Applied Energy 115 (2014) 1–8

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

# Toluene destruction in thermal stage of Claus reactor with oxygen enriched air

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## HIGHLIGHTS

- Examined $H_2S$ and $H_2S/C_7H_8$ combustion using $O_2$ enriched air at Claus condition ($\Phi = 3$).
- Oxygen enrichment allowed examination at increased reactor temperatures.
- Presence of toluene reduced $SO_2$ formation and increased $S_2$ formation.
- Toluene triggered the formation of $CS_2$ and hydrocarbons (methane and acetylene).
- Increased $O_2$ enrichment in air helped to mitigate the impact of hydrocarbons and $CS_2$.

## ARTICLE INFO

*Article history:*
Received 20 May 2013
Received in revised form 18 October 2013
Accepted 30 October 2013
Available online 21 November 2013

*Keywords:*
Hydrogen sulfide combustion
Sulfur chemistry
Toluene addition and destruction
Oxygen enrichment in Claus process

## ABSTRACT

Results are presented on the toluene destruction using oxygen enriched air as the oxidant with addition of defined amounts of $H_2S$ and toluene into $H_2$/air flames under fuel-rich mixture conditions at equivalence ratio of $\Phi = 3$ (Claus condition). The oxygen enrichment allowed variation of temperature in the reactor and reduced nitrogen and total volumetric gas flow while maintaining the same equivalence ratio. The formation and destruction of hydrocarbons and other gas phase species during the combustion of $H_2S$ and $C_7H_8$ mixture are presented with oxygen enrichments (0%, 19.5% and 69.3% $O_2$) to air. Toluene is often present in acid gas consisting of mainly $H_2S$ and $CO_2$ so that combustion of $H_2S/C_7H_8$ is of practical value. The formation of $SO_2$ increased with oxygen enrichment to air. Increased oxygen in air reduced oxidation rate of $H_2$ and increased $H_2S$ oxidation rate which enhanced faster rate of $SO_2$ production to result in reduced formation of elemental sulfur. Addition of toluene to $H_2S$ reduced the rate of $H_2$ oxidation and increased that of $H_2S$. In contrast to the case of 100% $H_2S$ combustion, toluene favored faster increase in mole fractions of $SO_2$ to a peak value but the formed $SO_2$ decomposed with increased distance along the reactor. The decay of $SO_2$ is attributed to the reactions between $SO_2$ and other sulfur containing radicals or hydrocarbons formed (such as methane and acetylene) to produce elemental sulfur and carbon disulfide. Oxygen enrichment to the combustion air enhanced the rate of hydrocarbons decomposition which helped to reduce the amounts of $CS_2$ formed. Formation of $CS_2$ and hydrocarbons adversely impact the performance and efficiency of sulfur capture in a Claus process. These results assist in identifying conditions on the role of oxygen enrichment in designing compact Claus reactors.

## 1. Introduction

In an effort to produce cleaner air with sulfur bearing fuels, stringent regulations on emission of pollutants from the combustion of hydrogen sulfide are set by various environmental regulatory agencies worldwide [1]. Hydrogen sulfide is present in most natural gas wells so that it must be separated out from the natural gas and treated in a Claus reactor wherein both the energy and sulfur recovery occurs [1–5]. The efficiency of the Claus reactor can vary significantly depending on the gas composition, rector design configuration and operational condition [2]. This has stimulated significant demands for improved sulfur recovery efficiency in both new and existing gas processing plants and refineries. Moreover, as light and sweet feedstock is becoming increasingly scarce, there is a shift towards utilization of heavier and sourer feedstock that contains increased amounts of acid gas [1–5]. Most often, these feedstock contain various contaminants, such as $H_2S$, $CO_2$, $N_2$, $NH_3$, $CS_2$, COS and hydrocarbons such as benzene, toluene and xylene also known as (BTX) and mercaptans [2]. Combustion of any crude natural gas containing the aforementioned contaminants results in the formation of highly toxic compounds (such as $SO_2$, $H_2SO_4$, CO, COS and $CS_2$). Hence, it is a necessity to separate

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http://dx.doi.org/10.1016/j.apenergy.2013.10.060

out and oxidize hydrogen sulfide and other acid gases from crude natural gas prior to its utilization in any application.

Separation of hydrogen sulfide gas from crude natural gas commonly takes place through the so called 'Amine extraction' process [1,2]. This process involves the removal of acidic gases, mainly $H_2S$ and $CO_2$ from crude natural gas. In this process, alkaline-based organic compounds are used to absorb hydrogen sulfide from crude natural gas. During the separation of $H_2S$ and $CO_2$, small concentrations of methane, mercaptans and BTX often accompany the separated gas. The collected hydrogen sulfide even in small amounts must be treated to hinder its harmful effects on human health and environment. The well-known Claus process [1–5] is used for the treatment of hydrogen sulfide. In this process, reaction between $H_2S$ and $O_2$ occurs under fuel-rich conditions (at equivalence ratio of $\Phi = 3$) to form elemental sulfur. However, these reactions occur in two stages as described below in Eqs. (1) and (2) [2].

$$3H_2S + 1.5O_2 \rightarrow H_2O + SO_2 + 2H_2S; \quad \Delta Hr = -518\ \text{kJ/mol} \tag{1}$$

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

The elemental sulfur is captured in either liquid or solid form [1,2]. In practice, the Claus process is commonly divided into two main stages; thermal stage and catalytic stage. In both stages, similar chemical reactions occur in the reactor, but catalysts are used in the later stage to further enhance the conversion of hydrogen sulfide to sulfur. The presence of contaminants (such as $CO_2$, $CH_4$ and BTX) in the separated hydrogen sulfide gas stream, even in very small concentrations can alter the chemical kinetics of hydrogen sulfide combustion significantly. As a consequence, this often causes hydrocarbon depositions, resulting in rapid deactivation of catalyst. This leads to higher operational cost and reduced process efficiency. Therefore, it is crucial to oxidize and recover energy from BTX completely in the thermal stage.

