Effect of Carbon Dioxide and Nitrogen in Hydrogen Sulfide on Optimum Reactor Temperature in Claus Process

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Abstract

This paper provides detailed examination of the effect of presence of N_2 and CO_2 in acid gas on the composition of the subsequent equilibrium product gas stream, in order to seek the optimum operating temperature for high sulfur removal efficiency. The study provides the important role of the incoming gas composition on the fate of sulfur recovery in the Claus reactor. Our studies reveal that the presence of N_2 and CO_2 in the acid gas stream impacts the sulfur recovery efficiency by altering the optimum temperature of the reactor as well as the conversion efficiency. The results show that the reactor temperature should be precisely monitored in order to enhance the sulfur recovery. The simulations provided here assist in quantifying the role of acid gas composition on sulfur recovery under different operational conditions of the reactor with minimal adverse effect on the environment.

1. Introduction

Hydrogen sulfide occurs naturally as a contaminant accompanying crude natural gas. Crude natural gas comes in sour form, i.e., it contains "sour" acid-forming gases, such as H_2S and CO_2, as well as undesired non-combustible impurities, such as nitrogen[1]. Table 1 provides a characteristic composition of sour natural gas. Removal of H_2S is crucial for several reasons including health, safety, corrosion, environmental and material recovery. H_2S induces several health hazards, such as eyes, skin, and respiratory system irritation. According to the air pollution regulations on sulfur compounds, the removal of hydrogen sulfide is environmentally beneficial, as it is a source of several dangerous chemical compounds, such as, SO_2, SO_3, H_2SO_3 and H_2SO_4, which all contribute to acid rain.

Table 1. Characteristic composition of natural gas.[1]

Constituent	Chemical formula	Typical concentration
Methane	CH_4	70-90%
Ethane	C_2H_6	
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulfide	H_2S	0-5%
Rare gases	Ar, He, Ne, Xe	trace

Crude natural gas must undergo treatment processes prior to its usage as fuel, so that the undesirable sour gases are removed. The removal of hydrogen sulfide as well as carbon dioxide is achieved through the amine extraction process2-3. In this process the sour gas is passed over an aqueous solution of alkanolamines, wherein the CO2 and H2S (acid gases) are absorbed from the upflowing sour gas to produce a sweetened gas stream, i.e., H2S- and CO2-free natural gas. The alkanolamines, used in the amine extraction process, are organic chemical components, which have at least one hydroxyl group and one amino group. Each of these two groups has its own role in the process. The hydroxyl group reduces the vapor pressure in the aqueous solution, in order to increase the water solubility. On the other hand, the amino group provides the required alkaline medium in this aqueous solution, in order to increase the tendency of acid gas absorption. The most common alkanolamines, which have been widely used commercially, are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Alkanolamines are classified as primary, secondary, or tertiary, based on the number of hydrogen atoms in the amino group. Primary amines have two hydrogen atoms, secondary have one atom, and tertiary have none. MEA, DEA, and MDEA are examples of primary, secondary, and tertiary amines, respectively.

The resulting sour or acid gas after amine extraction contains primarily H_2S and CO_2 with traces of nitrogen, as part of the ammonia in the aqueous alkanolamine solution disintegrates into water and nitrogen[4]. The produced H_2S gas is treated thermally through the widely implemented Claus process[5-9], which mainly consists of two stages (thermal stage and catalytic stage). The main reactions of Claus thermal stage begin with the oxidation of one third of the hydrogen sulfide in order to form SO_2, i.e.,

$$H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O \qquad \Delta Hr = -518\ KJ/mol$$

The remainder of hydrogen sulfide then reacts with the produced sulfur dioxide from the previous reaction to produce elemental sulfur.

