.15	0.12	0.43	0.26	0.00
N ₂	0.48	0.17	0.28	0.28	79.05
O ₂	0.00	0.00	0.00	0.00	20.95

Saturation conditions:

T (°C)	32.2	32.2	84.1	87.7	21.1
P (kPa)	182.3	183.8	176.9	175.7	99.9
Humidity (%)	100.0	100.0	100.0	100.0	75.0

Note: Actual hydrocarbon distribution assumed to be C₂H₆ in this work.

Alberta, Canada. Also, the gas was assumed to be saturated with water at 43.3°C and 133.1 kPa, which are typical inlet conditions to a Claus plant reaction furnace. This results in a water content of 6.61 mol %. The remainder of the acid gas was assumed to be CO₂, with no other impurities. The air fed to the furnace was assumed to be 20.63 mol % O₂, 77.62 mol % N₂ and 1.75 mol % H₂O, which corresponds to being water saturated at 15.5°C and 101.3 kPa. From a polytropic calculation with an efficiency of 70% and with the air assumed to be entering the blower at standard conditions, the discharge temperature was calculated to be 60°C, again a typical temperature for air entering the reaction furnace. These results were used to compare equilibrium calculations of the furnace effluent with some plant data based on the waste heat boiler effluent and empirical models and are shown in Figures 3 to 15. The feed gas composition is summarized in Table 6.

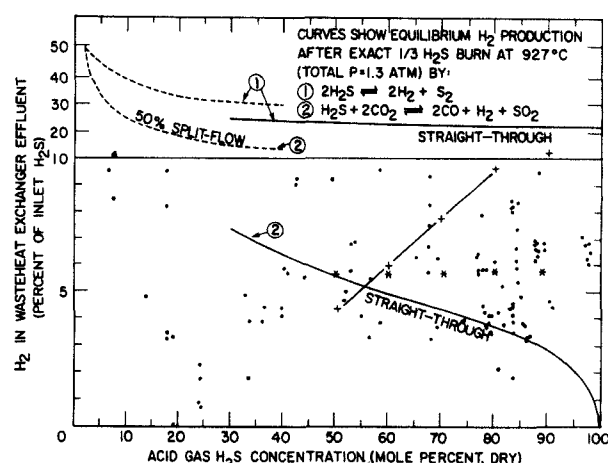


Figure 3 — H₂: Equilibrium results vs empirical correlation and plant data.

- = Plant data
- + = Equilibrium (adiabatic flame temperature)
- * = Western Research correlation

The second set of results were used to compare equilibrium calculations and empirical predictions of the furnace effluent with plant data from the reaction furnace effluent from Sames et al. (1990). These results are shown in Figures 16 to 18 and the feed composition to the furnace is summarized in Table 7. Note that in both cases, the concentrations of the components H₂, CO, COS and CS₂ in the furnace effluent as well as sulphur conversion in the furnace were studied.

COMPARISONS WITH PLANT DATA — WHB EFFLUENT

Figures 3 to 7 compare the generated equilibrium data with the Western Research empirical correlations, plotted on graphs reproduced from Paskall (1979) which show actual plant data based on samples taken from the WHB effluent. Figure 3 compares hydrogen (H₂) data. This figure shows that, in general, equilibrium predicts concentrations of H₂ too high for acid gas feeds with an H₂S content of about 65% or higher and too low below this value. However, the data is highly scattered, showing no obvious trend, indicating that perhaps it needs to be correlated with additional variables such as residence time and/or flame temperature. In fact, Western Research's correlation is simply an average value of 5.6%, which is a somewhat better estimate than the equilibrium results.

Figure 4 compares carbon monoxide (CO) data. This figure indicates that the equilibrium calculations tend to overpredict the concentration of CO in the furnace effluent. The free energy minimization calculations appear to favour the H₂S + CO₂ reaction to form CO although the plant data shows that CO formation is probably due to a combination of this reaction and CO₂ dissociation. Again, the data is scattered although an increasing trend is evident. Western Research's correlation reflects this as it increases through the middle of the data, again a better estimate than the equilibrium results.

Figure 5 compares carbonyl sulphide data (COS) data. In this case, equilibrium predicts a constant 1% of total inlet carbon forms COS. From the actual data, it can be seen that this is a substantial underprediction. Again, the plant data is scattered with an increasing trend, with Western Research's correlation through the middle of the data similar

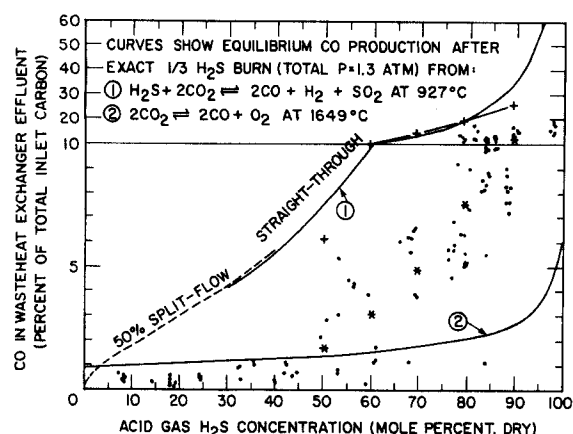


Figure 4 — CO: Equilibrium results vs empirical correlation and plant data.

