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Catalytic Processing of High-Sulfur Fuels for Distributed Hydrogen Production

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Abstract

In this work, the development of a new on-demand hydrogen production technology is reported. In this process, a liquid hydrocarbon fuel (e.g., high-S diesel) is first catalytically pre-reformed to shorter chain gaseous hydrocarbons (predominantly, C_1-C_3) before being directed to the steam reformer, where it is converted to syngas and then to high-purity hydrogen. In the pre-reformer, most sulfurous species present in the fuel are catalytically converted to H_2S. In the desulfurization unit, H_2S is scrubbed and converted to H_2 and elemental sulfur. Desulfurization of the pre-reformate gas is carried out in a special regenerative redox system, which includes Fe(II)/Fe(III)-containing aqueous phase scrubber coupled with an electrolyzer. The integrated pre-reformer/scrubber/electrolyzer unit operated successfully on high-S diesel fuel for more than 100 hours meeting the required desulfurization target of >95% sulfur removal.

1 Introduction

A major challenge facing future Hydrogen Economy is the issue of hydrogen fuel delivery to end-users. Due to an enormous cost of building a new hydrogen delivery infrastructure, in the interim, it might be economically feasible to deliver high-energy density hydrocarbon fuels (e.g., diesel fuel) and reform them to H_2 on-site. The advantages are three fold: (1) an existing fuel delivery infrastructure can be utilized, (2) more energy can be delivered per trip when the tanker is filled with diesel instead of liquid or compressed hydrogen, and (3) the fuel dispensing station would be able to service both internal combustion and fuel cell powered vehicles at the same time.

Reforming high-sulfur (high-S) hydrocarbon fuels is particularly challenging due to rapid deactivation of conventional reforming catalysts by sulfurous compounds, and it has been a focus of intensive worldwide R&D efforts with a particular emphasis on vehicular (on-board) applications (e.g., [1-4]). Moreover, if sulfurous compounds (mostly, H_2S) are not removed from the reformate gas, they could poison the catalysts in the anode compartment of FC substantially decreasing its performance or permanently damaging it [5]. Florida Solar Energy Center (FSEC), in collaboration with the Chevron Technology Ventures (CTV), has developed a new on-demand hydrogen production technology for distributed applications. The objective of this work is to catalytically convert high-S liquid hydrocarbon fuels to an essentially sulfur-free gaseous feedstock for steam reformation, while consuming only a fraction of hydrogen product. The experimental results on the development and performance testing of the catalytic pre-reformer and desulfurization systems are presented in this paper.

2 Experimental

Hexadecane (98% purity) was obtained from Fisher and used without further purification. Thiophene (99%) was obtained from Alpha Aesar and used as received. Commercial diesel fuel was purchased from a local Chevron gas station. Since commercial diesel fuel contains low levels of sulfur (approximately 5.5 ppmw), the fuel was supplemented with thiophene (C_4H_8S) to elevate the sulfur content to 3180-5240 ppmw level. This thiophene-spiked diesel was then used in all experiments as a surrogate high-S fuel. The same was carried out with hexadecane. Alumina-supported Ni-Mo hydroprocessing catalyst in the form of 1 mm by 5 mm extruded pellets was provided by Haldor Topsoe. The composition of the Ni-Mo catalyst was (%w/w): NiO (2-5), MoO_3 (12-18), Al_2O_3 (68-80), $AlPO_4$ (5-11). Analysis of the products of pre-reforming was performed by means of gas chromatography (GC) as follows: Shimadzu GC-14B (flame ionization detector, helium carrier gas, capillary column). Analysis of sulfurous compounds (H_2S, thiophene, methyl-mercaptan) was conducted using Perkin Elmer GC (flame photometric detector, capillary column).

3 Results and Discussion

Description of the concept. Fig. 1 depicts a simplified block-diagram of the process for conversion of a high-S fuel to hydrogen. A high-S liquid hydrocarbon fuel (e.g., diesel fuel) is first catalytically processed in a pre-reformer (or hydro-reformer) to shorter chain hydrocarbons (C_1-C_3) in the presence of hydrogen (this process is similar to a hydrocracking process, therefore, hereafter we will also refer to this process “hydro-reforming”). In the pre-reformer, most sulfurous species present in the fuel are catalytically converted to hydrogen sulfide (H_2S).

