Roles of hydrogen sulfide concentration and fuel gas injection on aromatics emission from Claus furnace

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HIGHLIGHTS

- Role of fuel gas in destructing aromatic contaminants present in lean acid gas is presented.
- Experimental data from industrial furnace is used to validate a detailed Claus mechanism.
- Furnace simulations predict fates of undesired aromatics, COS, and CS_2 with varying H_2S concentrations.
- Fuel gas is found to be ineffective for aromatics destruction in Claus process for lean acid gas feeds.

ARTICLE INFO

ABSTRACT

Acid gas (H_2S and CO_2) recovered from sour feedstocks is treated in Sulfur recovery units (SRU) to obtain sulfur. The frequent changes in acid gas composition often result in lean acid gas, containing higher volume of CO_2 than H_2S. Lean acid gas causes flame instability that result in inefficient destruction of feed impurities in Claus furnace. To mitigate this problem, fuel gas (with >90% CH_4) is co-fired with acid gas to increase furnace temperature and prevent flame extinction. The addition of fuel gas in Claus furnace may aggravate the production of polycyclic aromatics hydrocarbons (that cause frequent catalyst deactivation), and CS_2 and COS (that reduce sulfur yield). Clearly, the amount of fuel gas injected into Claus furnace needs to be optimized. The previous optimization studies have given less importance to the roles of H_2S concentrations in acid gas and the injected fuel gas on the production of aromatics and organosulfur species. This paper explores the fate of undesired aromatics, COS and CS_2 in the Claus furnace over a wide range of H_2S concentrations in acid gas using a detailed reaction mechanism. Experimental data on species concentration from a SRU is presented, and is used for mechanism validation. The effect of fuel gas co-firing with typical Claus feed containing 30–50% H_2S is presented alongside detailed analysis of species compositions in the thermal section. An increase in fuel gas flow rate (from 0 to 200 kmol/h) increased aromatics production in the furnace for lean acid gases. For rich acid gas, a decrease in aromatics production occurred as fuel gas flow rates was increased. The divergent trends were found to be occurring due to the reduced reactivity of methane in comparison to H_2S at low flame temperatures, the dilution effect of unburnt CH_4, CO_2, and N_2 in the furnace, and the endothermic hydrocarbon pyrolysis reactions leading to aromatics formation and growth. Fuel gas addition also led to COS and CS_2 formation to reduce sulfur yield. The results indicate that fuel gas may not be the best solution for aromatics destruction in the Claus process for lean acid gas feeds.

1. Introduction

Claus process is the most widely used technology for the treatment of hydrogen sulfide (H_2S), found in raw natural gas and in by-product gases derived from oil refineries, by producing sulfur from it (Zarei et al., 2016). This process is responsible for approximately 90–95% of elemental sulfur production (Rameshni and Street, 2001). It consists of a thermal stage (with a Claus furnace and a heat recovery system) and catalytic reactors. In the furnace, partial oxidation of H_2S takes place through the reaction, $H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$. The unburnt H_2S undergoes Claus reaction with SO_2 ($2H_2S + SO_2 \rightarrow 3/8S_8 + 2H_2O$) to produce sulfur. The exhaust gas (containing sulfur, sulfur dioxide, water, unreacted H_2S, and other byproducts) then flows through a heat exchanger, which is called waste heat boiler (WHB), to recover thermal energy, condense the sulfur, and produce steam (Yeh, 2016). The Claus furnace operates at temperatures of 1027–1477 K, and in

the catalytic reactors, H_2S and SO_2 remaining from the furnace undergoes Claus reaction to produce sulfur at low temperatures (Rameshni, 2002).

The acid gas (H_2S and CO_2) fed into Sulfur Recovery Unit (SRU) is often accompanied by other impurities such as benzene, toluene, ethylbenzene and xylenes (collectively known as BTEX), small hydrocarbons, ammonia, carbon dioxide, N_2, carbon disulfide (CS_2), and carbonyl sulfide (COS) (Bullin and Brown, 2004; Rameshni, 2010). These impurities should be oxidized in the Claus furnace, as the presence of unburnt hydrocarbons in the catalytic reactors causes frequent catalysts deactivation (Crevier et al., 2002), and reduces sulfur quality (Ibrahim et al., 2015a, 2015b) and the efficiency of Claus process (Chardonneaua et al., 2015). They also promote CO, COS (Jerzak et al., 2016), and CS_2 production (Selim et al., 2014). In practice, the acid gas composition changes significantly depending on the gas field, with CO_2 concentrations varying between 30% and 90% (Sassi and Gupta, 2008). This often results in lean acid gas, containing less than 50% H_2S (Crevier et al., 2002). The presence of higher concentrations of CO_2 (diluent) at the expense of combustible H_2S causes flame instability and extinction (due to a decrease in the adiabatic flame temperature), and results in an inefficient destruction of hydrocarbon impurities (especially BTEX) in the Claus furnace (Rameshni, 2010). Flame temperatures in the range of 1350–1600 K are suitable for Claus reactions and contaminant destruction including BTEX (ZareNezhad and Hosseinpour, 2008).