- = Plant data
- + = Equilibrium (adiabatic flame temperature)
- * = Western Research correlation

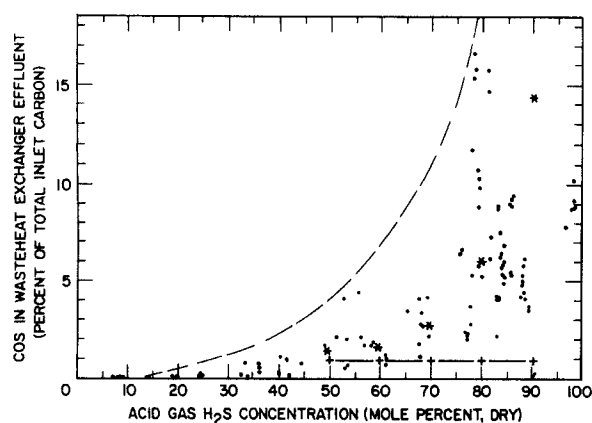


Figure 5 — COS: Equilibrium results vs empirical correlation and plant data.

- = Plant data
- + = Equilibrium (adiabatic flame temperature)
- * = Western Research correlation

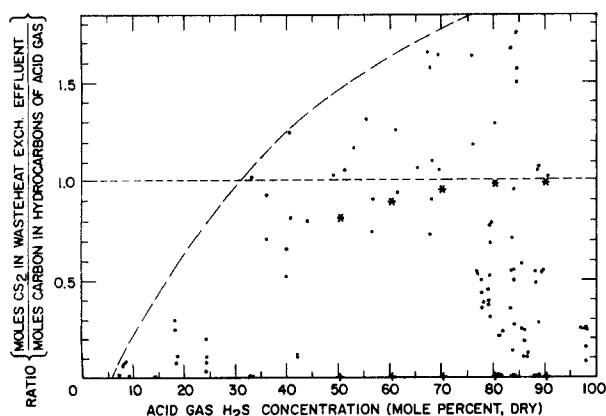


Figure 6 — CS₂: Equilibrium results vs empirical correlation and plant data.

- = Plant data
- + = Equilibrium (adiabatic flame temperature)
- * = Western Research correlation

to the delimited trend, again a better estimate than the equilibrium results.

Figure 6 compares carbon disulphide (CS₂) data. Again, equilibrium substantially underpredicts the concentration.

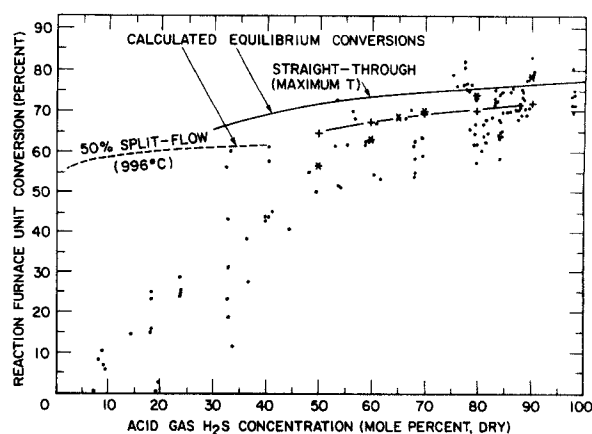


Figure 7 — Sulphur conversion: equilibrium vs plant data.

- = Plant data
- + = Equilibrium (adiabatic flame temperature)
- × = Sulsim® test point
- * = Western Research correlation

Both the COS and CS₂ underprediction can be attributed to hydrolysis being essentially complete at equilibrium, as previously discussed. The data in this figure is again very scattered and Western Research chose to fit their correlation through the middle of the data.

SULPHUR CONVERSION

Figure 7 compares sulphur conversion data. This figure shows that equilibrium sulphur conversion is only attained for relatively rich acid gas feeds (>80–90% H₂S), with the deviation from equilibrium increasing as the H₂S content is reduced. The equilibrium model developed in this work does not predict points on the Western Research equilibrium curve in the graph, deviating by about 6%. It is not evident why this occurs since this model's predictions matched those of Sulsim® and were within about 2% of the values of Kerr and Berlie (1977). However, this may simply be due to the equilibrium constant or free energy data used to generate the conversion values. The Western Research correlation fits the data better than the equilibrium results.

COMPARISONS WITH FISCHER NOMOGRAPH AND WESTERN RESEARCH CORRELATIONS — WHB EFFLUENT

Figures 8 to 12 compare equilibrium predictions with both the Western Research correlations (Sames et al., 1985) and the Fischer (1974) nomographs. The Western Research correlations give results as a percent of inlet composition while the Fischer nomographs give results as mol fraction in the furnace effluent. To compare the equilibrium and two empirical methods, a common basis was required. Hence, Figures 8–11 are presented as mol percent of H₂, CO, COS or CS₂ versus mol percent of H₂S (dry) of the acid gas feed. Since the Fischer nomographs appeared to be generated using stoichiometric air, this was also used with the Western Research correlations and equilibrium calculations to generate these figures.

Figure 8 shows that the equilibrium predictions for H₂ concentration in the furnace effluent are lower than the Western Research correlation below about 60% H₂S, after which they are higher which is similar behavior to that shown in Figure 3, where the data was presented differently.

