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Simulation of the Direct Production of Synthesis Gas from Sour Natural Gas by Noncatalytic Partial Oxidation (NCPO): Thermodynamics and Stoichiometry

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Noncatalytic partial oxidation of sour natural gas is proposed in this paper as a novel scheme for the production of synthesis gas, which is generally integrated with a process for ammonia or methanol. The proposed scheme has many potential advantages vis-à-vis the existing steam-reforming process of sweet natural gas. It is a noncatalytic process in which the sour feed does not require desulfurization. The combustion of sour natural gas in oxygen under noncatalytic partial oxidation (NCPO) conditions is investigated theoretically using AspenPlus simulation techniques. The main scope of the work is to study the stoichiometry and thermodynamics of the proposed scheme. A kinetics study and the reactor characteristics are not within the domain of this paper. Separation of SO_2 gas from the synthesis gas was carried out by absorption in water to produce sulfurous acid, the feedstock to what is known as the "modified Westinghouse cycle". The role of various operating parameters in establishing the optimum yield of the H_2/CO gas mixture was investigated. This included feed temperatures of 900 and 1200 °F, an equivalence ratio (moles of O_2/moles of CH_4) between 0 and 1, and a H_2S content in methane between 0 and 10%.

Introduction

Large reserves of natural gas are present in many oil-producing countries. Much of this natural gas is sour (i.e., it contains varying amounts of H_2S gas), and it has to be used as a feedstock for the manufacture of synthesis gas.

Currently, synthesis gas is produced by steam re-forming of sweet natural gas. This is a catalytic process in which the feed gas has to be sulfur free to avoid catalyst poisoning. As a result, acidic gas removal is a prerequisite for the steam-reforming process. H_2S is separated from the natural gas by one of the physio-chemical separation methods. The separation process is expensive and involves the use of amine solvents. The chemisorption of acidic gas into the solvents is followed by regeneration of these solvents. Although the bulk production of synthesis gas is done via catalyzed steam reforming of sweet natural gas, uncatalyzed partial oxidation of sour natural gas with appropriate conditions may prove to be more attractive.

The main theme of the proposed work is to propose a novel scheme for the direct manufacture of synthesis gas from sour natural gas by partial oxidation and in the absence of catalysts. Synthesis gas is the mixture of H_2 and CO used as a feedstock for petrochemical plants. This is a continuation of the work proposed earlier by Abdel-Aal and Shalabi.[1] Experimental work published by Mungen and Kratzer on the NCPO of sweet natural gas[2] will test the simulation algorithm proposed here.

The most common processes used worldwide for the production of synthesis gas are the steam reforming of natural gas, the steam reforming of naphtha, the partial oxidation of fuel oil, and the partial oxidation of
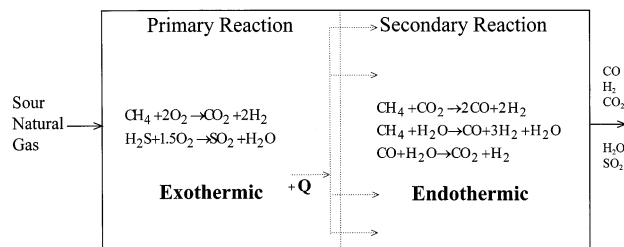
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Figure 1. Conceptual illustration of the two-stage mechanism of the noncatalytic partial oxidation of sour natural gas (proposed).

naphtha. Other advanced processes for the manufacture of synthesis gas are in the experimental stage. They have not been utilized industrially. These processes include catalytic partial oxidation (CPO) and noncatalytic partial oxidation (NCPO). Published work on the various processes for the production of sythesis gas is summarized elsewhere.[3]

Theoretical Background

Partial Oxidation. The actual reaction mechanism of the partial oxidation of sour natural gas is complex, but the behavior is consistent with a two-stage reaction mechanism, shown in Figure 1 involving complete combustion of some of the methane and all of the hydrogen sulfide in the first stage via highly exothermic reactions.[4] The large values of the equilibrium constants of these reactions[1] indicate that these reactions go to completion. The primary reactions are

