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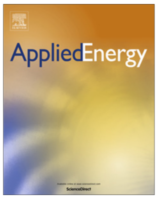

Experimental examination of syngas recovery from acid gases

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HIGHLIGHTS

- Examined syngas production from thermal decomposition of H_2S and CO_2.
- Temperature and acid gas composition directly impacts H_2 and CO produced.
- H_2S pyrolysis causes H_2 production to increase at higher reactor temperatures.
- CO_2 addition into H_2S decreased H_2 production at higher reactor temperatures.
- CO_2 easily reduced in the presence of H_2S pyrolytic environment.

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ABSTRACT

This paper shows the potential for valuable syngas (H_2 and CO) production from a laboratory-scale reactor, as an alternative and viable means for the treatment of acid gas (H_2S and CO_2). Claus process technology currently used for acid gas treatment often suffers from lack of high process efficiency due to various impurities present in acid gas that cause non-uniform gas composition. Increased environmental regulations on sulfur emissions have challenged environmental engineers to seek safe, reliable and efficient means of acid gas conversion to useful products. This paper provides suitable input and operational conditions of the reactor that helps to produce syngas from acid gas, having wide range of composition at high conversion rate of acid gas (H_2S and CO_2) to minimize environmental burden. The results reveal the importance of reactor temperature and the role provided by CO_2 in acid gas on the composition of syngas produced. The results show that a reactor temperature of 1373–1473 K and high residence time favors the production of syngas at high conversion efficiency of acid gas. The syngas produced can be utilized for energy generation or value added products. The operational conditions provide means to quantify reactor performance with different composition of the syngas to aid in the production of biofuels and value added products.

1. Introduction

Desulfurization of crude oil and natural gas continues to be a-serious problem in the chemical industry due to the continuous decrease in maximum allowable levels of sulfur content in gasoline, diesel and jet fuels, enforced by regulatory agencies [1,2]. The emergence of new approaches and technologies for greater sulfur removal is expected to increase the volume of generated acid gas (H_2S and CO_2) in the byproduct streams of various desulfurization units [1]. These acid gases often contain other impurities that include N_2, NH_3, CS_2, COS and hydrocarbons such as benzene, toluene and xylene (BTX). Claus process is commonly used for the treatment of acid gas to recover elemental sulfur. It consists of both thermal and catalytic stages in order to achieve very high conversion of acid gas [3]. However, the efficiency of Claus process is significantly hindered by the presence of impurities and compositional variations of acid gas in the feed stream to Claus plant [4–6]. The high content of CO_2 in most acid gases poses several environmental and technical issues in the operation of Claus plant [7]. Therefore, it is imperative to seek alternative utilization and more efficient treatment of acid gas, to preserve our environment from the use of sulfur-bearing fuels and enhance chemical energy generation from the conversion of acid gas to syngas.

Production of H_2 from H_2S has been examined by previous researchers [8–17]. Most studies have focused on the kinetics of H_2S decomposition into hydrogen and sulfur and the reported results are primarily on the various kinetic parameters [8–14]. The reported overall kinetic parameters show significant variations so that these results require substantiation and quantification prior to their use in practice. A vast number of studies have failed to

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provide a unified description of the reaction kinetics on H_2 production from H_2S despite examination over a wide range of conditions. Binoist and co-workers [15] reported experimental and modeling data on the pyrolysis of H_2S in diluted argon, using a continuous perfectly mixed reactor at residence time of 0.4–1.6 s and 1073–1375 K temperatures. They developed a detailed kinetic mechanism for H_2S pyrolysis. A revised version of this mechanism was later reported by Manenti and co-workers [16], which showed better comparison with the experimental data.

However, these studies have focused on the pyrolysis of H_2S alone, even though acid gas contains considerable amounts of CO_2. One viable option is to recover syngas and sulfur from acid gas over a defined temperature range to enhance conversion efficiency and mitigate the production of unwanted sulfur compounds [17]. Production of syngas from CO_2 reduction in H_2S pyrolytic environment has recently been discussed in theory [18]. However, experimental examination of the production of syngas from acid gas stream is not available in the open literature. This is an attractive alternative since the large volume of CO_2 in acid gas (lean acid gas) can be captured from the produced syngas. Acid gas thermal decomposition is well suited for the treatment of lean acid gas that poses serious operational issues in Claus process plants. Presence of impurities, such as hydrocarbons in acid gas will also be an added value since this will favor higher yield of syngas. The H_2 and CO (syngas) produced can then be used in industry for energy and power generation. Syngas is a valuable commodity for use as a fuel in gas engines, or to produce valuable chemicals, such as ammonia and liquid fuels. Therefore, this paper examines the pyrolysis of H_2S and CO_2 (acid gas) in diluted nitrogen. The results show that this path offers a more practical solution to the alternative treatment and utilization of acid gas.

