FUEL PROCESSING FOR PEM FUEL CELLS: IN-LINE ADSORBENT FILTERS FOR MEA PROTECTION

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Abstract

The present work deals with hydrogen generation from JP8 reformation and clean-up of the reformate to produce PEMFC quality hydrogen. The fuel processor has reformer, post-former, water gas shift reactors, H_2S removal, preferential CO oxidation, and CO_2 removal stages.

The processor also incorporates a final adsorbent fuel filter that can efficiently remove ppm level impurities that may poison the fuel cell catalyst. High contacting efficiency microfibrous media are used to entrap various reactive materials including heterogeneous catalysts and sorbents. These media are then layered so as to permit multiple staged chemical reactions to be achieved within the space of a few millimeters of thickness. As an example of this generic approach, microfibrous entrapped media containing sorbents to remove H_2S , NH_3 , CO, and CO_2 were sequentially layered. The enabling attribute is the high contacting efficiency afforded by microfibrous entrapment, and the thin layer design of these materials that permit facile and effective layering, packaging and sealing.

1. Introduction

Fuel cells offer a unique way to convert chemical energy of a fuel directly into electrical energy and are renewable resource. Unlike most other fuel cell types, Polymer Electrolyte Membrane Fuel Cells (PEMFC) are suitable for small, low power applications. These can be scaled down to small size without sacrificing performance and are suitable for applications ranging from microwatts to hundreds of kilowatts. Other advantages are low noise signature, pure water as by-product and the ability to refuel rather than recharge or discard. PEMFC are preferred in many applications like mobile power generation units, man-portable power generators and on-board power generation for automotive propulsion.

The bandwidth requirement for new electronic appliances demands more energy density than the existing batteries can offer (1). Due to the high cost of primary batteries and the large weight of rechargeable batteries, fuel cell technology is being developed to provide a power source for the individual soldier, sensors, communication equipment and other various applications in the United States army (2). PEMFC require hydrogen as a fuel to generate electricity. Hydrocarbon reforming is widely regarded as the best means of hydrogen generation for PEM Fuel Cells.

Various fuels such as methane, methanol, ethanol, gasoline, diesel and JP8 are being considered for fuel cell applications. Diesel and JP8 have salient advantages over other fuels mainly high energy density, safe handling and logistics (3).

Present work deals with development of a bread-board fuel processor for JP8 fuel. The fuel processor has its main components to be reformer, post-reformer, H₂S removal, water gas shift, carbon dioxide removal, preferential oxidation and fuel filter units. Most of these units contain microfibrous entrapped catalysts and sorbents. Microfibrous materials is a new class of proprietary materials that offer advantages such as high contacting efficiency, very low pressure drop and efficient thermal management over conventional packed bed approach thereby making the whole processor very compact (4).

2. Experimental

2.1. Experimental Set-up:

Figure 1 shows the schematic process flow diagram of the fuel processor. First reactor is steam reformer for JP8 fuel the outlet of which flows into post-former followed by H_2S removal reactor through intermediate gas storage tank by means of a compressor. After H_2S removal the reformate flows into high temperature water gas shift and low temperature water gas shift reactors followed by preferential oxidation of CO reactor. The reformate then flow through carbon dioxide removal absorption tower that has continuous circulation of alkaline absorbent. The reformate finally flows through fuel filter unit to remove trace quantities of all gases other than hydrogen before entering fuel cell.

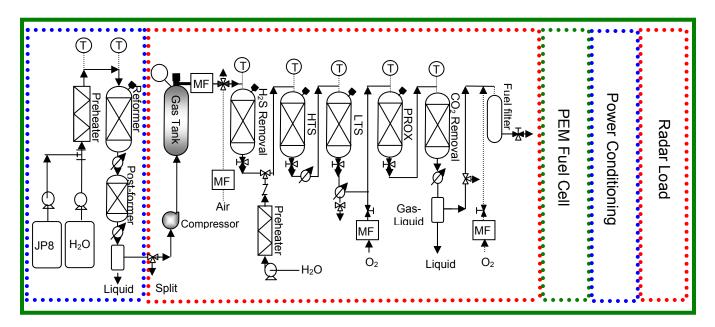


Figure 1: Process Flow Diagram of Fuel Processor unit

2.2. Catalysts and Sorbents

Catalysts for reformer, post-former (precious metal) and water gas shift reaction (Fe-Cr and Cu-Zn) were obtained commercially from Sud-chemie Inc. Sorbent used for H_2S removal was a microfibrous entrapped ZnO sorbent. The liquid sorbent used for CO_2 removal was alkaline solution. The solid sorbent in the fuel filter for CO_2 removal was microfibrous entrapped lime based sorbent. The PROX catalyst was a microfibrous entrapped metal oxide promoted precious metal catalyst (5). The fuel filter had microfibrous entrapped sorbents for CO, CO_2 , NH_3 and H_2S .

2.3. Preparation of Catalysts and Sorbents

The microfibrous entrapped catalysts and sorbents are prepared by wet-lay process followed by sintering at high temperature in presence of hydrogen. D. Cahela and B. Tatarchuk (6) discuss the process in details. This gives the support material for the catalyst /sorbent. The final catalysts/ sorbents were prepared using conventional incipient wetness method followed by calcination in air. Figures 2a and 2b show SEM images of microfibrous entrapped PROX catalyst and H_2S adsorbent.

