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Effect of benzene on product evolution in a H_2S/O_2 flame under Claus condition

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HIGHLIGHTS

- Effect of trace amounts of benzene (0.3%, 0.5% and 1%) to H_2S combustion process.
- Benzene favored formation of H_2 and reduced conversion of H_2S.
- Benzene reduced SO_2 formation to impact sulfur production.
- Benzene addition promoted CO and COS formation and degraded sulfur quality.

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ABSTRACT

Experimental results are presented on the role of benzene addition to H_2S combustion at an equivalence ratio of three with respect to H_2S (Claus condition) and complete combustion of benzene. The results are reported with 0.3%, 0.5% and 1% benzene addition to H_2S/O_2 flame. Combustion of H_2S and benzene mixtures is of practical value for sulfur recovery during combustion of acid gases. The results showed that H_2S combustion caused H_2S to decompose to a minimum mole fraction with high conversion of H_2S while the SO_2 mole fraction reached a maximum value. Addition of benzene decreased the conversion of H_2S with reduced mole fraction of SO_2 in the reactor to subsequently reduce the formation of elemental sulfur. Benzene also caused significant production of H_2, CO and COS formation along with faster decomposition of the formed SO_2. Presence of benzene, even in trace amounts, in acid gas hinders sulfur conversion in a Claus reactor and increases emission of unwanted sulfur bearing compounds. Increased hydrogen production with benzene offers potential value for hydrogen recovery under certain conditions.

1. Introduction

Sulfur is often present in the form of hydrogen sulfide in many crude natural gas and industrial gases, which exists mainly as an undesirable by-product of gas processing in chemical industries [1–5]. The pernicious hydrogen sulfide fumes that characterize many gas processing and operation sites of refinery and petroleum production represent a genuine threat to human health and the environment. Concentration levels of H_2S vary significantly depending upon the source of supply. For example, H_2S absorbed from amine treatment of natural gas or refinery gas, can contain 30–90% H_2S by volume or higher [4–6]. Many other processes can produce H_2S in small concentration, but even these small quantities cannot be discharged into the atmosphere without further treatment to alleviate its deleterious effects. Different processes are used to recover sulfur from H_2S [2,3].The most widely used process is called Claus process [2], but more recently, a novel chemical-looping process has been developed for converting sulfur dioxide (SO_2) in the flue gas generated from industries to elemental sulfur using oxygen carriers (such as Ca-based or Cu-based) [3]. However, Claus process technology is a more matured technology. It involves partial combustion of H_2S in a Claus furnace reactor under fuel rich conditions (at equivalence ratio of $\Phi = 3$) to produce SO_2. The formed SO_2 further react with the remaining H_2S to yield elemental S_2 and H_2O (see reactions (1) and (2)) [1,2].

$$H_2S + 1.5O_2 \rightarrow H_2O + SO_2; \quad \Delta Hr = -518\ \text{kJ/mol} \tag{1}$$

$$2H_2S + SO_2 \rightarrow 1.5S_2 + H_2O; \quad \Delta Hr = 47\ \text{kJ/mol} \tag{2}$$

Elemental sulfur is collected in either liquid or solid form [2]. It is desired to oxidize only one-third of the H_2S introduced into the reactor in order to partially convert H_2S to SO_2. The formed SO_2 reacts with H_2S to form liquid sulfur according to the stoichiometry shown in reactions (1) and (2).

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Acid gas stream, containing varying amounts of H_2S and CO_2, frequently has small amounts of hydrocarbons and other impurities in addition to the principal acid gas components (H_2S and CO_2). They often contain other undesirable compounds that include benzene, toluene and xylene (often referred to as BTX), C_1–C_4 hydrocarbons, N_2, NH_3, CS_2 and COS [1,2,4–7]. The efficiency of sulfur capture in a Claus reactor is significantly affected by the variation in the composition of acid gas feed into the Claus reactor and operational conditions, amongst other parameters [4–7]. The presence of BTX, even in small amounts can alter the chemical kinetics and product distribution of H_2S reactions [4,5]. For example, presence of hydrocarbons can result in the formation of other impurities, such as COS and CS_2 [1,4,5]. These often cause carbon depositions on catalytic pores (in the second catalytic stage of Claus reactor), resulting in rapid deactivation of catalyst, and leading to higher operational and maintenance cost and reduced process efficiency [1,8]. Therefore, any improvement in the performance and efficiency of Claus reactor requires good understanding of the role of BTX and other contaminants on the reactions in H_2S oxidation. The roles of CO_2, N_2, methane and toluene have been reported in previous investigations [1,2,4–10].

Selim et al. [9] reported experimental data on the effect of CO_2 and N_2 to H_2S combustion under Claus condition. Carbon dioxide acted as enhanced oxidizing medium which deteriorates the efficiency of Claus reactor significantly. On the other hand nitrogen provided dilution effects but did not affect the performance of Claus process significantly. Thus nitrogen acted as an inert gas, by reducing the reactants partial pressure. Ibrahim et al. [10] examined the role of toluene to H_2S combustion under Claus condition. They found that toluene triggers the formation of significant amounts of hydrogen that inhibits oxidation of H_2S, caused faster decomposition of SO_2 and created the mechanistic pathway for COS formation in the reactor. The effect of H_2 to H_2S oxidation has also been reported by other investigators [11–15].

