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Energy efficiency of hydrogen sulfide decomposition in a pulsed corona discharge reactor

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ABSTRACT

A novel pulsed corona wire-in-tube reactor with quartz view-ports allowed visual observation of the effect of charge voltage and gas composition on the corona distribution. The H_2S conversion and energy efficiency of H_2S decomposition in this pulsed corona discharge reactor varied at constant power (100 W) due to the selected values of the electrical parameters of pulse forming capacitance (720–2880 pF), charge voltage (11–21 kV), and pulse frequency (157–961 Hz). Low pulse forming capacitance, low charge voltage, and high pulse frequency operation produces the highest energy efficiency for H_2S conversion at constant power. H_2S conversion is more efficient in Ar–N_2 gas mixtures than in Ar or N_2. These results can be explained by corona discharge observations, the electron attachment reactions of H_2S at the streamer energies, and a proposed reaction mechanism of H_2S dissociation in the Ar–N_2 gas mixture. The energy consumption per molecule of converted H_2S in an equimolar mixture of Ar and N_2 (4.9 eV/H_2S) is the lowest that has been reported for any plasma reactor operated at non-vacuum pressures. The results reveal the potential for energy efficient H_2S decomposition in pulsed corona discharge reactors.

1. Introduction

The annual demand for hydrogen in the US chemical and refining industries for 2007 was about 8.9 million metric tonnes (www.epa.gov/climatechange/emissions/downloads/tsd/TSD%20HydrogenProduction%20EPA_2-02-09.pdf, 2008), mainly for use as a reactant in the synthesis of ammonia and methanol and in petroleum hydrodesulfurization, hydrocracking, and upgrading processes. Merchant hydrogen production for use in refineries and chemical plants was about 2.0 million metric tonnes per year (www.epa.gov/climatechange/emissions/downloads/tsd/TSD%20HydrogenProduction%20EPA_2-02-09.pdf, 2008). Although the total hydrogen consumption is growing at about 4% annually, growth in the merchant hydrogen business is higher, estimated to be about 10%, as refineries shift away from captive hydrogen production (http://www.the-innovation-group.com/ChemProfiles/Hydrogen.htm, 2008). With the cost of sweet crude oil increasing, refineries are processing more heavy sour crude, which requires additional hydrogen for sulfur removal. Legislation limiting sulfur content in gasoline and diesel require more hydrotreating process steps in refineries. In addition, as hydrogen is being developed as an energy carrier, the predominant hydrogen production method, steam reforming of natural gas, may be insufficient for future needs. For example, by 2040, the use of hydrogen in fuel cell powered cars and light trucks is anticipated to require annual production of approximately 136 million metric tonnes of hydrogen (Dresselhaus et al., 2004).

Hydrogen sulfide (H_2S) is a common contaminant (from ppm concentrations to 90% by volume) in many of the world's natural gas wells. In natural gas processing, it is viewed as a pollutant because it corrodes pipelines and deactivates metal-based catalysts used in steam methane reformation (Huang and T-Raissi, 2008). Traditionally, H_2S is converted via the Claus process to sulfur and water, resulting in a loss of the hydrogen content of the H_2S as low-grade steam. H_2S would be more economically valuable if both hydrogen and sulfur could be recovered. We estimate the US H_2S production rate from natural gas plants and oil refineries to be on order of 10 million metric tonnes per year. The theoretical energy required to produce hydrogen from H_2S is only 20.63 kJ/mol H_2 as compared to 63.17 kJ/mol H_2 for steam methane reforming and 285.83 kJ/mol H_2 for water electrolysis, all calculated from standard heats of formation at 298 K (Smith and Van Ness, 1987). Therefore, H_2S represents a significant potential future source of low-cost hydrogen, if efficient processes are developed to extract and recover the H_2.

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H_2S decomposition in various types of plasma reactors has been investigated as a method to recover the H_2. Unfortunately, the reported energy consumptions are much higher than the theoretical energy requirement of 0.21 eV per decomposed H_2S molecule (20.63 kJ/mol H_2). All but one of the reported efficiencies exceed the energy requirement of 3.6 eV per H_2 molecule produced required for conventional steam methane reforming, the predominant hydrogen production method, with all separation equipment included (Cox et al., 1998). Dalaine et al. (1998a,b) investigated H_2S conversion in gas systems with concentrations of 0–100 ppm H_2S in air using gliding arc discharges. This type of reactor is rather inefficient, with an energy consumption of 500 eV/H_2S molecule dissociated. A large amount of work on microwave decomposition of H_2S was carried out in the former Soviet Union (Asisov et al., 1985; Bagautdinov et al., 1992, 1993a,b, 1995, 1998). Very low energy consumptions of 0.76 eV/H_2S were reported in both laboratory and pilot units used for the decomposition of pure H_2S or mixtures with CO_2. Encouraged by these reports of high conversions and low energy requirements, a joint project for H_2S conversion using microwave plasmas was undertaken by the Alberta Hydrogen Research Program, Atomic Energy of Canada, and Shell Canada Limited. Unfortunately, this group reported the energy consumption for H_2S conversion to be about $\sim$4.5 eV/H_2S (Cox et al., 1998) and thus was unable to reproduce the low energy consumption reported by the Russian researchers. All microwave plasma experiments for H_2S conversion in the Canadian studies were performed at pressures below 1 atm, which requires additional energy consumption for compression and vacuum costs. Traus and Suhr (1992) and Traus et al. (1993) investigated conversion of H_2S at 10–100 mol% concentrations in Ar, N_2, and H_2 in a silent discharge reactor and in a rotating glow discharge reactor. They determined the energy consumption for H_2S conversion in a rotating glow discharge reactor ($\sim$27 eV/H_2S) to be less than that in a silent discharge reactor ($\sim$81 eV/H_2S). In addition, Abolentsev et al. (1995) and Ma et al. (2001) investigated decomposition of low (ppm) concentrations of H_2S in different balance gases, including air, N_2, H_2, He, and CH_4, using a silent discharge reactor. H_2S conversion in pulsed corona discharge reactors was also studied by several investigators (Averin et al., 1996; Helfritch, 1993; Ruan et al., 1999; Wiseman and Douglas, 1972). These investigations were conducted at low H_2S concentrations (< 2 mol%) with high (> 100 eV/H_2S) energy consumption, which are not practical conditions for commercial application.