Desulfurization of the pre-reformate gas is carried out in a special regenerative redox system, which includes a Fe-based scrubber coupled with an electrolyzer. Ferrous/ferric (Fe^{2+}/Fe^{3+}) redox couple is used for scrubbing and splitting H_2S to sulfur and hydrogen:

$$2Fe^{3+}_{(aq)} + H_2S_{(g)} \rightarrow 2Fe^{2+}_{(aq)} + S_{(s)} + 2H^{+}_{(aq)} \quad (1)$$

$$2Fe^{2+}_{(aq)} + 2H^{+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + H_{2(g)} \qquad \text{(electrolysis)} \quad (2)$$

$$\text{Overall: } H_2S_{(g)} \rightarrow H_{2(g)} + S_{(s)} \quad (3)$$

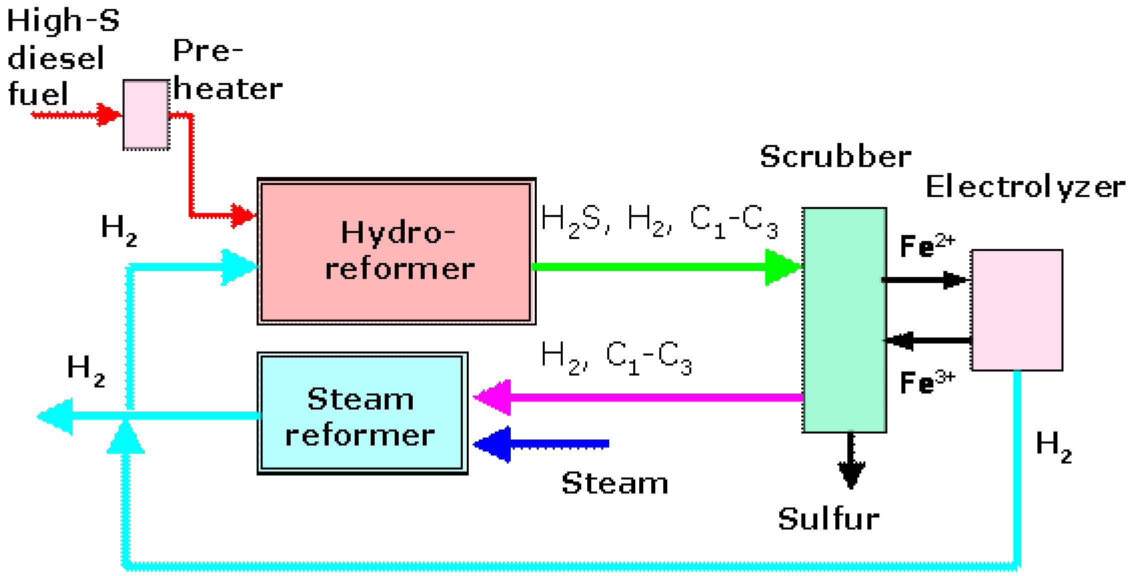

Figure 1: Block diagram of the proposed process for for conversion of high-S fuel to hydrogen.

Desulfurized pre-reformate gas is fed to the steam reformer, where it is mixed with steam and processed over Ni-catalyst to syngas. The syngas is further conditioned (or shifted) and purified (via pressure swing adsorption process) to high-purity H_2 according to a conventional steam methane reforming (SMR) process. A fraction of the output hydrogen product is recycled to the pre-reformer and used to conduct hydro-reforming of the high-S feedstock. It was estimated that the fraction of hydrogen product needed in the pre-reforming stage is in the range of 13-16%.

Hydro-reforming of high-S hexadecane and diesel fuel. Gas chromatogram of the effluent gas from high-sulfur (5240 ppm) hexadecane and diesel hydro-reforming over mixed Ni-Mo/Al_2O_3 - zeolite catalyst (1:2 ratio) at T=450 ^oC and P=14 atm is depicted in Figure 2, A and B, respectively.

