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Reformation of hydrogen sulfide to hydrogen in the presence of xylene

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HIGHLIGHTS

- Examined hydrogen production from thermal decomposition of H_2S contaminated with xylene.
- Temperature impacts H_2 production from hydrogen sulfide reformation with xylene.
- H_2 from H_2S reformation with xylene increased at higher reactor temperatures.
- Increased reactor temperature increased CS_2 concentration at the exit stream.

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ABSTRACT

Hydrogen sulfide is a hazardous gas from environmental, human health and equipment prospective. Hydrogen sulfide occurs naturally from crude oil and natural gas wells along with some other hydrocarbon impurities. Reformation of hydrogen sulfide without or with the presence of xylene (a common impurity present in hydrogen sulfide) has been investigated. Production of hydrogen concurrent with destruction of hydrogen sulfide provides a good alternative method to treat hydrogen sulfide. The role of xylene addition on the reformation of hydrogen sulfide was experimentally investigated. A laboratory-scale reactor was used to examine the effect of reactor temperature in the range of 1273–1573 K and various inlet stream composition on the production of hydrogen and destruction of both hydrogen sulfide and xylene. Results showed enhanced hydrogen production and higher hydrogen sulfide destruction at temperatures above 1273 K. Xylene was destructed completely at a relatively low temperature of 1373 K. Carbon disulfide formation increased with increase in temperature for all the inlet compositions of hydrogen sulfide and xylene examined. Reducing the formation of CS_2 and also mitigation of carbon deposition by reducing the amounts of carbon introduced to the reactor were investigated and quantified experimentally. The most favorable operational conditions for reaction between hydrogen sulfide and xylene were established. The results showed new potential of this binary mixture dissociation as an alluring treatment method of hydrogen sulfide.

1. Introduction

Hydrogen sulfide is an environmental contaminant that occurs naturally in crude petroleum oil and natural gas wells and other natural sources. Hydrogen sulfide can also occur from many industrial processes, mainly petroleum refineries. Hydrogen sulfide is a highly toxic, flammable, corrosive colorless gas that has characteristic rotten egg smell. Hydrogen sulfide toxicity is not only limited to environment but also this gas adversely affects human health and equipment. Despite the high heating value of hydrogen sulfide, its utilization as a fuel is forbidden in conventional combustion systems. Burning hydrogen sulfide in conventional combustion systems results in the formation of SOx, which are precursors to acidic precipitation. Hydrogen sulfide stream, commonly accompanied in natural gas and also from hydrodesulfurization process of petroleum oil products, is separated out using amine extraction process [1]. Other impurities that can also contaminate the separated hydrogen sulfide stream include carbon dioxide, nitrogen, ammonia, carbon disulfide, carbonyl sulfide and BTX (benzene, toluene and xylene). Most of these impurities are neither environmental friendly nor human health friendly. Environmental agencies strictly enforce limits on the maximum allowable levels of sulfurous compounds that can be vented out to the atmosphere. Thus, after the separation process, hydrogen sulfide stream has to undergo a highly efficient treatment process to meet the stringent environmental regulations on the maximum allowable sulfurous compounds that can be vented out from any

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petrochemical plant [2,3]. Claus process is the most common technology used for the treatment of hydrogen sulfide stream. In the thermal stage of this process, hydrogen sulfide is partially burnt under fuel rich conditions (at equivalence ratio of 3) that results in the formation of sulfur dioxide. The remaining hydrogen sulfide reduces the formed sulfur dioxide to produce elemental sulfur and thermal energy that is used to produce low quality steam in a boiler. In the subsequent catalytic stage of the Claus process, the reduction reaction occurs in several catalytic stages at progressively low temperatures with accelerated reaction and increased efficiency of sulfur recovery process, to result in high levels of destruction of the original hydrogen sulfide stream. The more stringent environmental regulations means more extensive cleanup of the tail gases. Extensive studies have been made to lessen extensive cleanup burden of the process to improve the efficiency of Claus process and mitigate sulfur emissions by optimizing the input and operational conditions of the Claus reactor [4–7]. The performance of thermal stage of Claus reactor is affected by the inlet gas stream composition. In addition, the catalytic stage suffers from the existence of carbonaceous species in the reacting stream that poisons and deactivates the catalyst.

Although direct utilization of hydrogen sulfide as a fuel is forbidden in any industry for the aforementioned reasons, hydrogen sulfide is a hydrogen rich feedstock that is used in the Claus process for sulfur recovery (primary) and steam production (secondary). Therefore, rather than consuming the hydrogen constituent in hydrogen sulfide in Claus process, simultaneous recovery of sulfur and hydrogen production is more attractive approach. Dissociation of hydrogen sulfide can be made using several different technologies; the most direct method being the thermal decomposition of hydrogen sulfide. Many investigators have studied hydrogen production via catalytic/non-catalytic thermal dissociation of hydrogen sulfide, both experimentally and numerically. Most of these studies have focused on overall H_2S thermal decomposition reaction [8–19]. The numerical studies had focus on developing detailed reaction mechanisms of H_2S thermal decomposition [20,21]. The treatment of pure hydrogen sulfide to produce hydrogen and sulfur was the focus of these studies. However, hydrogen sulfide stream separated out from petroleum products had considerable amounts of CO_2, N_2 as well as other impurities given above. Syngas recovery from acid gas containing hydrogen sulfide and carbon dioxide has been examined experimentally [22] and numerically [23–25]. Reactor temperature and inlet acid gas composition affected the recovered syngas composition.