$$2H_2S + SO_2 \rightarrow (3/n)\ S_n + 2\ H_2O$$

where S_n indicates different sulfur isotopes (n = 2 – 8) that could be formed, specifically in the catalytic step. Since the presence of CO_2 and N_2 in acid gas is inevitable, they can have a great effect on the optimum operating conditions of the reactor. Khudenko et al. [4] examined the effect of air enrichment with oxygen on the treatment of acid gases, mainly containing H_2S and CO_2. They concluded that oxygen enrichment has significant effect on Claus process, as this reduces the equipment size and provides sufficiently higher sulfur recovery compared to the conventional Claus process. Fisher [10] and Gray et al. [11] investigated the use of oxygen in Claus processes treating lean gases, in order to increase the furnace temperature and to reduce the amount of bypass in the split flow modification. This improvement involved the addition of pure oxygen to the process air and is commonly referred to as the oxygen enrichment.

Studying the effect of different gases accompanied with hydrogen sulfide in the sour gas is critical for determining the optimum operating temperature which will provide maximum sulfur recovery. Carbon dioxide and nitrogen are the most prominent gases contained in the hydrogen sulfide acid gas stream to be treated. This paper provides detailed examination of the effect of presence of N_2 and CO_2 in acid gas on the composition of the subsequent equilibrium product gas stream, in order to seek the optimum operating temperature for high sulfur recovery from H_2S.

2. Simulation Assumptions and Test Matrix

In this paper we examine the effect of CO_2 and N_2 present in H_2S gas stream on the optimum temperature of the thermal reactor of Claus process for enhanced sulfur recovery. Numerical simulations have been carried out to determine the optimum reactor temperature (i.e., temperature that yields peak sulfur-recovery efficiency) for various combinations of CO_2 and N_2 concentrations in the inlet H_2S gas stream to the reactor. Sulfur recovery efficiency is defined here as:

$$\text{conversion efficiency} = \frac{\text{mass of recovered sulfur}}{\text{mass of sulfur in inlet } H_2S}$$

Wide ranges of CO_2 and N_2 concentrations have been studied. Nitrogen has been changed from 10-50% with a step of 10%, and CO_2 has been changed from 10-90% with a step of 10%. Hydrogen sulfide is always the remainder part of acid gas with a concentration not less than 10%. H_2S number of moles was kept constant (3 moles), while changing total number of moles of acid stream, in order to facilitate comparisons based on conversion efficiency.

The following equation gives the total number of moles of acid gas for any combination of nitrogen and carbon dioxide concentrations:

$$\text{Total number of mole for the acid gas streams} = 3/\ (1\text{-}X\text{-}Y)\ \text{moles}$$

where X is the nitrogen percentage (0.1-0.5) and Y is the carbon dioxide percentage (0.1-0.9).

Note that the concentration of H2S is always greater than or equal to 10%. For example, for 60% CO_2 in the acid gas stream, nitrogen would be 10%, 20%, or 30%, but not 40%. For each test case (i.e., combination of CO_2 and N_2 mole fractions in the acid gas stream) a range of reactor temperatures was considered (1000 – 2000 K).

CHEMKIN (4.1) software by reaction design has been used in the chemical equilibrium analysis along with the detailed sulfur reaction mechanism developed by Leeds university[12] as well as the GRI mechanism provided by reaction design.

3. Results and Discussion

In order to decouple the effects of nitrogen and carbon dioxide on the reactor optimum temperature, the analysis starts by introducing each separately with hydrogen sulfide, and the behavior is compared to that of a H_2S-argon mixture, since argon represents a perfectly inert gas under the given operational conditions. Initially it was believed that both nitrogen and carbon dioxide behave as inert gases in chemical reactions. However, this is not entirely accurate at the elevated temperatures needed for sulfur removal within the Claus process.