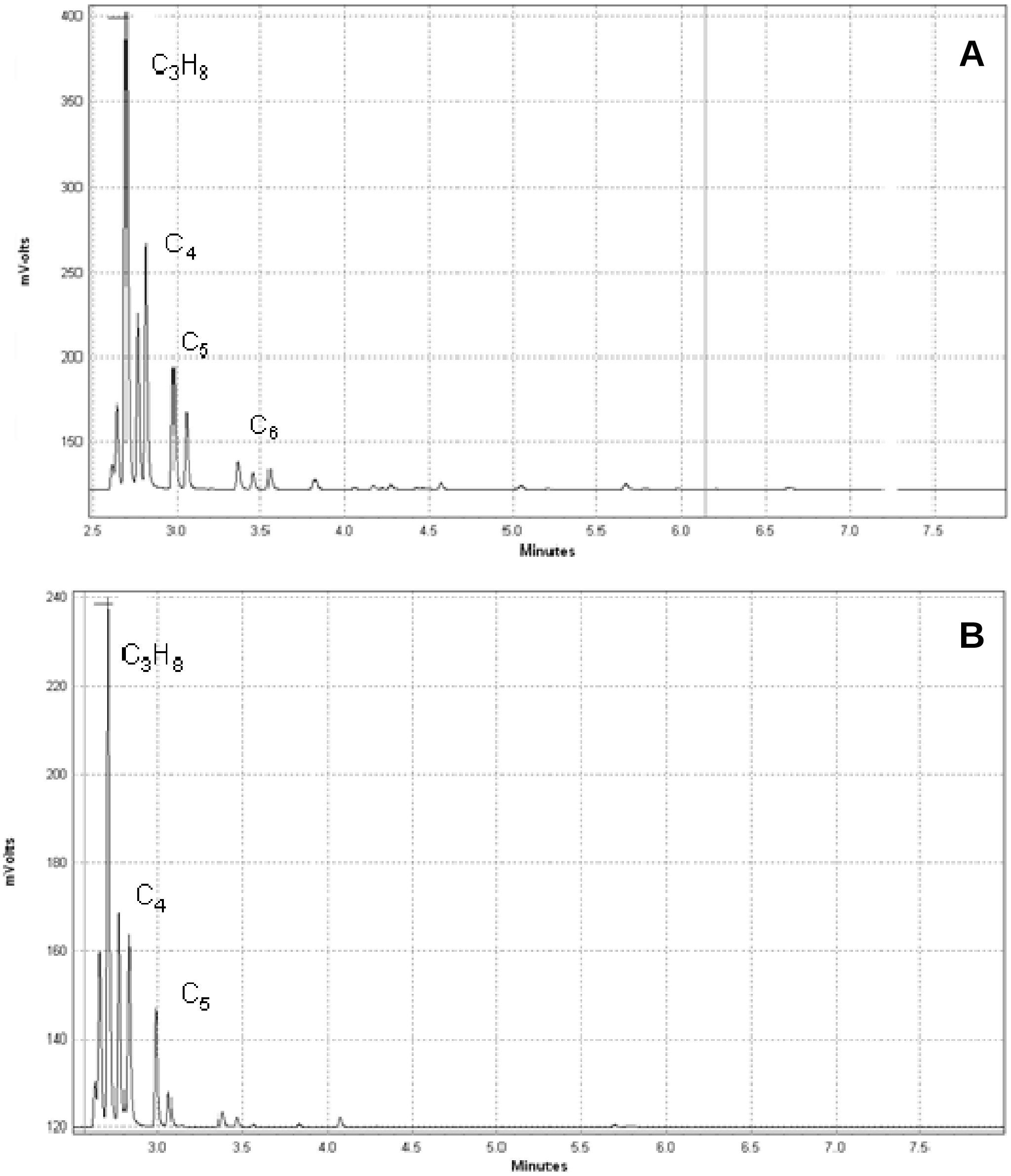

Figure 2: Gas chromotograms of the effluent gas from high-S hexadecane (A) and diesel fuel (B) hydro-reforming over mixed Ni-Mo/Al_2O_3 - zeolite catalyst (1:2 ratio). Thiophene content of the fuels: 5240 ppm. T=450 °C, P=14 atm.

The results revealed that the composition of the pre-reformate gas obtained from hexadecane and diesel fule are quite similar. After about 50 h a steady state regime is reached characterized by production of the pre-reformate gas consisting of C_1-C_5 hydrocarbons with propane being a predominant component of the product gas. There are practically no hydrocarbons higher than C_5 in the effluent gases. Overall, the experiment was run for about 100 h, with the average conversion of hexadecane and diesel fuel to gaseous products of 98% for and 95-97%, respectively.