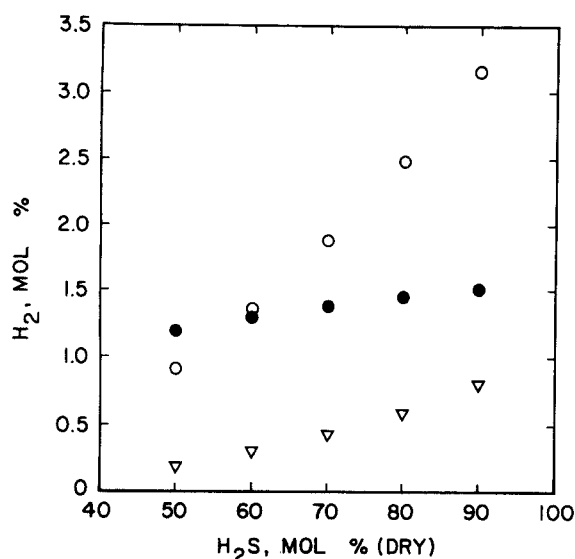


Figure 8 — Comparison of predicted H_2 concentration in furnace effluent.

○ = Equilibrium
● = Western Research correlation
▽ = Fischer nomograph

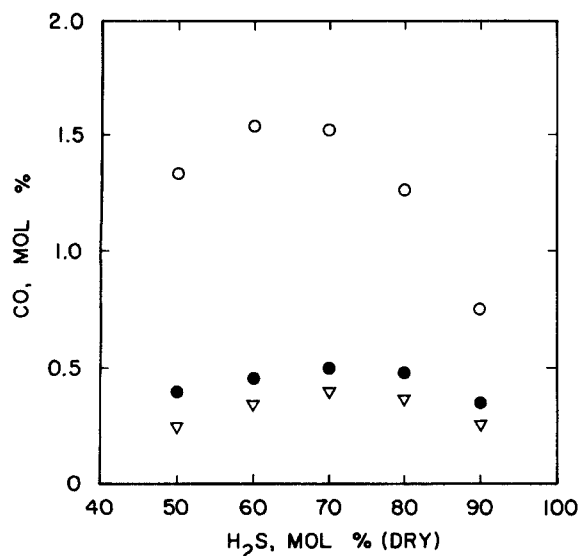


Figure 9 — Comparison of predicted CO concentration in furnace effluent.

○ = Equilibrium
● = Western Research correlation
▽ = Fischer nomograph

The Fischer nomographs predict values which are substantially lower than both equilibrium predictions and the Western Research correlation. Since the Fischer nomograph is based on the reaction of $CH_4 + H_2O$ to form H_2 , for a low hydrocarbon content, which is common, low values of H_2 are predicted. Conversely, Western Research believes that the major source of H_2 is the thermal cracking of H_2S . All models show an increase in H_2 concentration with H_2S content in the acid gas feed, although as indicated, the equilibrium results show the steepest trend.

Figure 9 shows that the equilibrium predictions for CO concentration in the furnace products are considerably greater than both of the empirical models, which in this case are in reasonable agreement for both trend and magnitude. Even though CO_2 concentration in the feed is decreasing as

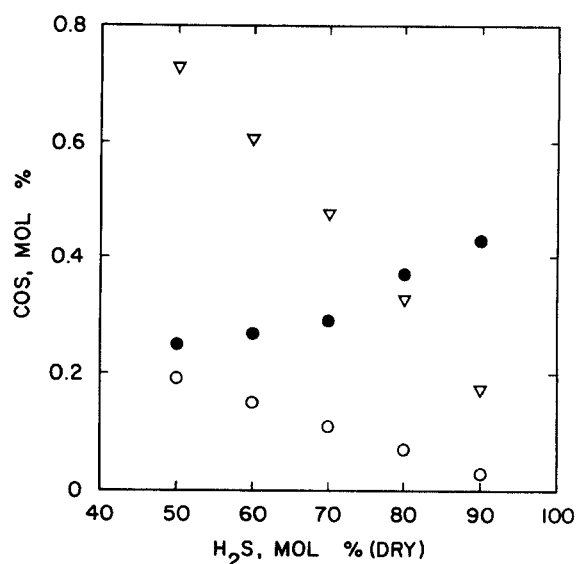


Figure 10 — Comparison of predicted COS concentration in furnace effluent.

○ = Equilibrium
● = Western Research correlation
▽ = Fischer nomograph

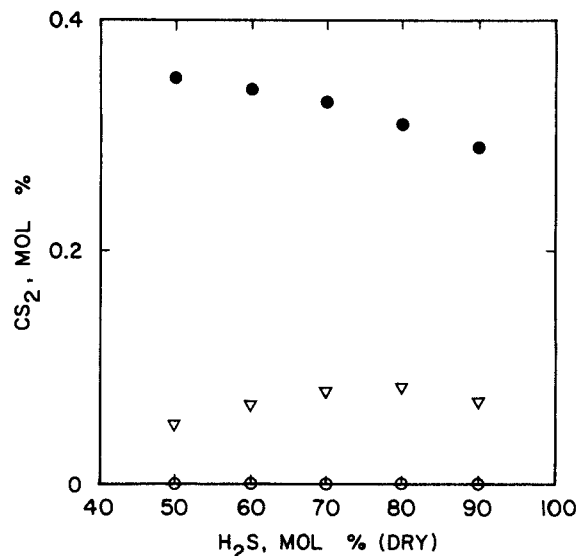


Figure 11 — Comparison of predicted CS_2 concentration in furnace effluent.