4. Effect of Nitrogen

In order to highlight the effect of nitrogen presence in sour gas, its behavior is compared to that of a perfectly inert gas, namely argon (Ar). Two acid gas compositions are considered. The first one being 90% hydrogen sulfide and 10% N_2, while the other contains 90% hydrogen sulfide and 10% argon. Argon was chosen as it represents a purely inert gas that contributes to nothing but decreasing the mole fraction of reactants. The percentages of nitrogen and argon were each increased to 50% to facilitate two more acid gas compositions. The results obtained on the efficiency-temperature plot shown in Figure 1a show that the presence of nitrogen has no significant effect on variation of conversion efficiency. This supports that nitrogen behaves as an inert gas, similar to argon, and that it does not affect the mechanism rates of H_2S/O_2 reaction. If the inert gas concentration is increased to 50%, at the expense of decreasing hydrogen sulfide concentration down to 50% as shown in figure 1b, the behavior of both Ar and N_2 is similar. However, the optimum temperature (corresponding to peak efficiency) is slightly decreased. This is attributed to the fact that the lower partial pressures of all species (including S_2) in this latter case promote their tendency to dissociate. Therefore, the reactor temperature has to be decreased to hinder the dissociation and loss of S_2, in order to maintain maximum sulfur recovery efficiency.
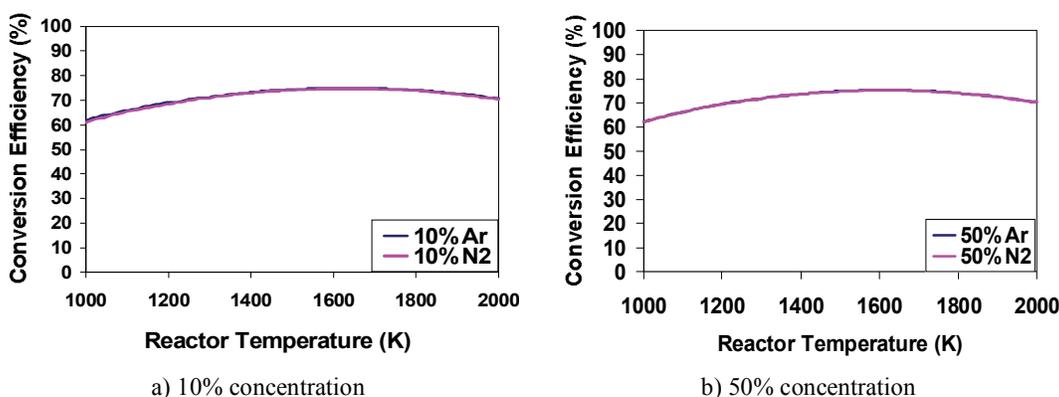

a) 10% concentration   b) 50% concentration

Figure 1. Effects of nitrogen and argon concentrations in acid gas on conversion efficiency.