Bernez-Cambot et al. [11] studied experimentally the flame structure of H_2S/air diffusion flame under Claus condition. They reported that the flame could be divided into three distinct zones. The First zone involved the thermal and chemical decomposition of H_2S, wherein H_2 was the major product formed. Oxidation of formed H_2 and H_2S occurred in the second zone, whereas the third zone was characterized by partial consumption of hydrogen. Similarly, Azatyan et al. [12] reported that H_2S oxidation takes place in stages. In the first stage, H_2, SO_2 and SO are formed and authors conjectured that H_2S hinders the oxidation of H_2 in the reactor. The second stage involves H_2 oxidation along with the formation of OH-radical. These results have further been supported by Pierucci and co-workers [13] who compared conversion of different fuels during stoichiometric combustion of pure H_2S, H_2 and CH_4 and their mixtures against contact times at reactor temperature of 1500 K. They found that H_2S exhibited faster reactivity than H_2 and CH_4.

Chin et al. [14] studied numerically and experimentally oxidation of hydrogen sulfide and hydrogen sulfide-methane mixtures in a tubular reactor over a narrow temperature range of 1273–1473 K and pressure of 110–180 kPa. They showed that H_2S is consumed much faster during H_2S–CH_4 mixture combustion, but reduces the amounts of produced SO_2 in the reactor. They postulated that methane is less competitive for oxygen than H_2S which results in methane reacting with other major sulfur containing species to form carbon disulfide. Chin et al. in the same paper also examined the reaction of methane with sulfur dioxide to determine if this reaction is directly responsible for COS formation. They deduced that COS is not a direct product of reaction between methane and sulfur dioxide but rather methane is partially oxidized to CO which then serves as a precursor to COS formation. Karan et al. [15] studied experimentally the kinetics of CH_4–S_2 and CH_4–H_2S reactions within a temperature range of 1073–1523 K and residence times of 90–1400 ms. Their results revealed that methane is kinetically favored to react with sulfur to produce CS_2 and this reaction occurs rapidly. Conversely, reaction of methane with H_2S also forms CS_2 with the rate of CS_2 formation limited by the H_2S thermal decomposition at the initial stage of reaction.

Although it is conventionally accepted that BTX poses technical problems to the Claus process plant, it is not well known how each component in the BTX alters the chemical composition of hydrogen sulfide combustion in Claus reactors. The effect of toluene, xylene, carbon dioxide and nitrogen has been examined in our previous work [9,10]. However, it is expected that benzene would behave much differently than toluene and/or xylene due to the greater thermal stability of benzene. Therefore the focus of this paper is on examining the gas phase combustion behavior of H_2S and benzene mixtures under Claus condition. Composition of the gas phase combustion products is examined to characterize the role of benzene to hydrogen sulfide combustion in a Claus reactor. Characterizing the individual effect of each contaminant (CO_2, N_2, benzene, toluene, and xylene) on the composition of combustion generated species of hydrogen sulfide provides significant implications for operators, designers and program developers of sulfur plants. This will also facilitate modeling efforts and justifiable assumptions for practical applications.

2. Experimental facility

A schematic diagram of the experimental setup is shown in Fig. 1. The facility consisted of a quartz tube reactor with a diameter and length of 4 cm and 19 cm, respectively. Detailed description of the experimental facility used here is available in our previous paper [10]. A major difference here is that hydrogen sulfide was premixed with benzene and injected into the central tube of the burner, while oxygen was introduced into the outer annulus of the burner. The sampled gas was split inside the GC into two streams. First stream was injected into the thermal conductivity detector which provided the detection of carbon monoxide and hydrogen. Second stream was injected into flame photometric detector (FPD) which provided gas analysis of stable sulfur compounds (such as, hydrogen sulfide, sulfur dioxide and carbonyl sulfide). Calibration was performed by analyzing known concentration of pure gases to identify their retention times. Subsequently, analysis of known concentrations of gas mixtures from calibration bottles was performed. Calibration gases were allowed to flow through the GC in order to saturate the sampling line prior to starting the GC analysis. Both TCD and FPD were calibrated using different concentration ranges of known gas mixtures in the calibration bottles. This ensured that the sampled gases composition from the experiments had similar range of concentrations to that of the calibration gases. A calibration curve that related the peak areas from the gas chromatographs to the gas mixture composition was then generated. The relative peak areas were then used to calculate the concentration of each gas in the mixture. Mean temperatures were measured using a K-type thermocouple that was also connected to a traverse mechanism and an online data acquisition and data analysis system.

3. Experimental conditions

Experimental examination of the effect of benzene to hydrogen sulfide combustion was carried out with emphasis on the formation and decomposition of selected stable end-species. Table 1 shows the test matrix for all experiments reported here. Combustion of H_2S alone gas stream was first examined followed by a