○ = Equilibrium
● = Western Research correlation
▽ = Fischer nomograph

H_2S increases, all models indicate that the mol percent of CO first increases, goes through a maximum and then decreases.

Figure 10 shows that the COS concentration predicted in the furnace product from equilibrium is lower than both of the empirical models. In this case, the trend of the equilibrium and Fischer nomographs, which decrease with H_2S content, are opposite to the Western Research correlation which increases with H_2S content. This may be because the Western Research correlation reflects the formation of COS in the waste heat boiler.

Figure 11 shows that equilibrium predicts practically no CS_2 in the furnace effluent. On the other hand, the correlation of Western Research predicts a relatively significant CS_2 concentration. The Fischer nomograph predicts the

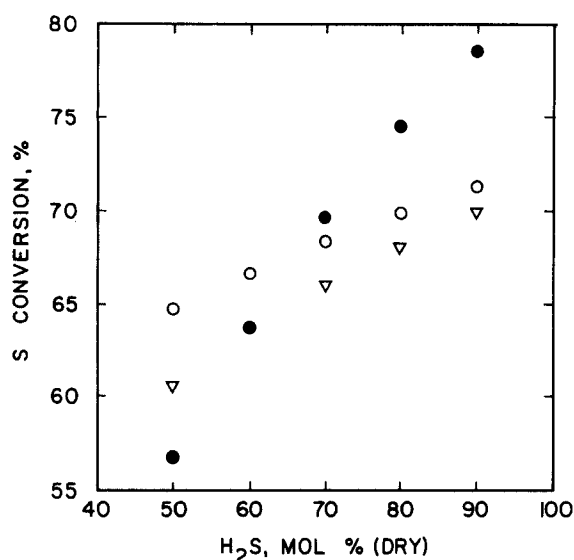


Figure 12 — Comparison of sulphur conversion at furnace exit.
 ○ = Equilibrium
 ● = Western Research correlation
 ▼ = Fischer nomograph

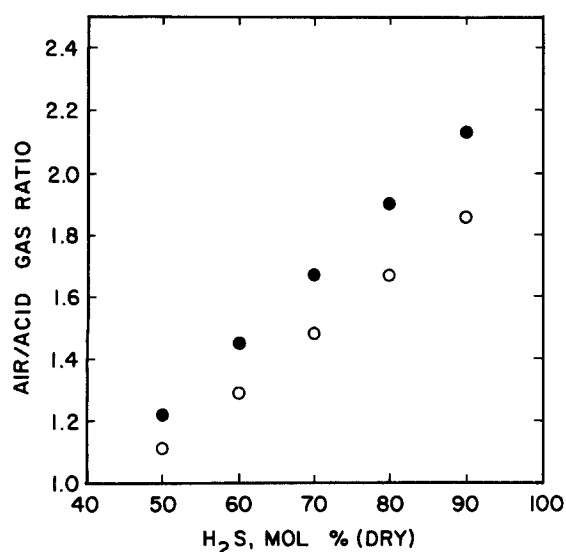


Figure 13 — Comparison of equilibrium vs Stoichiometric air required in furnace.
 ○ = Equilibrium air
 ● = Stoichiometric air

concentration of CS₂ greater than equilibrium but 4–7 times lower than the Western Research correlation. Also, the trends of the two empirical methods do not agree. The Western Research correlation predicts a monotonically decreasing trend while the Fischer nomograph predicts a trend which increases, goes through a maximum and then decreases.

Finally, furnace sulphur conversion is shown in Figure 12. Equilibrium values agree to within 1% of the “classic” equilibrium curves, such as those published in the GPSA Engineering Data Book (1987) or by Bennett and Meisen (1973) and Meisen and Bennett (1974). The Fischer nomograph gives slightly lower conversions whereas the Western Research correlations predict a lower conversion up to about 67% after which they exceed equilibrium results, an apparent contradiction.

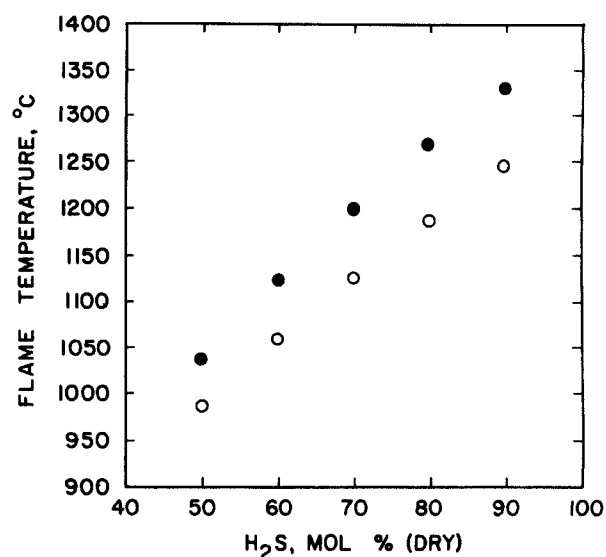


Figure 14 — Effect of excluding key components on flame temperature.
 ○ = Including H₂, CO, COS, CS₂
 ● = Excluding H₂, CO, COS, CS₂