To avoid spillover of unburnt BTEX and smaller hydrocarbons into the catalytic section, a significant amount of fuel gas (with >90% CH_4) is co-fired with lean acid gas (Deixonne and Sharma, 2010). Fuel gas combustion increases the furnace temperature to assist in aromatics destruction. The effect of fuel gas on adiabatic temperature in Claus furnace has been reported in ZareNezhad and Hosseinpour (2008) and Mohammed et al. (2016). In ZareNezhad and Hosseinpour (2008), through equilibrium calculations, the adiabatic temperatures during the combustion of feeds containing 20–40 mol% H_2S along with fuel gas were determined, and it was shown that fuel gas addition can result in significant temperature increase, if H_2S concentrations in feed is increased. It was also found that fuel gas addition is incapable of increasing the furnace temperatures above 1400 K, even with 40 mol% H_2S in feed. Although the use of equilibrium assumption makes the results less reliable, they offer valuable insight on the effect of fuel gas on temperature, as the H_2S concentration decreases in acid gas stream. In Mohammed et al. (2016), a detailed reaction mechanism was used to predict the effect of fuel gas on furnace temperatures and species concentrations, including polycyclic aromatic hydrocarbons (PAHs) in Claus furnace and WHB. They used an industrial feed gas, in which the acid gas stream was composed of more than 60% H_2S (rich gas), while lean acid gas streams were not investigated. An increase in fuel gas flow rate from 70 to 210 kmol/h was accompanied by a corresponding increase in air flow rate from 4720 to 5910 kmol/h. Thus, the total feed flow rate to the Claus furnace varied from 8013 to 9343 kmol/h. It was found that an increase in fuel gas flow rate from 70 to a high value of 210 kmol/h enhanced the adiabatic temperature by 345 K in the furnace. The significant temperature rise facilitated BTEX destruction and suppressed growth of higher aromatics, while aggravating CS_2 production. The significant increase in CS_2 production makes the injection of high amounts of fuel gas (above 100 kmol/h) undesirable. The destruction of CS_2 requires titanium dioxide catalysts that cost more than the alumina catalysts used in the sulfur recovery units (Clark et al., 2001). Thus, fuel gas injection into Claus furnace needs to be optimized to reduce undesired byproduct formation, and some other techniques such as feed preheating (John, 1975) and oxygen enrichment (Norman et al., 2006) are required to be explored to ensure sufficiently high furnace temper-

atures for the destruction of BTEX impurities. Increase in the inlet temperature of acid gas and/or air induces higher adiabatic temperatures in the furnace, though preheating temperature is limited to 645 K due to metallurgical constraints (ZareNezhad and Hosseinpour, 2008). Oxygen enrichment, i.e., enriching or replacing air with oxygen, is more suitable for high temperature rise in the Claus furnace (up to 1800 K adiabatic temperature) (ZareNezhad and Hosseinpour, 2008; Goar, 1985). However, temperatures above 1800 K damage the refractory linings in the Claus furnace (Goar, 1985). A detailed review of the effect of feed preheating and oxygen enrichment on Claus reactions can be found in Rahman et al. (2016) and Gupta et al. (2016), while studies on the co-oxidation of CH_4 and H_2S are briefly discussed below.

The effect of CH_4 on the oxidation of H_2S under Claus reaction conditions have been published in several studies (Chin et al., 2001; Karan and Behie, 2004; Bongartz and Ghoniem, 2015; Li et al., 2017; Gersen et al., 2017). In Chin et al. (2001), experiments were conducted in a flow reactor to study the combustion of H_2S in the presence and absence of CH_4. The reported data proved that H_2S reaction with oxygen occurs more rapidly when compared to CH_4. In Karan and Behie (2004), the interaction between CH_4 and sulfur-containing compounds was studied experimentally to determine the kinetics of key reactions that result in the formation of CS_2. In Bongartz and Ghoniem (2015), a reaction mechanism for the oxy-fuel combustion of H_2S and CH_4 in the presence of CO_2 was proposed. The results from the mechanism were compared with different sets of experimental data over a wide range of conditions for H_2S oxidation. In Gersen et al. (2017), the effect of H_2S on the ignition delay and the oxidation of CH_4 was studied, while in Li et al. (2017) and Selim et al. (2011), the flames of CH_4 and air in the presence of H_2S for different equivalence ratios were investigated. Under fuel-rich conditions, the formation of CS_2 and hydrocarbons such C_2H_2, C_2H_4, C_2H_6, and C_3H_8 were observed in flames (Selim et al., 2011). In Mohammed et al. (2016), the injection of CH_4 (fuel gas) in Claus furnace resulted in the production of significant quantities of CS_2 and large PAHs. From these studies, it can be conjectured that the addition of CH_4 to Claus feed alters the reaction pathways of H_2S oxidation, and could aggravate the formation of organosulfur complexes (such as CS_2 and COS) that reduce sulfur production. Moreover, the uncombusted CH_4 may produce large hydrocarbons in the furnace through pyrolysis.

Since a significant amount of fuel gas is used in SRU, it is important to accurately predict the implication of changing fuel gas flow rate on the production of chemically active species in the furnace in order not to aggravate the impact of feed impurities. Numerous side reactions involving aromatics, CO, COS, and CS_2 can be promoted, if the furnace temperature decreases beyond a certain level that does not support hydrocarbon oxidation. As mentioned earlier, the adiabatic temperature in Claus furnace is dependent on the relative concentration of H_2S and CO_2 in acid gas stream. Clearly, fuel gas optimization studies are required over a wide range of H_2S concentrations found in lean acid gases due to frequent changes in practical acid gas composition. For such studies, the use of a detailed kinetic reaction mechanism is necessary, as the equilibrium assumption (used in some previous works) is not valid for the formation of species such as COS, CO, CS_2, and aromatics from hydrocarbons that are kinetically controlled (Karan and Behie, 2004; Clark et al., 2001).

The objective of this paper is to use a detailed and validated reaction mechanism for Claus feed combustion to study the effects of fuel gas flow rate and H_2S concentration in acid gas on the amounts of aromatics (BTEX and PAHs) and organosulfur complexes formed in the thermal section of the SRU that reduce sulfur recovery efficiency and catalyst performance. A detailed reaction mechanism, published in our previous work (Rahman et al., 2016), will be adopted for the kinetic simulations of the furnace