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

$$H_2S + {}^3/_2O_2 \rightarrow SO_2 + H_2O \qquad (2)$$
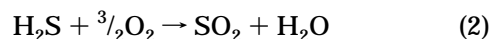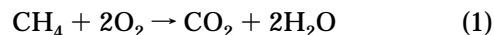
A large surplus of methane remains unreacted in the gases exiting the primary reactions. The surplus meth-
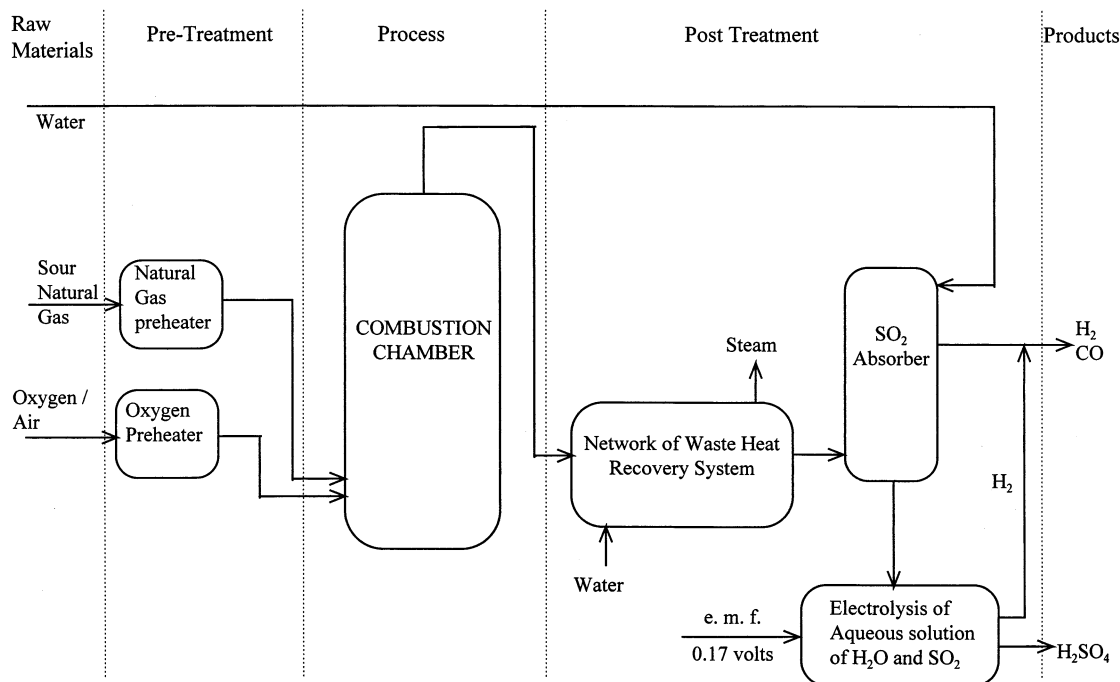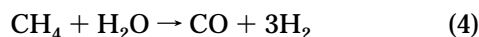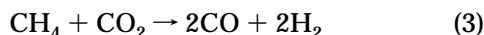
Figure 2. Schematic diagram of the proposed process of noncatalytic partial oxidation.

ane then reacts with the products of the primary reaction in the second stage as follows:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (3)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (4)$$

Whereas primary reactions 1 and 2 are highly exothermic, both reactions 3 and 4 are highly endothermic. The excess heat liberated in the primary reactions is supplied to the secondary reactions. Hence, the reactions are self-regulating (autothermal). Equilibrium is very far to the right in reactions 3 and 4, and no measurable amount of oxygen remains. The overall reaction is

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad (5)$$
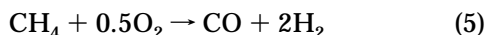
These reactions can be classified into two categories as shown in Figure 1.