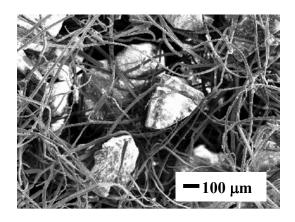


Figure 2a: Microfibrous Entrapped PROX catalyst

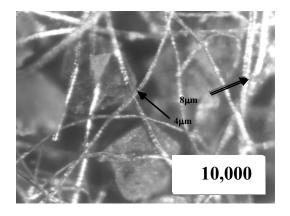


Figure 2b: Microfibrous Entrapped H₂S sorbent

3. Results and Discussion

3.1. Reformer and Post-former

The steam reforming of JP8 at 900°C and atmospheric pressure over the commercial catalyst gives reformate with composition 60 - 65% H₂, 18-22% CO₂, 8-12% CO, 5 - 12% C₁-C₃ and around 60 ppm H₂S. Post-former reduces the light hydrocarbons to below detection limits. The reforming and post-forming catalyst is sulfur tolerant hence the sulfur removal phase was employed after these stages. Figure 3 shows the sulfur tolerance tests for the catalyst. As seen in figure 3, there is no change in the H₂ concentration in reformate as a function of sulfur content over a period of time. Gasoline was used as a model fuel with Dibenzothiophene as sulfur doping agent for the fuel.

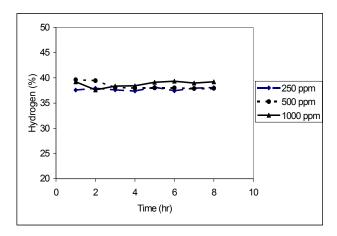


Figure 3: Sulfur Tolerance Tests of the Catalyst

3.2. Hydrogen Sulfide Removal

This section of the processor implements polishing sorbent concept. A composite bed consisting of the packed bed of 1-2mm Sud-Chemie ZnO extrudates followed by the above mentioned microfibrous entrapped ZnO/SiO₂ sorbent particulates has been demonstrated for H₂S removal from H₂ fuel stream. Figure 4 shows the breakthrough curves for 2vol% H₂S challenge in H₂ in single and composite beds at 400°C and a face velocity of 1.2cm/s (30mL(STP)/min dry gas flow rate). Two single beds, 7mm(dia.)×3mm(thick) microfibrous entrapped ZnO/SiO₂ (A) and 7mm(dia.)×7mm(high) packed bed of 1-2mm Sud-Chemie ZnO sorbent extrudates (B), provided breakthrough times (@1ppmv H₂S detection limit) of 5min and 28min, respectively. The breakthrough curve with small particulates (ZnO/SiO₂) alone is very sharp. But the breakthrough curve in packed bed with large particulates (B) is very sigmoidal. When the polishing sorbent was placed behind the packed bed (B+A), the outlet from the packed bed B, where the H₂S concentrations increased very slowly with the time on stream after the breakthrough point in bed B, was encountered immediately with the high

contacting efficiency polishing sorbent A. As a result, a very large extension in gas life was obtained due to high contacting efficiency, compared to that either the polishing sorbent or the packed bed alone will do. For this demonstration, 60 ppm H_2S is reduced to less than 0.6 ppm at the outlet.

3.3. Water Gas Shift Reaction

High temperature and low temperature water gas shift reactions operate respectively at 350-400 and 180-200°C and atmospheric pressure. The inlet CO concentration of 10-15% is reduced to around 0.75-1% in presence of microfibrous entrapped catalysts.

3.4. PROX Stage

The PROX reactor operates at $180-200^{\circ}$ C and atmospheric pressure. The carbon monoxide content is reduced to less than 10 ppm at the exit of the reactor. Figure 5 compares the performance of microfibrous entrapped catalyst with pellets of the size 1.5 - 2.5 mm.

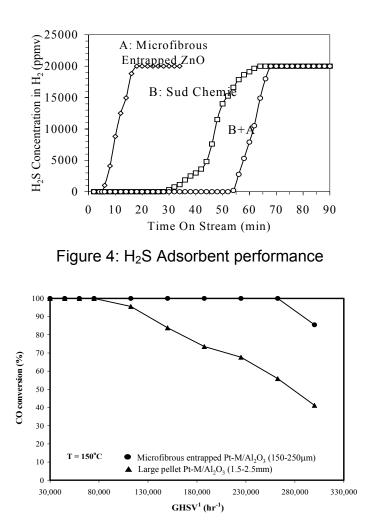


Figure 5: Comparison of microfibrous entrapped PROX catalyst with pellets

3.5. CO₂ Removal Section

The absorption in alkaline solution reduces the CO_2 content from 35% to about 200 ppm at the outlet. The absorption unit is operated in a continuous circulating fashion.

3.6. Fuel Filter Section

All the ppm level gases such as H_2S CO, CO_2 , NH_3 and organic vapors are removed by means of various microfibrous entrapped sorbents. This unit operates at room temperature and atmospheric pressure.

3.7. Fuel Cell and Radar Operation

The hydrogen generated from the fuel processor was fed to a 200 W PEM fuel cell (Ballard Nexa®), which operated a RPT radar testbed.

4. Conclusions

(1) Logistical fuel to radar power is possible by means of a fuel processor followed by PEM fuel cell.

(2) Traditional processes are applicable for reformate clean-up processing technologies can be reduced in weight and volume by means of new materials such as microfibrous entrapped sorbents and catalysts and regenerable continuous – batch operation.

(3) With additional process integration, mainly energy, the fuel processor can become an attractive means of hydrogen generation.

5. Acknowledgments

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6. References

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