Hydrogen-constituted impurities, such as ammonia and hydrocarbons, in hydrogen sulfide stream enriches its hydrogen feedstock. Pyrolysis of hydrogen sulfide contaminated with hydrogen-constituted impurities is expected to produce more hydrogen. Traditionally, investigating reactions with hydrocarbons start with methane.

Investigation of reaction between hydrogen sulfide and methane has been examined from different perspectives, as discussed hereafter. In 1939, Waterman and Vlodrop [26] studied the reaction between hydrogen sulfide and methane experimentally for carbon disulfide production using a tubular quartz reactor over a temperature range of 1350–1550 K. They could infer the occurrence of the following reaction:

$$CH_4 + 2H_2S \rightleftharpoons CS_2 + 4H_2 \tag{1}$$

Erekson [27] investigated production of gasoline via chemical looping of hydrogen sulfide in two-step reaction shown below:

$$CH_4 + 2H_2S \rightleftharpoons CS_2 + 4H_2 \tag{1}$$

$$CS_2 + 3H_2 \rightleftharpoons [-CH_2-] + 2H_2S \tag{2}$$

Erekson employed the reaction between hydrogen sulfide and methane to produce hydrogen and carbon disulfide over a range of temperatures (973–1473 K) as shown in the first step of his cycle. Note that neither production of hydrogen nor hydrogen sulfide treatment was a prime focus of the study. Hence, neither data on the amounts of hydrogen produced nor the hydrogen sulfide conversion was reported.

Interest in production of hydrogen via reaction between hydrogen sulfide and methane has grown considerably as hydrogen is the cleanest fuel. This reaction was studied with a focus on hydrogen production by Megalofonous and Pappayanakos [28] both numerically, using equilibrium calculations, and experimentally over a relatively low temperature range of 985–1133 K. This temperature range was not high enough for significant production of hydrogen from homogeneous reaction between hydrogen sulfide and methane. They also investigated accelerating the reaction using MoS_2 as catalyst. In addition, the production of hydrogen via this method has been proposed in theory [27,29].

Enhanced hydrogen production via thermal reformation of hydrogen sulfide in presence of methane were investigated experimentally and numerically [30,31]. A potential of more than 95% recovery of hydrogen constituent in hydrogen sulfide from a mixture of hydrogen sulfide and methane has been depicted [31]. This finding agreed well with the hydrogen sulfide conversion reported by Karan and Behie [32] during their examination of the reaction between hydrogen sulfide and methane.

Reaction between hydrogen sulfide and other hydrocarbon impurities, such as benzene, toluene and xylene, that naturally accompany hydrogen sulfide after its separation from natural gas has also been studied [33,34]. Ibrahim et al. [33,34] reported detection of hydrogen emanating from hydrogen sulfide and xylene during the early stages of combustion. They also reported that amounts of hydrogen formed increased with the increase in xylene amounts in the hydrogen sulfide stream. They attributed the increased amounts of hydrogen produced to increased decomposition of hydrogen sulfide as well as xylene. However, they did not determine if the increased thermal decomposition rate was due to higher temperatures in combustion from the presence of xylene or from increased hydrogen constituent in the mixture.

Other hydrocarbon impurities in hydrogen sulfide have potential to enhance hydrogen production via hydrogen sulfide reformation such as benzene, toluene and xylene. One of the hydrocarbon impurities that already exists in hydrogen sulfide stream separated out from the refined petroleum products and that also causes problems in the Claus reaction is xylene. This is a volatile liquid aromatic hydrocarbon. Reforming hydrogen sulfide in the presence of xylene would definitely produce more hydrogen, which can improve the economics of hydrogen production via decomposition of H_2S. However, paucity of experimental data on the thermal decomposition of hydrogen sulfide in presence of such impurities is lacking to impede evaluating these routes. The objective of this study was to provide experimental data on hydrogen sulfide reformation in the presence of xylene as a practical alternative method to treat hydrogen sulfide in addition to hydrogen production from hydrogen sulfide stream. The role of input and reactor operational parameters has been identified for the production of hydrogen from reforming hydrogen sulfide with xylene.

2. Experimental facility and condition

Fig. 1 shows a schematic diagram of the experimental facility. The facility consisted of a quartz tubular reactor of 0.006 m in diameter, which was housed inside a temperature-controlled electrically-heated horizontal tubular furnace. Quartz was chosen over other materials for its superior thermal stability at high