In addition to the above reactions of methane, the products can react via the exothermic water gas shift reaction:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad (6)$$
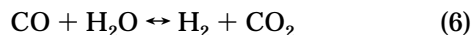
Open Sulfur Cycle Process. In the proposed process of production of synthesis gas by noncatalytic partial oxidation of sour natural gas as shown in Figure 2, effluent synthesis gas from the combustion chamber containing SO_2 is absorbed by water in a column. The aqueous solution of SO_2 (sulfurous acid) is introduced as the "Westinghouse" process or sulfur cycle process, where hydrogen and sulfuric acid are produced:

$$2H_2O(l) + SO_2(aq) \rightarrow H_2SO_4(aq) + H_2(g)$$
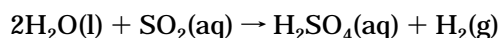
It is more beneficial to use an open sulfur cycle instead of a closed sulfur cycle.[5] The open sulfur cycle continuously produces sulfuric acid as the main product.

Process Description

Sour natural gas and oxidant are preheated separately prior to the partial oxidation. Sour natural gas

undergoes cracking above 1200 °F followed by the deposition of carbon, and the oxidant is highly reactive above 1000 °F, which is highly undesirable. Sour natural gas is preheated only up to 1200 °F, and the oxidant is preheated only up to 1000 °F.

The sour natural gas and the oxidant should be thoroughly mixed as soon as they are introduced into the combustion chamber, prior to the partial oxidation. As shown in Figure 2, the noncatalytic reaction of CH_4 and O_2 proceeds as a flame in the combustion chamber. All of the oxidant is consumed in the process. H_2 and CO are the major components of the combustion chamber effluent gas. The mechanism of the reactions is very complex, but this behavior is consistent wih the two-stage combustion chamber mechanism involving complete combustion in the first stage via the highly exothermic reactions (1) and (2). A large surplus of methane remains unreacted. This surplus methane can then react with either of the products of the primary reactions (as indicated by eqs 3 and 4).

Simulation Procedure

The combustion chamber was simulated using two reaction stages. Exothermic reactions (1) and (2) take place in the first stage. Endothermic reactions (3) and (4) take place in the second stage. All reactions were simulated using AspenPlus. One hundred moles of sour methane gas was used in the feed for simulation. The oxidant used in the simulations was pure oxygen.

Thermodynamic Relationships

In the simulation, it was necessary to carry out first some basic calculations of the thermodynamic properties. These calculations were carried out for different reactions to estimate the equilibrium constants. The range of temperatures selected in our study was chosen because the majority of reaction furnaces used in Claus processes [involving partial oxidation of acid gas] operate in the 1700−2200 °F range.[6,7]
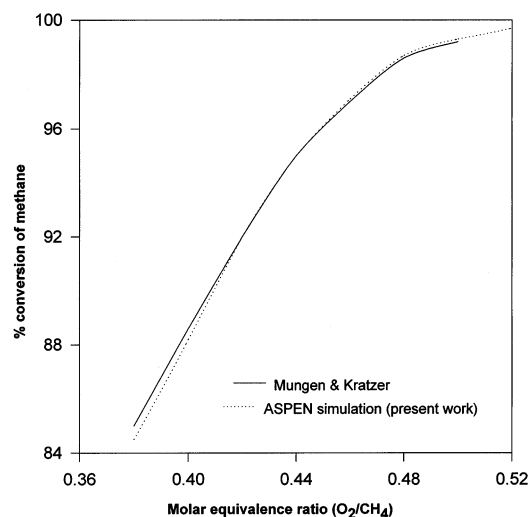
Figure 3. Comparison of the AspenPlus simulation results with published work.
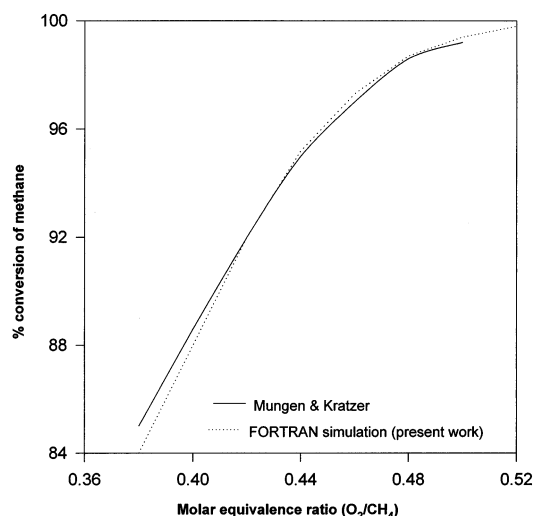

Figure 4. Comparison of the results of the mathematical model with published work (% conversion of methane).