2. Experimental facility and test condition

The experimental setup consists of a tubular reactor, horizontal furnace, sampling system, condenser, supply of feed streams and appropriate control system. Fig. 1 shows a schematic diagram of the experimental setup.

The quartz tube reactor was 0.019 m in diameter and 0.35 m long. The quartz reactor had a high thermal stability up to 1800 K and was housed inside a high temperature laboratory scale tubular furnace. The furnace was equipped with a temperature controller to ensure temperature uniformity throughout the furnace. Operating temperature of the furnace ranged up to 1475 K with an overall hot zone length of 0.28 m. Prolonged use of this reactor revealed no noticeable effects on inner surface of the quartz reactor from the pyrolysis of acid gas, revealing the absence of any catalytic activity of quartz reactor with the acid gas used. This was in agreement with the findings of Adesina et al. [9] and Binoist et al. [15] who also reported no catalytic activity. The reactor was stabilized at the desired temperature, prior to the injection of reactant gases. Thermal flow meters/controller was used to supply the required flow rates of industrial grade hydrogen sulfide, nitrogen and carbon dioxide. The temperature inside the reactor was measured using a K-type thermocouple and was maintained to ±2.1 K of the set point. Nitrogen was first injected into the reactor to ensure no residual gas was present. H_2S and CO_2 were then premixed with N_2 and injected into the reactor. The resulting mixture composition consisted of 5% acid gas with different ratio of H_2S to CO_2, while nitrogen makes up the remaining 95% of the total mixture. The flow rates and resulting mixture of the reactant gases are given in Table 1. Residence time in the reactor was controlled using flow rates of the injected gases.

Gas sampling and analysis at the exit of the reactor was conducted using a sonic-throat sampling probe that was mounted on a computer controlled traverse mechanism and positioned at the longitudinal centerline axis of the reactor. A suction pump was used to inject the sampled gases into the online gas chromatograph (GC) that was equipped with a thermal conductivity detector. Several samples (3–4) were collected for each condition so that an average data is reported at each condition. Error in the experimental measurements was estimated to be <2.1% of the measured values. The whole experimental setup was placed in a closed fume hood to ensure controlled and safe environments for the experiments. The fume hood was connected to an exhaust duct, wherein a fan was used to induce air into the fume hood for unidirectional flow and to assure safe operation of the facility. The environment in the chamber was continuously monitored for the presence of H_2S, H_2 and CO gas.

3. Results and discussion

The results on pyrolysis of H_2S, diluted in nitrogen gas were examined and are presented. The experimental data, obtained from the experimental facility are compared with other data available in the literature. Subsequently, results on the pyrolysis of H_2S and CO_2 are presented. The goal here was to quantify experimentally, the speciation of syngas (H_2 and CO) production from the pyrolysis of acid gas (H_2S and CO_2) over a range of temperatures and gas composition.

3.1. Calibration of experimental facility

Pyrolysis of H_2S and N_2 mixtures was examined using a mixture of 5% H_2S/95% N_2 injected into the reactor. The residence time in the reactor was kept constant at 1.45 s, while the temperature of the reactor was changed incrementally from 1273 to 1475 K. Gas composition at the exit of the reactor were quantified during all the experiments. The input and reactor operational conditions were chosen to facilitate comparison with experimental data from the literature. The chosen residence time of 1.45 s also meant that comparison with equilibrium simulation was feasible. The amounts of H_2S conversion within the examined temperature range of 1213–1475 K was between 33% and 68%, which agrees with the equilibrium data. The conversion of H_2S at different temperatures resulted in different amounts of hydrogen production. Fig. 2 shows a comparison of hydrogen production from the pyrolysis of 5% H_2S/95% N_2 mixture. The results are also compared to the data reported by Binoist et al. [15]. Since the residence time was high enough for the reaction products to reach equilibrium, a comparison is also made with equilibrium simulations. The equilibrium simulations were conducted using the chemical equilibrium code from NASA Glenn research center [19].

The data from Binoist et al. [15] were obtained under similar input conditions but with a different reactor type. While our data are from a simulated plug flow reactor, Binoist et al.'s data were obtained from pyrolysis of 5% H_2S/95% Ar, at a residence time of 1.45 s in a small bulb reactor that provided perfect mixing of gases. Our data showed a satisfactory agreement with the data reported by Binoist et al. [15], between 1273 and 1375 K. However, they did not examine temperatures above 1375 K, but our data compares well with the equilibrium predictions at these higher temperatures (above 1375 K). The equilibrium prediction matched well with the experimental data, except for temperatures below 1275 K. The production of hydrogen was undepreciated at lower temperatures, signifying that the residence time of 1.4 s was not sufficient for the reactions to reach equilibrium values. Overproduction of H_2 above equilibrium value at 1323 K and 1473 K could be due to complex chemistry that is precluded in the equilibrium calculation.