5. Effect of Carbon Dioxide

In contrast to N_2, the effect of CO_2 presence is more complicated. Unlike N_2, CO_2 is not entirely inert. It has the capability to dissociate to CO and O radicals at the elevated temperatures of Claus process[13-14]. If the same above analysis of the effect of nitrogen is repeated for carbon dioxide, the results obtained show that small quantities of CO_2 in acid gas slightly promote sulfur recovery, see Figure 2a. In contrast, higher CO_2 concentrations result in decreased efficiency, as shown in Figure 2b. At low concentrations of CO_2 and Ar the conversion efficiencies are similar over a range of temperatures (Figure 2a). However, at high concentrations (Figure 2b) the behavior of carbon dioxide deviates from that of argon at reactor temperatures above 1400 K. Beyond this temperature of 1400 K, a steep decrease in the conversion efficiency is observed. At these high temperatures CO_2 dissociates excessively, especially at high CO_2 concentrations, and the amount of oxygen radicals produced is considerably high. This oxygen radical attacks hydrogen sulfide to form SH intermediately, which then eventually transforms to SO_2[15]. This will lead to an unbalance in the adjusted ratio of oxygen and SO_2 of the abovementioned Claus process reactions. Figures 3 and 4 show the equilibrium mole fractions of the main species along the reactor, where the black bar is the equilibrium mole fraction, and the gray one is the complementary to the maximum mole fraction that could be obtained of this particular species in the reaction. It can be noticed that the equilibrium mole fraction of SO_2 is always higher in Figure 3 than in Figure 4 for the same temperature. Therefore, higher CO_2 concentrations always tend to enhance the production of SO_2, due to the aforementioned reasons. However, this effect becomes significant at about 1400 K, which justifies the sudden deterioration in conversion efficiency in Figure 2 that starts at about 1400 K.
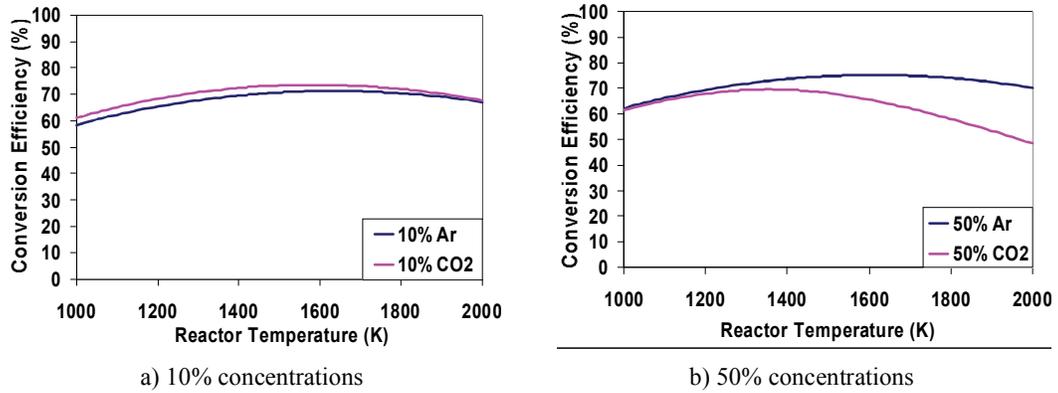
a) 10% concentrations   b) 50% concentrations

Figure 2. Effects of carbon dioxide and argon concentrations in acid gas on conversion efficiency.

a) 1500 K

b) 1800 K
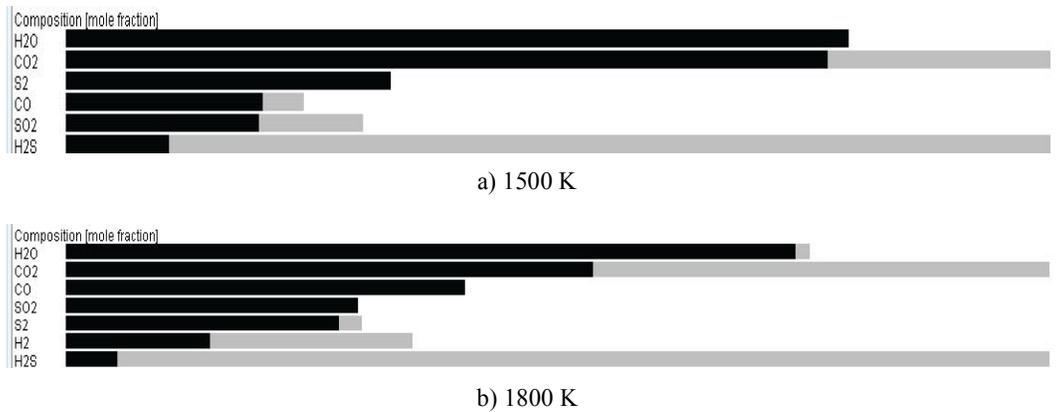
Figure 3. Main species equilibrium mole fraction for 50% H_2S, 50% CO_2 sour gas inlet conditions.
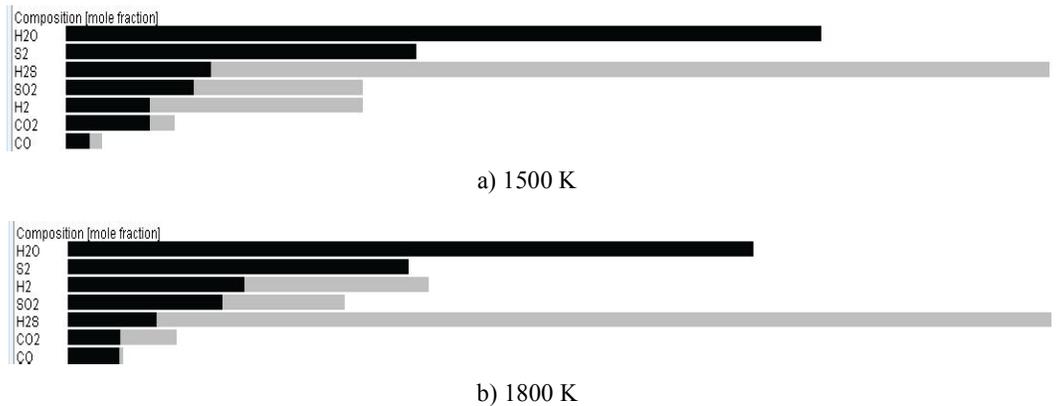