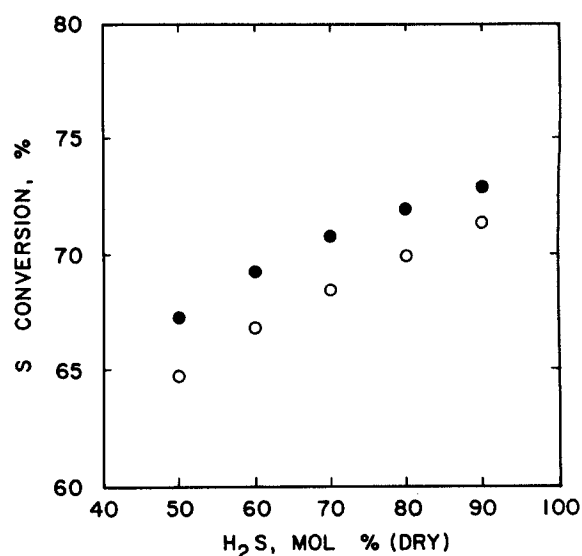


Figure 15 — Effect of excluding key components on sulphur conversion.
 ○ = Including H₂, CO, COS, CS₂
 ● = Excluding H₂, CO, COS, CS₂

FURNACE AIR REQUIREMENTS

Figure 13 shows the air to acid gas ratio versus the feed H₂S mol percent (dry). The equilibrium curve represents the values which correspond to a H₂S/SO₂ ratio of 2/1 leaving the furnace, based on an equilibrium calculation. The stoichiometric curve represents the air required to burn 1/3 of the H₂S to SO₂ plus all of the CH₄ in the acid gas feed(s). This amount of air results in an H₂S/SO₂ ratio leaving the furnace of about 1/1, much less than the ideal 2/1. Stoichiometric air only gives a 2/1 ratio if H₂, CO, COS and CS₂ are not included in the calculation. Kerr and Berlie (1977) showed that actual air requirements fall between these two limits.

EFFECT OF NEGLECTING H₂, CO, COS AND CS₂

Figures 14 and 15 show the effect of neglecting H₂, CO, COS and CS₂ in furnace calculations, as is done in

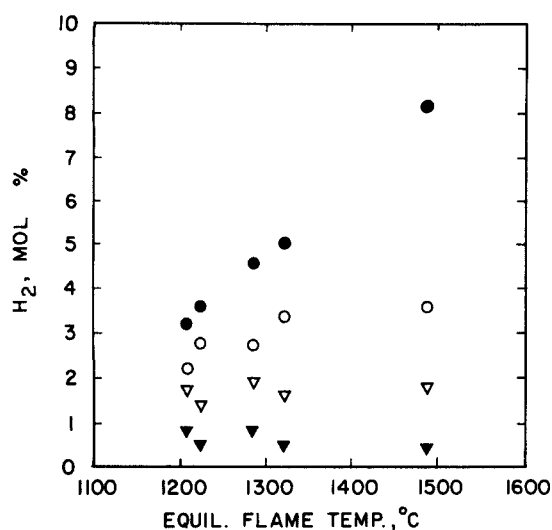


Figure 16 — H_2 concentration — actual data (Sames et al., 1990) vs. equilibrium and empirical models.

○ = Measured furnace exit
● = Equilibrium
▽ = Western Research correlation
▼ = Fischer nomograph

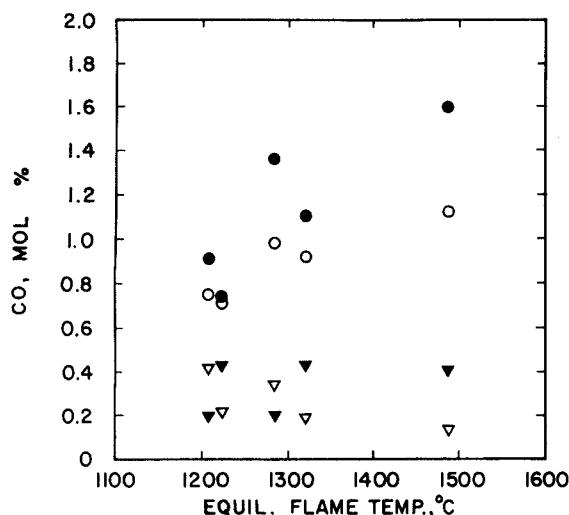


Figure 17 — CO concentration — actual data (Sames et al., 1990) vs. equilibrium and empirical models.

○ = Measured furnace exit
● = Equilibrium
▽ = Western Research correlation
▼ = Fischer nomograph

many simplified hand calculations. If these compounds are excluded, the flame temperature and sulphur recovery are higher than if they are included. Adiabatic flame temperatures were 5–7% higher while sulphur conversions are 1.5–2.5% higher.