The furnace reactions are very complex. It is very likely that a large number of free-radical intermediates would be involved. Nonetheless, the net reactions (reactions 1−4 and 6) are sufficient for most practical applications in the partial oxidation of methane.[8]

Results and Discussion

To believe the predictions of the simulation based on the proposed model for the NCPO of sour natural gas, a comparison was made with two sources:

(a) Experimental work was published by Mungen and Kratzer on the NCPO of sweet natural gas.[2] No other published work on the NCPO of sour gas was available. The model was modified for sweet natural gas, and the simulation was carried out keeping all the conditions identical to that reported by Mungen and Kratzer. The composition presented in Figure 3 shows very close agreement between the present work and the one reported by Mungen and Kratzer. Further verification was carried out by using Fortran simulation based on the solution of the set of balances derived for carbon, hydrogen, oxygen, and sulfur. The results are shown in Figure 4, confirming the agreement between simulation and experiment results.

Table 1. Comparison of the Results of the Proposed Process with the Plant Data

	Ibn Sina, Jubail, steam reforming	proposed process partial oxidation
feed natural gas	50 MMScfd (sweet)	75 MMScfd (sour)
fuel	30 MMScfd	0 MMScfd
feed steam	200 MMScfd	0 MMScfd
product synthesis gas	194 MMScfd	194 MMScfd
heat input from furnace	1240 MMBtu/h	0 MMBtu/h
radiant section	676.5 MMBtu/h	0 MMBtu/h
convection	563.5 MMBtu/h	0 MMBtu/h
waste heat recovered	645 MMBtu/h	1615 MMBtu/h
synthesis gas compos	$H_2 = 0.453$	$CO = 0.081$
	$CO_2 = 0.056$	$H_2O = 0.01$
	$CH_4 = 0.001$	$N_2 = 0.399$
	$SO_2 = 0$	$H_2 = 0.5479$
	$CO = 0.3643$	$CO_2 = 0.0035$
	$H_2O = 0.065$	$CH_4 = 0$
	$N_2 = 0$	$SO_2 = 0.0193$

Table 2. Recommended Optimum Operating Parameters (NCPO of Sour Natural Gas)

operating parameters	opt values
molar equivalence ratio: mol of O_2/mol of CH_4	0.5^a
combustion chamber temp	2200 °F
combustion chamber pressure	15 psi
preheat tempeature	1200 °F

[a] Depending upon the H_2S content in the feed (sour natural gas) (0.5 for sweet methane).
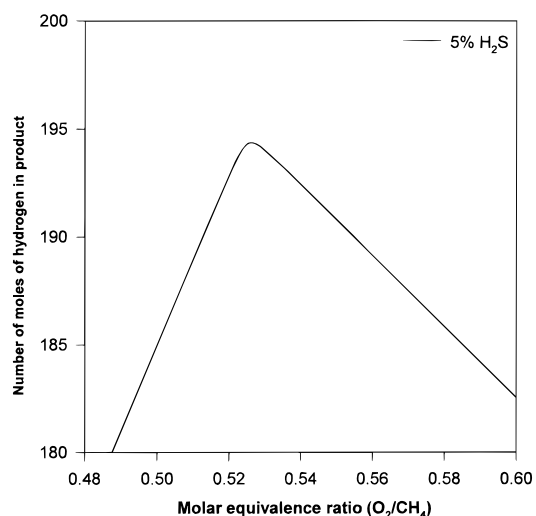

Figure 5. Variation of the moles of H_2 with the molar equivalence ratio.