a) 1500 K

b) 1800 K

Figure 4. Main species equilibrium mole fraction for 90% H_2S, 10% CO_2 sour gas inlet conditions.

6. Combined Effect of Carbon Dioxide and Nitrogen

By combining the effects of carbon dioxide and nitrogen, the efficiency-temperature plots of Figure 5 can be obtained for all cases presented in this study. It is worth recalling that nitrogen behaves as an inert gas, whereas higher CO_2 concentrations result in lower recovery efficiencies. It can be observed from Figure 5 that the conversion efficiency increases at low reactor temperatures, which is due to the higher tendency of the H_2S to dissociate eventually forming S_2. Increasing the reactor temperature triggers carbon dioxide to dissociate forming oxygen radical, which attacks hydrogen sulfide to form higher amounts of

SO$_2$. The effect of H$_2$S dissociation is dominant at low reactor temperatures since the rate of dissociation of H$_2$S is much higher than that of CO$_2$, which allows for an increasing conversion efficiency, until the maximum conversion efficiency point is reached at the optimum operating temperature. If the reactor temperature is increased beyond this optimum temperature, the effect of oxygen radical dissociated from carbon dioxide dominates the process. At higher values of N$_2$ and CO$_2$ the optimum temperature shifts to smaller values, because of the higher tendency of CO$_2$ to dissociate and form oxygen radicals, which attack H$_2$S to form SO$_2$ instead of S$_2$.

Figure 6 shows the effect of changing CO$_2$ and N$_2$ concentrations on the maximum conversion efficiency. It can be observed that the general effect of increasing carbon dioxide percentage in acid gas is to decrease the conversion efficiency. However, the effect of nitrogen involves an inflection point. At low concentrations of CO$_2$ up to 6% of acid gas, increasing nitrogen concentration affects the conversion efficiency positively. This could be attributed to the reduction in partial pressure of the reactants and the higher tendency for dissociation. On the other hand, at CO$_2$ concentrations above 6%, increasing nitrogen concentration results in reduction in maximum conversion efficiency. This is because of the higher concentrations of CO$_2$ in the reactants, which means higher amount of oxygen radical is liberated due to CO$_2$