FURNACE EFFLUENT COMPARISONS

Figures 16 to 18 compare equilibrium results for H_2 , CO and COS with actual plant data from the furnace effluent and the two previously compared empirical methods. Figures 16 and 17 show that equilibrium predictions for H_2 and CO concentrations in the furnace effluent are higher than the measured furnace effluent quantities. For H_2 , equilibrium overpredictions range from about 30% to more than double, while for CO they range from about 3% to about 45%. The

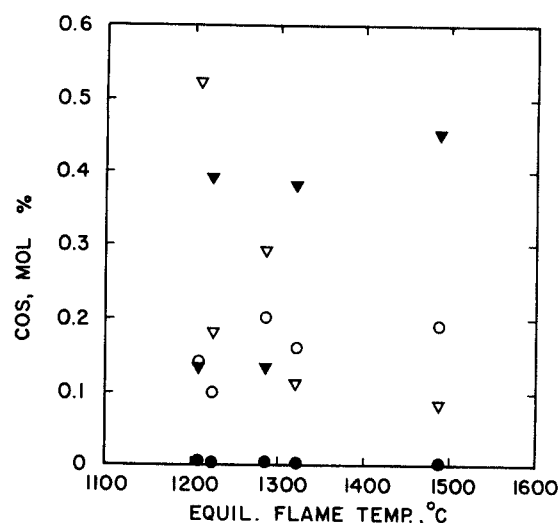


Figure 18 — COS concentration — actual data (Sames et al., 1990) vs. equilibrium and empirical models.

○ = Measured furnace exit
● = Equilibrium
▽ = Western Research correlation
▼ = Fischer nomograph

maximum overpredictions occurred for a case where a significant amount of air enrichment was used, resulting in a high adiabatic flame temperature. In terms of trend, only the equilibrium calculations remotely followed the furnace effluent plant data. Both empirical models tended to underpredict H_2 and CO quantities, and did not follow the trend of the furnace effluent plant data. For COS, Figure 18 shows that equilibrium predictions were much too low and in this case, the predictions were so low that it is difficult to determine the trend. Both empirical models predicted COS production but neither model matched the trend of the furnace effluent data, although in magnitude, the Western Research correlation compared reasonably well. For CO and COS, the two empirical models did not follow each other in terms of trend.

Process design implications and sulphur recovery

In order to compare the implications of the reaction furnace model on design, overall sulphur recovery and emissions, a two-stage modified Claus plant was simulated using SULSIM®. The 60 mol % H_2S (dry) and 80 mol % H_2S (dry) hypothetical acid gas cases were used as feed gases at a molar flow rate of 45.36 kmol/h (100 lbmol/h). These cases were selected because the 60 mol % H_2S (dry) case represents a feed for which the sulphur conversion in the furnace based on the Western Research correlations is lower than the result of an equilibrium calculation while the 80 mol % H_2S (dry) case represents a feed for which the sulphur conversion in the furnace based on the Western Research correlations is higher than the result of an equilibrium calculation.

For each feed, one simulation was performed using the equilibrium furnace model and a second simulation was performed using the Western Research empirical model. All pressures, temperatures and equilibrium approaches which are set, were set the same for both simulations. The outlet temperatures of the WHB, thermal condenser, first and second stage condensers were set at 371, 182, 160 and 138°C respectively. The outlet temperatures of the first and second

TABLE 8
Comparison of Design Variables and Sulphur Recovery for
Equilibrium vs Western Research Correlations

Case:	60% H ₂ S (Dry)		80% H ₂ S (Dry)	
	Equil.	West. Res.	Equil.	West. Res.
Air Requirement (kmol/h)	58.26	60.50	74.91	79.41
Furnace Effluent Molar Flow (kmol/h)	103.63	105.01	120.79	124.24
Furnace Effluent Molecular Weight (kg/kmol)	32.13	32.32	30.84	31.02
Furnace Flame Temperature (K)	1286	1333	1398	1463
Overall Sulphur Recovery (%)	96.4	95.2	96.6	95.7
Stack Gas Sulphur Emissions as SO ₂ (kmol/h)	0.91	1.23	1.14	1.47

Notes: 1. Based on 2-stage Claus plant simulations run on SULSIM® with identical parameters set for all cases. The molar flow of feed was 45.36 kmol/h (100 lbmol/h).

stage (indirect) reheaters were set to 232 and 216°C, respectively. The pressure at the reaction furnace exit was set to 133.03 kPa and a typical pressure drop of about 3.45 kPa was taken across the reheaters and condensers and 4.14 kPa was taken across the (one-pass) WHB and converters. Approach to equilibrium for the Claus reaction in the catalytic converters was set to 95% while the approach to equilibrium for the COS/CS₂ hydrolysis in the first converter was set to 80% (typical for new catalyst). The air requirement was calculated to achieve a H₂S/SO₂ ratio of 2/1 in the tailgas. The salient results of the simulation are summarized in Table 8. Using the results in Table 8, equipment sizes based on using the Western Research correlations to model the furnace were ratioed to sizes based on equilibrium results. Although all the detailed calculations are not presented here, example calculations for the reaction furnace waste heat boiler and catalytic converters are presented below.