(b) The plant operating in Saudi Arabia (Jubail) utilizes the steam-reforming process of sweet natural gas. If the NCPO of sour natural gas is to replace the existing process, the simulation results are reported in Table 1 and are compared with the plant data. There is a close agreement between the compositions of hydrogen, methane, steam, and the product synthesis gas flow rates. Variations in the SO_2 and nitrogen compositions between plant and simulation are due to the sweet natural gas feed and air oxidant in the Jubail plant data.

Finally, the recommended optimum values of operating a process based on the NCPO of sour natural gas are given in Table 2.

Since the simulation has been tested successfully with two experimental data available, then we can be confidant with the simulation obtained from AspenPlus. The results of the simulation by changing variables are illustrated.
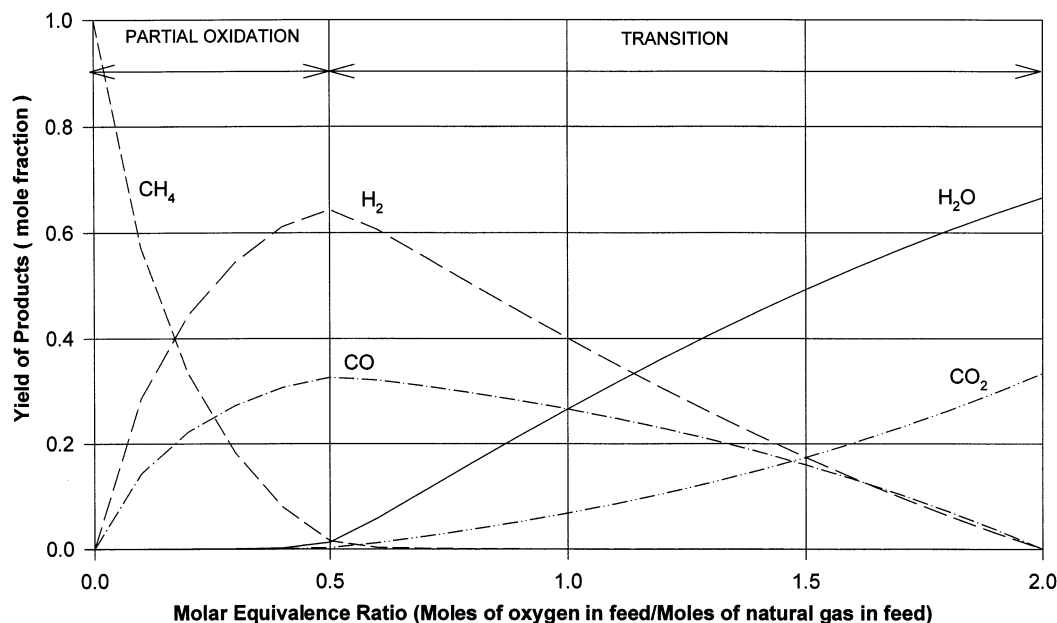
Figure 6. Transition from partial oxidation to complete oxidation.

1. Effect of the Equivalence Ratio (O_2/CH_4). The effect of the equivalence ratio (ER) on the number of moles of hydrogen in the product is shown in Figure 5. There is an indication of a change in the number of moles of hydrogen with increasing equivalence ratio. The number of moles of hydrogen in the product increase with an increase in the equivalence ratio and reach a maximum value at the optimum equivalence ratio. This maximum occurs at ER = 0.525 for a feed of 95% methane and 5% H_2S.

At lower equivalence ratios, the amount of oxygen supplied is low, so a small amount of methane reacts with this oxygen to form low amounts of steam and carbon dioxide which react with the methane in secondary reactions (3) and (4) and produce low amounts of hydrogen. Therefore, initially no steam and carbon dioxide appear in the product. Only a small amount of hydrogen appears in the product along with a large amount of unreacted methane.