We previously reported the lowest energy consumption of 17.4 eV/H_2S molecule for moderately high concentrations of H_2S, 16% H_2S in Ar, (Zhao et al., 2007) at non-vacuum pressures (134 kPa). Also, at higher H_2S concentrations (> 16 mol%), H_2S decomposition in Ar produced higher conversions and reaction rates, as compared to those in He, N_2, and H_2. Therefore, Ar was selected as the balance gas for most of the future experiments. Although Ar can be separated from H_2S and H_2 at the reactor outlet and recycled to the process, it is relatively expensive compared to N_2. Therefore, Ar diluted with N_2 was also used as a balance gas with improved performance.

The electrical parameters of charge voltage (V_c), pulse frequency (f), and pulse forming capacitance (C_p) have been reported to impact the conversion of various reactants in plasma reactors. For methane conversion, the moles of methane converted per unit of energy supplied decreased with increasing charge voltage and increased with increasing pulse-frequency (Ma et al., 2001), while methane conversion and energy efficiency were higher at a pulse forming capacitance of 1280 pF as compared to 1920 pF at different power inputs (Zhao et al., 2006b). H_2S conversion increased with increasing charge voltage for ppm concentrations of H_2S in an ozonizer (Haas and Khalafalla, 1973). NO conversion at ppm concentrations (Mok, 2000) increased with increasing pulse frequency and capacitance. In all these studies, the total power supplied to the reactor changed as each of these parameters changed because power input is defined as $P = 1/2C_pV_c^2f$, where C_p is the pulse forming capacitance, V_c is the charge voltage, and f is the pulse frequency. This study reports the effect of these parameters at constant power to isolate the effects on H_2S conversion as these parameters were varied at constant power input.

2. Experimental

The experimental system, shown in Fig. 1, consists of a stainless steel reactor, a flow control and distribution system, and an electrical system. The reactor is a vertical wire-in-tube design, with gas flow from top to bottom. The anode is a 0.001 m diameter stainless steel wire passing axially through the center of the cathode tube. The cathode is a stainless steel tube, 0.024 m in diameter and 0.914 m long, with seven quartz view-ports and seven ports for sampling and temperature measurement placed equidistantly along its length. The 0.01 m diameter quartz view-ports permitted visual inspection of the corona discharge. At the same operating conditions, similar H_2S

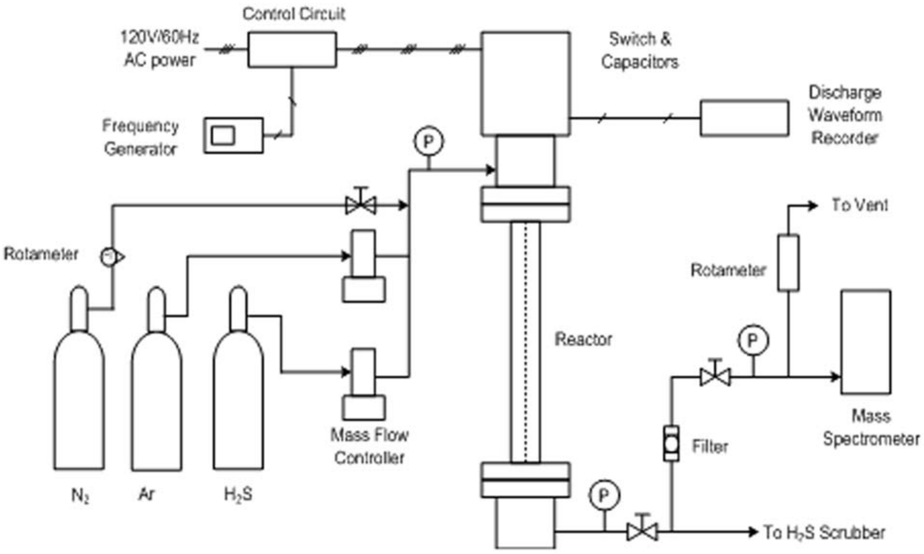

Fig. 1. Experimental setup.