Furnace Volume Ratio:

The volume of the reaction furnace is calculated from the following equation.

$$V_{fur} = (FRT/P)t_r \quad (5)$$

Since pressure and residence time are set the same for both models, the ratio of the volumes is stated as follows.

$$V_{fur,WR}/V_{fur,EQ} = (F_{WR}/F_{EQ})(T_{WR}/T_{EQ}) \quad (6)$$

Waste Heat Boiler Heat Transfer Area Ratio:

The area of any heat exchanger is calculated according to the following equation.

$$A = Q/(U \cdot LMTD) \quad (7)$$

For the WHB, the overall heat transfer coefficient is predominantly a function of the mass flux through the tubes and if the ratio of the mass flow rates is close to unity, the ratio of the coefficients will be close to unity. The duty of any heat exchanger is calculated according to the following equation.

$$Q = W C_p \Delta T \quad (8)$$

If the compositions entering the WHB from both models are similar, then the ratio of the specific heat values will be close to unity. From the values of molar flow and molar mass given in Table 8, both of the above assumptions are reasonable and as such, the ratio of the heat exchange areas may be stated as follows:

$$A_{WR}/A_{EQ} = (W_{WR}/W_{EQ})(\Delta T_{WR}/\Delta T_{EQ}) \\ (LMTD_{EQ}/LMTD_{WR}) \quad (9)$$

Catalytic Converter Catalyst Volume Ratio:

The volume of catalyst required in a converter is calculated from the following equation.

$$V_{cat} = Q_g/SV \quad (10)$$

The gas flow rate, Q_g , in standard m³/h may be calculated from the molar flow rate multiplied by the constant 23.69 m³/kmol and since the space velocity is set the same for both models, the ratio of the catalyst volumes is stated as follows:

$$V_{cat,WR}/V_{cat,EQ} = F_{WR}/F_{EQ} \quad (11)$$

Using equations (6), (9) and (11), the values from Table 8 and the temperature profile given previously resulted in the furnace volume and WHB and condenser heat transfer areas being 6% larger for the 60 mol % H₂S (dry) case and 8% larger for the 80 mol % H₂S (dry) case when the Western Research correlations were used to model the reaction furnace. Catalytic converter catalyst volumes and reheater duties were 2% larger for the 60 mol % H₂S (dry) case and 3% larger for the 80 mol % H₂S (dry) case. Hence, using the Western Research correlations to model the furnace result in a slightly more conservative plant design.

Table 8 also indicates that the overall sulphur recovery is 1.2% lower for the 60 mol % H₂S (dry) case and 0.9% lower for the 80 mol % (dry) using the Western Research correlations to model the furnace, compared to using the equilibrium model. These small differences, however, are substantial for sulphur recovery. The decrease in the difference between the two cases can be attributed to the sulphur conversion in the furnace based on the Western Research correlations exceeding the equilibrium result after about 67% H₂S, as shown in Figures 7 and 12. Corresponding sulphur emissions as SO₂ are 35% and 29% higher for the 60 mol % H₂S (dry) and 80 mol % H₂S (dry) cases, respectively. Hence, using the Western Research correlations to model the surface results in conservative estimates for overall sulphur recovery and sulphur emissions.

Conclusions and implications

The results of equilibrium calculations for the exit composition and temperature of a modified Claus plant reaction furnace tend to not agree with actual plant data, both before and after the WHB. Typically, CO composition is overpredicted, while COS and CS₂ are significantly underpredicted. H₂ is underpredicted at lower temperatures (and H₂S contents) and overpredicted at higher temperatures (and H₂S contents). Equilibrium sulphur conversion is only attained for relatively rich acid gas feeds (>80–90% H₂S). It is difficult to quantify these observations due to a lack of data based on the reaction furnace effluent. Most plant data that are supposed to represent the reaction furnace products are based on the waste heat boiler effluent.

Empirical models, based on fitting data from the waste heat boiler effluent, did not match the trends of the actual furnace effluent data. This is due to the simplified approaches of correlating the formation of a particular component in the furnace effluent as a function of a single variable, such as H₂S content in the feed, or attempting to attribute the formation of the component to a single reaction with a fitted equilibrium constant, correlated as a function of major feed constituents as evident from the significant scatter of plotted plant data, both before and after the WHB. Comparison of the empirical models showed that usually they were not consistent with one another. The scatter of the plant data when it was plotted as functions of a single variable indicates that additional variables are probably required to properly characterize the system. Nonetheless, of the two empirical models studied, the Western Research model appears to better represent plant data.

Overwhelmingly, the above discussion indicates that "kinetic" limitations in the furnace need to be addressed further in order to better quantify the composition of H₂, CO, COS and CS₂ in the furnace effluent. These limitations are presently not well understood and may or may not be due to reaction rates. However, it is believed that the effectiveness of the mixing of the acid gases and air in the furnace, which is more of a mass transfer limitation, is a dominant factor.

The components H₂, CO, COS and CS₂ should be included in furnace calculations. Excluding them results in optimistic sulphur conversion in the furnace. It also results in the adiabatic flame temperature being predicted too high and an incorrect air to acid gas ratio, subsequently affecting the plant material and heat balances.

Acknowledgement

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).