At an equivalence ratio in the vicinity of one-half, the oxygen is supplied in a sufficient amount for partial oxidation. Thus, the primary reactions (1) and (2) produce sufficient steam and carbon dioxide to consume all of the unreacted methane in the secondary reactions (3) and (4). Consequently, no unreacted methane appears in the product and complete conversion is achieved at this equivalence ratio. The region marked by zero equivalence ratio and 0.525 equivalence ratio for a feed with 5% H_2S is the region of partial oxidation. At an equivalence ratio higher than 0.525, the oxygen supplied is more than sufficient for partial oxidation. Therefore, the primary reactions (1) and (2) produce more steam and carbon dioxide than required for partial oxidation at the expense of methane. More oxygen consumes a larger amount of methane in the primary stage, so a lower amount of methane is available to secondary reactions (3) and (4). Hence, as a result, surplus steam and carbon dioxide appear in the product. This affects the production of hydrogen. Hydrogen drops until an equivalence ratio of 2 is reached, where the hydrogen concentration becomes 0 as a result of stoichiometry (Figure 6). At this equivalence ratio, all of the methane is consumed by the primary reactions and the secondary reactions will not take place.
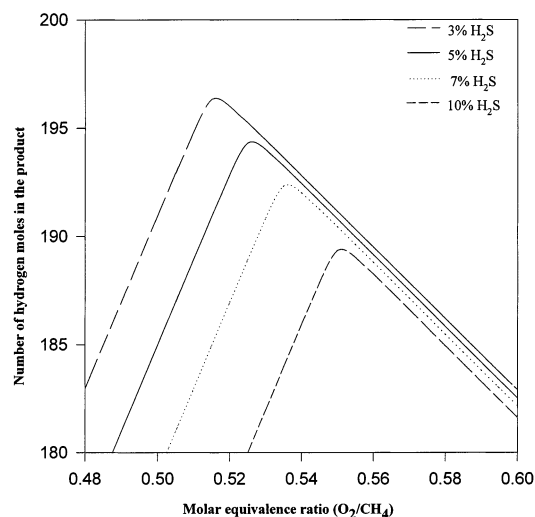

Figure 7. Effect of the H_2S content on the moles of H_2 in the product.

2. Effect of the Hydrogen Sulfide Content in the Feed. The content of hydrogen sulfide in the sour natural gas has a direct effect on the number of the moles of hydrogen in the product. The number of moles of hydrogen in the product decrease with the increase in the hydrogen sulfide content of the sour natural gas as shown in Figure 7. The partial oxidation of hydrogen sulfide is highly exothermic. There is a gradual shift in the optimum equivalence ratio with an increase in the hydrogen sulfide content of the sour natural gas. This is due to the fact that hydrogen sulfide requires 1.5 times more oxygen than that required by the methane.

The partial oxidation of the hydrogen sulfide does not produce any hydrogen, whereas methane and other hydrocarbons produce hydrogen upon partial oxidation. Therefore, there is a decrease in the hydrogen production with an increase in the hydrogen sulfide content of the feed. The same trend of a decrease in carbon monoxide similar to hydrogen is observed with an increase in hydrogen sulfide of the feed (Figure 8).

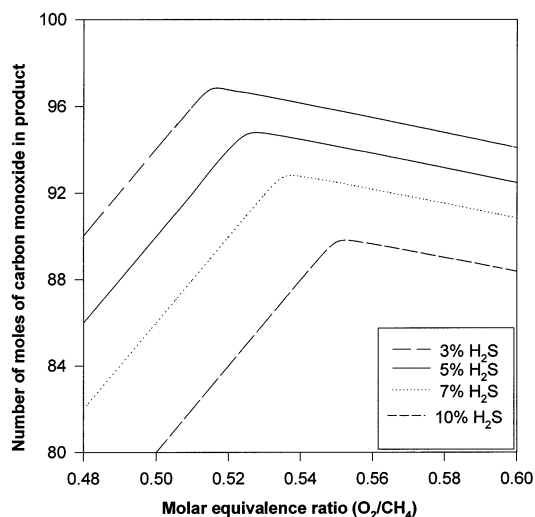**3. Effect of the Preheat Temperature.** The number of moles of hydrogen and of carbon monoxide in the