Several investigators have studied the flame structure of $H_2S$/air over a wide range of operational conditions. Selim, AlShoaibi and Gupta examined the chemical kinetics of hydrogen sulfide combustion under various experimental conditions [6–9]. In one of our previous papers [6], hydrogen sulfide combustion in methane/air flame was examined at three different equivalence ratios of 0.5, 1 and 3 that represented fuel lean, stoichiometric and rich conditions, respectively. Authors reported that oxygen availability in the reaction pool, $H_2S$ combustion tends to form $SO_2$, while with the depletion of oxygen net reaction tends to form elemental sulfur rather than sulfur dioxide. In another paper [7], authors investigated experimentally the effect of acid gas composition on sulfur recovery. The results revealed that the presence of carbon dioxide reduces the sulfur recovery wherein most of $H_2S$ is transformed to $SO_2$. However nitrogen did not make the same effect as it acted mainly as an inert medium. Also, same authors examined the sulfur chemistry with the acid gas ($H_2S$ and $CO_2$) addition in $H_2$/air flame at different equivalence ratios [8]. It was reported that presence of $CO_2$ enhances the oxidizing medium of the reaction pool while simultaneously promoting formation of carbonaceous–sulfurous compounds (such as COS and $CS_2$). These compounds deteriorate the performance of Claus process. Selim et al. [9] also investigated the effect of oxygen enrichment of air on acid gas combustion under Claus condition. It was found that oxygen enrichment increases the oxidizing role of $CO_2$ which enhanced the formation of $SO_2$. The results also showed that oxygen enrichment reduces the formation of $CS_2$ while enhancing the formation of COS due to the increased concentration of CO in the reactor at high temperatures. Our investigation of sulfur chemistry in both $H_2S/O_2$ and $H_2$/Air flames under Claus condition showed that hydrogen sulfide inhibits $H_2$ oxidation which agrees with the earlier findings by Bernez-Cambot et al. [10] and Azatyan et al. [11]. Bernez-Cambot et al. carried out experiments to study the flame structure of $H_2S$/air diffusion flame under Claus condition. They used a gas analyzer to measure the concentrations of selected combustion products at different locations in the reactor. They reported that the flame is divided into three distinct zones. The First zone involved the thermal and chemical decomposition of $H_2S$, wherein hydrogen was observed as the major product, while the second zone involved the oxidation of both $H_2S$ and the formed $H_2$. However, third zone is characterized by partial consumption of hydrogen and to a lesser extent that of sulfur diffusing from the flame. Azatyan et al. examined the behavior of hydrogen sulfide, carbon disulfide, and carbonyl sulfide combustion at low-pressure using electron spin resonance technique along with gas chromatography. These authors showed that first stage of $H_2S$ oxidation involves the formation of $H_2$, $SO_2$ and SO and they hypothesized that the presence of $H_2S$ is considered inhibitor to $H_2$ oxidation. They also showed that the second stage includes hydrogen oxidation coupled with the formation of OH-radical. These results agree with the findings of Bernez-Cambot et al. [10].

Frenklach et al. [12] studied numerically and experimentally the ignition delay of $H_2S$ combustion in a reflected shock wave tube. They performed numerical modeling using an adopted reaction mechanism, consisting of 57 elementary reactions. Muller III et al. [13] investigated sulfur chemistry in fuel-rich $H_2/O_2/N_2$ flames using 0.25%, 0.5% and 1% of $H_2S$ in the mixture. They measured concentrations of SH, $S_2$, SO, $SO_2$, and OH radicals using quantitative laser fluorescence measurements. They used this information to predict kinetic parameters for various possible intermediate chemical reactions of sulfur compounds.

Chin et al. [14] studied numerically and experimentally oxidation of hydrogen sulfide and hydrogen sulfide–methane mixtures in a tubular reactor in a temperature range of 1000–1200 °C and pressure of 110–180 kPa. They reported that $H_2S$ consumption is faster in the presence of methane while the amounts of $SO_2$ formed reduces. Their results also revealed that methane is much less competitive for oxygen than $H_2S$ which results in methane reacting with other major sulfur containing species to form carbon disulfide. In the same paper, they examined the reaction of methane with sulfur dioxide to determine if this reaction is directly responsible for COS formation. They concluded that COS is not a direct product of reaction between methane and sulfur dioxide, rather methane is partially oxidized to CO which then serves as a precursor to COS formation. Karan and Behie [15] studied experimentally the kinetics of $CH_4$–$S_2$ and $CH_4$–$H_2S$ reactions within a temperature range of 800–1250 °C 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. On the other hand, 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. Hawbolt et al. [16] studied pyrolysis of hydrogen sulfide in the temperature range of 850–1150 °C under Claus condition. They determined a pyrolysis rate expression for hydrogen sulfide and reported that hydrogen sulfide dissociation is minimal at temperatures below 1000 °C. This justifies the need for high temperatures in the Claus thermal reactors.

However, oxygen enrichment to combustion air has been commonly used in the Claus process to destroy contaminants and several undesired compounds present in natural gas wells, mercaptans, benzene, toluene and xylene [17–19]. With oxygen enrichment, the nitrogen concentration in combustion air is reduced and this caused two simultaneous effects in the reactor. First it increased the temperature of gases in reactor and second it reduced the total volumetric flow of gases (from decrease in nitrogen flow) in the Claus reactor. This caused a change in the mixing characteristics (decrease in average gas flow velocity and Reynolds number) and increased the average residence time in the reactor. The reduction in the flow of nitrogen, which acts as a