Desulfurization of pre-reformate gas. Figure 3 provides a schematic diagram of the desulfurization sub-unit for the continuous removal of hydrogen sulfide from the pre-reformate gas and its splitting to hydrogen and sulfur.

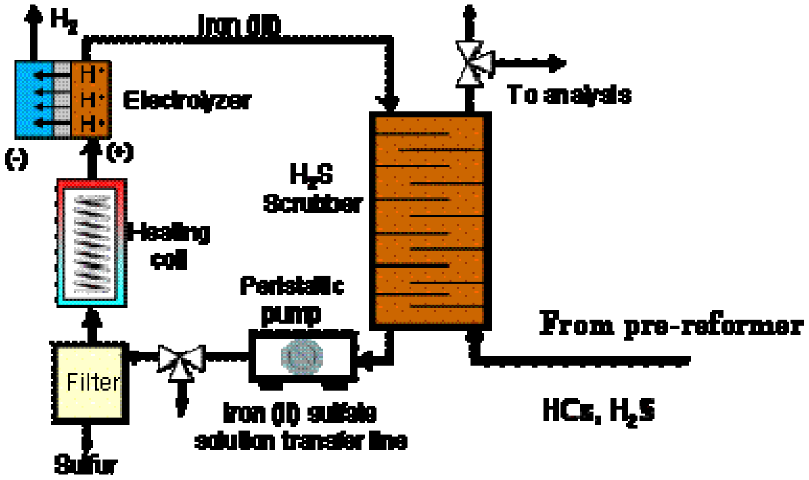

Figure 3: Schematic diagram of the desulfurization sub-unit for the continuous removal of hydrogen sulfide from the pre-reformate gas.

A gaseous mixture from the pre-reformer is directed to a scrubbing unit, which includes an absorption column filled with aqueous ferric sulfate solution, $Fe_2(SO_4)_{3(aq)}$ (total volume of solution 2.3 L). H_2S when dissolved in the aqueous solution is oxidized by ferric ion (Fe^{3+}) to elemental sulfur, and simultaneously ferric sulfate is reduced into ferrous sulfate, $FeSO_4$ (see Equation 1). Elemental sulfur is removed from the system by a filter, and the remaining ferrous sulfate solution is fed to an electrolyzer, where ferrous sulfate is oxidized back to ferric sulfate, and protons are reduced to hydrogen gas at the cathode. The regenerated ferric sulfate solution is then fed back to the absorption column of the scrubber for scrubbing hydrogen sulfide, forming a closed cycle with the net reaction being hydrogen sulfide decomposition to elemental sulfur and hydrogen gas. Electrolysis of acidic $FeSO_4$ aqueous solutions was carried out using a modified proton exchange membrane (PEM) electrolyzer. An electrolyzer potential of 0.80 to 1.03 volts was necessary for the electrochemical process to regenerate the scrubber solution at a rate sufficient to match the H_2S flow rate into the scrubber. The electrolytic system can be operated at the range of temperatures from ambient to 90 °C. In our experiments, desulfurization of the pre-reformate gas occurred optimally at the following process conditions: iron sulfate (total) concentration of 0.1 M, pH of 1.7-1.8, and electrolyte temperature of 50 °C.

In the combined diesel pre-reforming/desulfurization experiment, diesel fuel with 3180 ppmw of thiophene produced a pre-reformate gas with H_2S content of 185 ppmv, which was fed to the desulfurization unit. On average, about 3 ppmv of H_2S was detected exiting the ferric sulfate scrubber during the experiment. Based on the collected data from high-S diesel and hexadecane pre-reforming-desulfurization experiments, the fuel desulfurization yields were determined to be higher than 95%.

4 Conclusions

A novel process for converting high-sulfur diesel to hydrogen that employs a catalytic pre-reformer coupled with an efficient sulfur-scrubbing unit suitable for distributed hydrogen production applications has been developed. The integrated pre-reformer and sulfur-scrubbing unit operated successfully for 100 hours, while achieving the desulfurization efficiencies of higher than 95%.

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