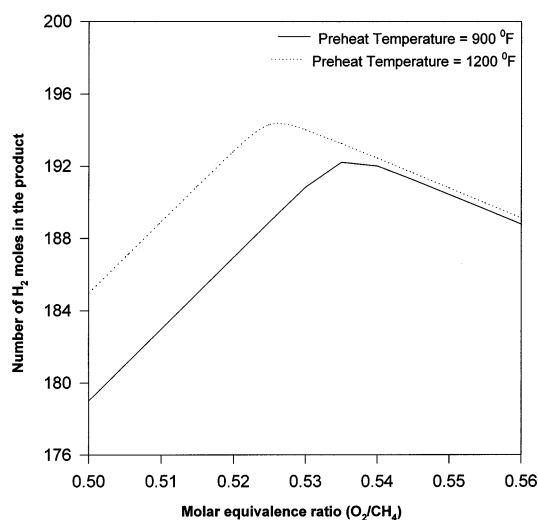**Figure 8.** Effect of the H_2S content on the number of moles of CO in the product.

Figure 9. Effect of the preheat temperature on the moles of H_2 in the product.
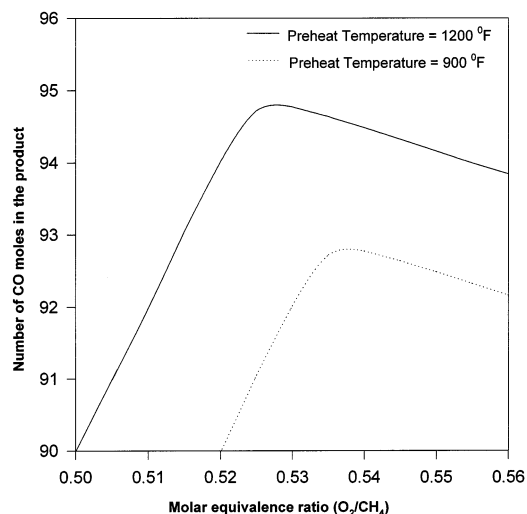

Figure 10. Effect on the preheat temperature on the CO moles in the product.

product is higher for the higher preheat temperatures of sour natural gas as shown in Figures 9 and 10. The higher preheat temperatures result in high hydrocarbon
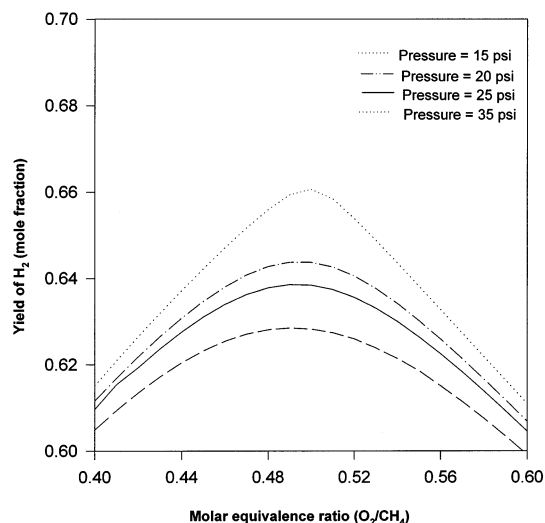

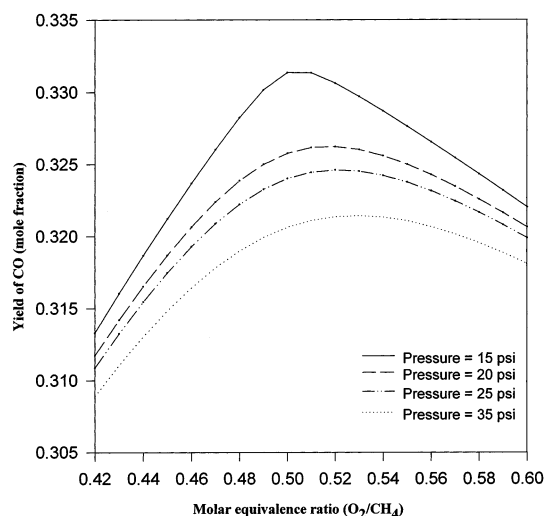**Figure 11.** Effect of pressure on the yield of H_2.