Nomenclature

<i>A</i>	= heat transfer area (m ²)
<i>B</i>	= burner
<i>BFW</i>	= boiler feed water
<i>C_p</i>	= specific heat [J/(kg · s)]
<i>F</i>	= molar flow rate (kmol/h)
<i>HPS</i>	= high pressure steam
<i>LMTD</i>	= log mean temperature difference (°C or K)
<i>LPS</i>	= low pressure steam
<i>P</i>	= pressure (kPa)
<i>Q</i>	= heat exchanger duty (W)
<i>Q_g</i>	= gas volumetric flow rate at STP (m ³ /h)

<i>R</i>	= gas constant
<i>RF</i>	= recovery furnace
<i>SV</i>	= space velocity (h ⁻¹)
<i>t_r</i>	= residence time (s)
<i>T</i>	= temperature (°C or K)
<i>TGCU</i>	= tail gas clean-up unit
<i>ΔT</i>	= temperature difference across heat exchanger (°C or K)
<i>U</i>	= overall heat transfer coefficient [W/(m ² · K)]
<i>V</i>	= volume (m ³)
<i>W</i>	= mass flow rate (kg/s)
<i>WHB</i>	= waste heat boiler

Subscripts

<i>cat</i>	= catalyst
<i>fur</i>	= furnace
<i>EQ</i>	= equilibrium
<i>WR</i>	= Western Research

References

- Bennett, H. A. and A. Meisen, "Hydrogen Sulphide — Air Equilibria under Claus Furnace Conditions", *Can. J. Chem. Eng.*, **51**, 720–732 (1973).
- Chase, M. W., C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald and A. N. Syverud, JANAF Thermochemical Tables, 3rd Edition, American Chemical Society and the American Institute of Physics for the National Bureau of Standards, Washington, DC (1985).
- Dowling, N. I., J. B. Hyne and D. M. Brown, "Kinetics of the Reaction between Hydrogen and Sulphur under High-Temperature Claus Furnace Conditions", *Ind. Eng. Chem. Res.*, **29**, 2327–2332 (1990).
- Fischer, H., "Burner/Fire Box Design Improves Sulfur Recovery", *Hydrocarbon Process.* October, 125–130 (1974).
- Gas Processors Suppliers Association (GPSA), Engineering Data Book, Ch. 22, GPSA, Tulsa, OK, (1987).
- Hyne, J. B., "Design and Chemistry of Front End Reaction Furnaces", *Canadian Gas Journal (Gas Processing/Canada)* **12**, (March/April, 1972).
- Kerr, R. K., "The Claus Process: Capability/Thermodynamics", *Energy Process, Can.*, 28–35 (July/Aug., 1976).
- Kerr, R. K. and E. M. Berlie, "The Claus Process: Reaction Furnace/Burner Operation", *Energy Process. Can.*, 42–46 (May/June, 1977).
- Luinstra, E. A. and P. E. d'Haene, "Catalyst Added to Claus Furnace Reduces Sulfur Losses", *Hydrocarbon Process.*, 53–57 (July, 1989).
- Meisen, A. and H. A. Bennett, "H₂S–CO₂–H₂O–Air Equilibria Under Claus Furnace Conditions" *Canadian Sulphur Symposium*, Dept. of Chem., Univ. of Calgary, Alberta, Canada (1974).
- Paskall, H. G., "Capability of the Modified-Claus Process. A Final Report to the Department of Energy and Natural Resources of the Province of Alberta", Ch. IV (1979).
- Paskall, H. G., "Reaction Furnace Chemistry and Operational Modes", *Sulphur Recovery*, Western Research Calgary, Alberta, Canada (1990) (originally published in 1981).
- Reid, R. C., J. M. Prausnitz and B. E. Poling, "The Properties of Gases and Liquids", McGraw-Hill Book Company, New York (1986).
- Sames, J. A. and H. G. Paskall, "So You Don't Have a COS/CS₂ Problem, eh?" *Sulphur Recovery*, Western Research, Calgary, Alberta, Canada (1990), (originally published in *Sulphur*, June, 1984).
- Sames, J. A. and H. G. Paskall, "Simulation of Reaction Furnace Kinetics for Split-Flow Sulphur Plants", *Sulphur Recovery*, Western Research, Calgary, Alberta, Canada (1990) (originally published as a paper for the Sulphur '85 conference, November, 1985).

- Sames, J. A., P. R. Dale and B. Wong, "Evaluation of Reaction Furnace Variables in Modified Claus Plants", Sulphur Recovery, Western Research, Calgary, Alberta, Canada (1990), (originally published for the Laurence Reid Gas Conditioning Conference, March, 1987).
- Sames, J. A., H. G. Paskall, D. M. Brown, M. S. K. Chen and D. Sulkowski, "Field Measurements of Hydrogen Production in an Oxygen Enriched Claus Furnace", Sulphur Recovery, Western Research, Calgary, Alberta, Canada (1990), (also in preprints of Sulphur 1990 International Conference, April, 1990).
- Walas, S. M. "Phase Equilibria in Chemical Engineering", Butterworth Publishers, Boston, MA, (1985).
- Wen, T. C., D. H. Chen, J. R. Hopper and R. N. Maddox, "Claus Simulation with Kinetics" *Energy Process. Can.*, 25-32 (July/Aug., 1987).
- Younger, A. H., Natural Gas Processing Technology Course Notes, University of Calgary, Calgary, Alberta (1991).

Manuscript received October 10, 1992; revised manuscript received April 30, 1993; accepted for publication May 18, 1993.