a) 0% Nitrogen

b) 10% Nitrogen

c) 20% Nitrogen
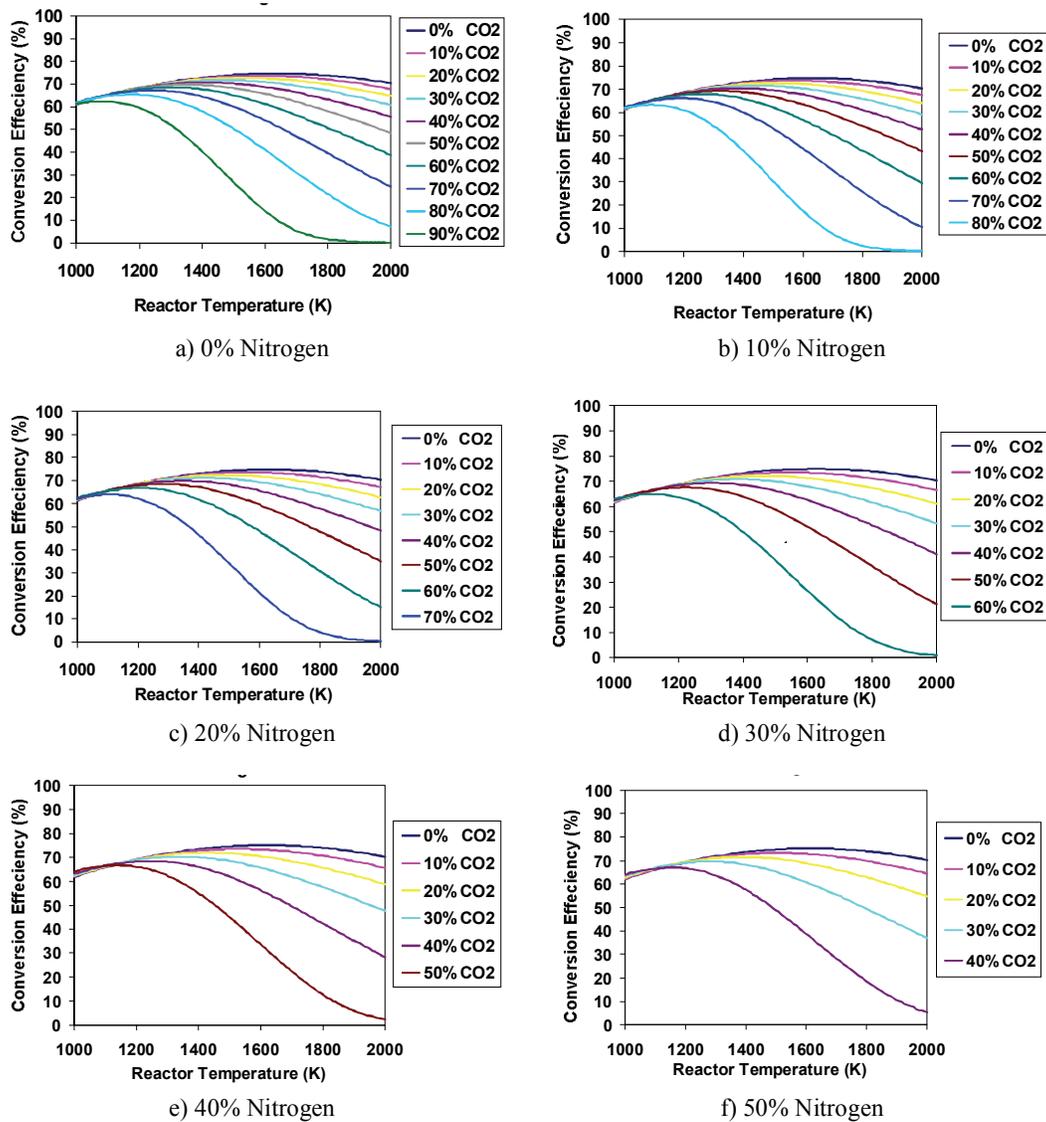
d) 30% Nitrogen

e) 40% Nitrogen

f) 50% Nitrogen

Figure 5. Effect of carbon dioxide and nitrogen concentrations in acid gas on conversion efficiency. CO$_2$ is changed from 10 to 90% and nitrogen is changed from 10 to 50% with the remainder being hydrogen sulfide.

dissociation. Subsequently the reaction mechanism goes in the direction of forming SO_2. Therefore, the adjusted Claus conditions will deviate from the required balance, which conclusively reduces the maximum conversion efficiency.