Figure 12. Effect of pressure on the yield of CO.

conversion, as the higher temperatures favor the endothermic secondary reactions.

The preheat temperature is limited by two factors. First is the design of the preheater, which should be such that there are no local hot spots or stagnant pockets where methane could decompose. Second is the temperature at which spontaneous ignition could occur when the oxidant and methane are premixed. Sour natural gas is not preheated above 1200 °F to avoid cracking and carbon deposition. The oxidant is very reactive above 1000 °F, so it is not preheated above 1000 °F.

4. Effect of Pressure. Hydrogen and carbon monoxide are basically produced in the secondary reactions (3) and (4). Because of the stiochiometry of the reactions, increases in the pressure will shift the reactions to the left. Higher pressures reduce the amount of hydrogen and carbon monoxide produced, and this effect is observed in Figures 11 and 12.

Conclusions and Recommendations

A two-stage reaction mechanism is proposed and simulated for the partial combustion of sour natural gas: oxygen reacts with some of the methane and the hydrogen sulfide to produce carbon dioxide, water, and sulfur dioxide followed by the reactions of carbon dioxide

and water with the rest of the methane to give carbon monoxide and hydrogen.

Using this scheme of noncatalytic partial oxidation (NCPO), simulation was carried out using AspenPlus.

The transformation of hydrogen sulfide into sulfur dioxide and, hence, sulfuric acid along with the production of synthesis gas via NCPO offers a novel scheme that could compete with the conventional steam reforming with the elimination of both the expensive gas desulfurization process and the steam generation. In this respect, NCPO is described as a self-sufficient steam producer for the reaction.

The optimum conversion of the sour natural gas is achieved in the vicinity of $\frac{1}{2}$ M equivalence ratio depending on the content of hydrogen sulfide in the feed of sour natural gas.

The proposed process is recommended for ammonia and urea production from sour natural gas. Partial oxidation takes place using air which provides nitrogen used in ammonia fixation. The material balance for oxygen needs to be modified to use air as in the present simulation algorithms.

For methanol production, where synthesis gas consists only of carbon monoxide and hydrogen, the partial oxidation process of sour natural gas has to be implemented using pure oxygen. The economics of such a process has to be considered carefully.

The proposal offers a new approach to produce sulfuric acid via the noncatalytic process, known as the open sulfur cycle along with additional hydrogen, thus increasing the yield of synthesis gas.

The potential of implementing this scheme in the future, particularly in oil-producing countries, should be considered by carrying out experimental work on the NCPO of sour natural gas, followed by an economic feasibility.

Literature Cited

(1) Abdel-Aal, H. K.; Shalabi, M. A. Noncatalytic partial oxidation of sour natural gas versus catalytic steam reforming of sweet natural gas. *Ind. Eng. Chem. Res.* **1996**, *35*, 1787.

(2) Mungen, R.; Kratzer, M. B. Partial Combustion of Methane with Oxygen. *Ind. Eng. Chem.* **1951**, *12*, 2782.

(3) Hakeem, Tariq. Non-Catalytic Partial Oxidation of Sour Natural Gas. MS Thesis, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia, 1997.

(4) Eastman, D. Synthesis Gas by Partial Oxidation. *Ind. Eng. Chem.* **1956**, *48*, 1118.

(5) Abdel-Aal, H. K. Opportunities of Open Loop Thermochemical Cycles: a case study. *Int. J. Hydrogen Energy* **1984**, *9*, 767.

(6) Hyne, J. B. Design and Chemistry of Front End Reaction Furnaces. *Can. Gas J., Gas Proces., Canada.* **1972**, No. 3−4, 12.

(7) Estep, J. W.; McBride, G. T., Jr.; West, J. R. *The Recovery of Sulfur from Sour Natural and Refinery Gases*; Advances in Petroleum Chemistry and Refining; McKetta, J. J., Jr., Eds.; John Wiley & Sons: New York, 1962; Vol. 6, Chapter 7.

(8) Paskal, H. G. Capability of Modified-Claus Process. Report published by Western Research, Alberta, Canada, 1983.