To conclude the analysis of effect of acid gas composition on optimum reactor temperature, a color map of this temperature is depicted in Figure 7a within the investigated ranges of CO_2 and N_2 mole fractions (0 – 90% and 0 – 50%, respectively). Figure 7a shows direct results from the equilibrium calculations, while Figure 7b shows numerical fits obtained from the correlation equation given by:

$$T[K] = -556 \left(\frac{CO_2}{0.9 - N_2} \right) + 1659.5$$

This equation provides the value of optimum temperature directly for a given sour-gas composition. The maximum error associated with this fit equation was calculated to be 4%.
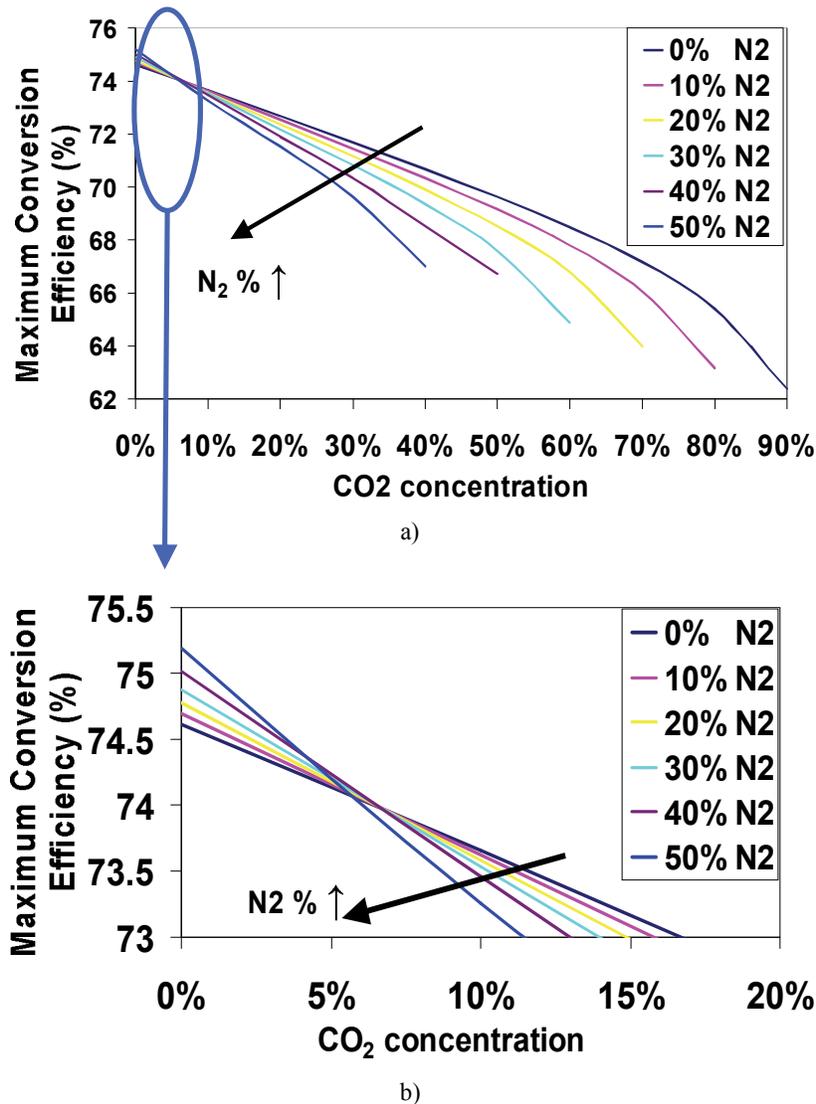

a)

b)

Figure 6. Effect of CO_2 and N_2 concentrations on the maximum conversion efficiency.
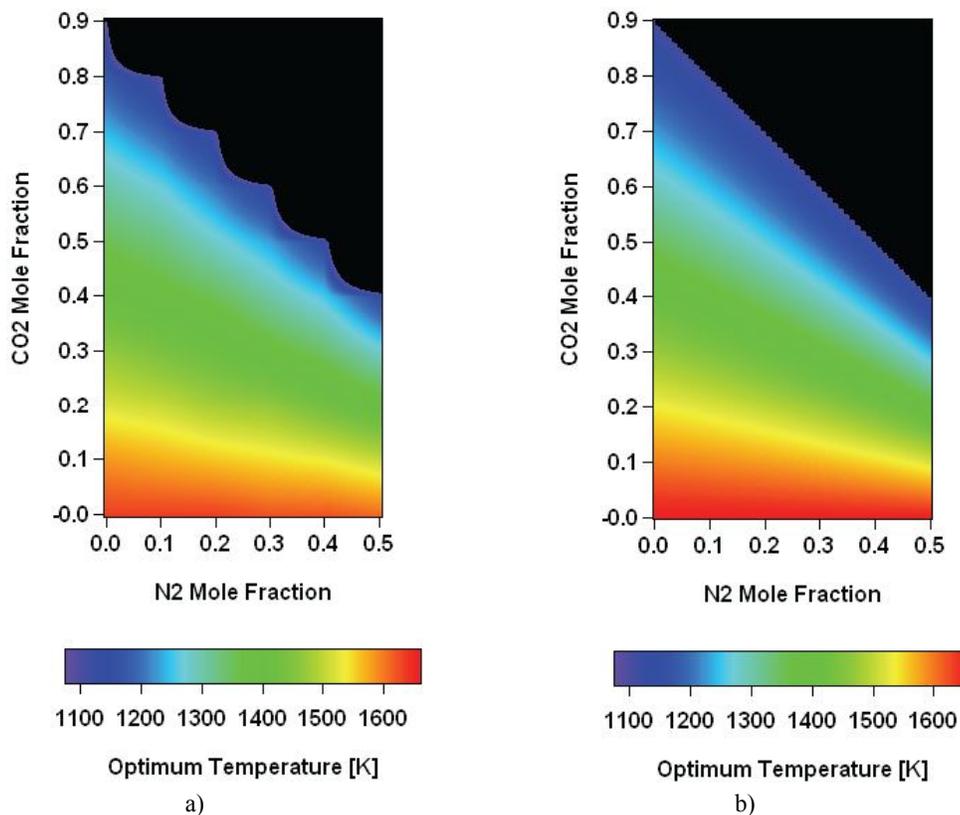
Figure 7. Mapping of optimum reactor temperature at different sour-gas compositions, (a) numerical results obtained from equilibrium calculations, (b) results from fit equation given above.

7. Conclusions

The effects of acid gas composition on optimum reactor temperature and sulfur recovery efficiency within thermal step of Claus process have been investigated. Carbon dioxide and nitrogen were considered as primary constituents of acid gas to accompany hydrogen sulfide. Variation of conversion efficiency of sulfur has been studied over a wide range of temperatures (1000 - 2000 K). The equilibrium mole fractions of different species were determined numerically. The results indicate that carbon dioxide affects the reactor temperature as an inert gas at low temperatures. The presence of CO_2 reduces the partial pressures of reactants and subsequently changes the equilibrium mole fractions of the products. However, at higher temperatures CO_2 starts to liberate considerable amounts of oxygen radical, especially at higher CO_2 concentrations, which causes a reduction in conversion efficiency. This is attributed to the fact that the amount of available oxygen deviates away from the balanced ratio required for optimum sulfur recovery in Claus process. In contrast, nitrogen affects the process by reducing the reactants partial pressure and subsequently reducing the optimum operating temperature. An analytical expression has been obtained that could be used to determine the optimum temperature from given concentrations of CO_2 and N_2 in the sour gas.

Acknowledgments

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