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Simulation of a fuel reforming system based on catalytic partial oxidation

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ABSTRACT

Catalytic partial oxidation (CPO) has potential for producing hydrogen that can be fed to a fuel cell for portable power generation. In order to be used for this purpose, catalytic partial oxidation must be combined with other processes, such as water-gas shift and preferential oxidation, to produce hydrogen with minimal carbon monoxide. This paper evaluates the use of catalytic partial oxidation in an integrated system for conversion of a military logistic fuel, JP-8, to high-purity hydrogen. A fuel processing system using CPO as the first processing step is simulated to understand the trade-offs involved in using CPO. The effects of water flow rate, CPO reactor temperature, carbon to oxygen ratio in the CPO reactor, temperature of preferential oxidation, oxygen to carbon ratio in the preferential oxidation reactor, and temperature for the water-gas shift reaction are evaluated. The possibility of recycling water from the fuel cell for use in fuel processing is evaluated. Finally, heat integration options are explored. A process efficiency, defined as the ratio of the lower heating value of hydrogen to that of JP-8, of around 53% is possible with a carbon to oxygen ratio of 0.7. Higher efficiencies are possible (up to 71%) when higher C/O ratios are used, provided that olefin production can be minimized in the CPO reactor.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) offer significant potential as portable power sources. In particular, the United States military is considering them as replacements for batteries, since battery power density and lifetime are often not ideal. PEMFCs operate by reacting hydrogen and oxygen to generate electricity. However, hydrogen is difficult to store and transport, so PEMFCs are likely to be powered by liquid fuels, where the liquid fuels are first converted to hydrogen before being fed to the fuel cell.

Converting liquid fuels to high-purity hydrogen is a significant technical challenge, as discussed by a number of authors [1–6]. Sulfur must first be removed from the fuel, since the noble metal catalysts used in the conversion process are susceptible to deactivation by sulfur. Next, the fuel must be reformed to make hydrogen. This reforming step can be achieved by steam reforming, autothermal reforming, or catalytic partial oxidation [7]. The reformed stream contains a high concentration of carbon monoxide, which must be removed before feeding to the fuel cell. A first step to accomplish this is the water-gas shift reaction, which reacts carbon monoxide and water to make carbon dioxide and hydrogen. The carbon monoxide concentration is still too high following this reaction, so selective oxidation is next used to oxidize carbon monoxide to carbon dioxide.

Catalytic partial oxidation (CPO) at short contact times has been proposed as an efficient means for producing hydrogen from alcohol and hydrocarbons [8–12]. In this process, fuel and oxygen are fed to a noble metal catalyst at high flow rates. The catalyst is initially heated to ignite the reaction; reaction then proceeds autothermally, where the heat from surface oxidation reactions allows further reaction to occur. Running CPO in this fashion offers several advantages. A high production rate of hydrogen is achieved from a small catalyst bed. In addition, hydrogen can be produced almost on demand. Finally, there are no additional heating requirements.

While CPO appears attractive for portable power generation applications, there may be trade-offs for using it. For example, if no water is added to the feed stream of CPO, more carbon monoxide is formed compared to other reforming processes. This will require more intense downstream processing to clean the hydrogen for use by the PEMFC. This paper evaluates the use of CPO in an integrated system for generation of high-purity hydrogen for a PEMFC from a military logistic fuel, JP-8. A fuel processing system using CPO as the first processing step is simulated to understand the trade-offs involved in using CPO. The effects of water flow rate, CPO reactor temperature, carbon to oxygen ratio in the CPO reactor, temperature of preferential oxidation, oxygen to carbon ratio in the preferential oxidation reactor, and temperature for the water-gas shift reaction

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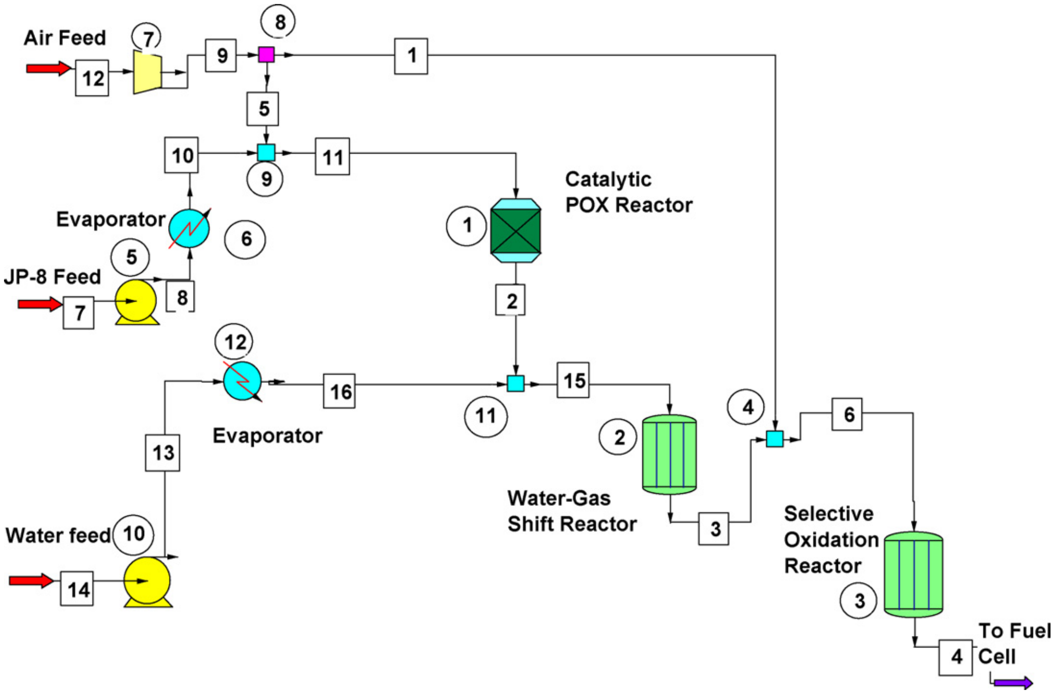

Fig. 1. Flowsheet for JP-8 reforming process.

are evaluated. The possibility of recycling water from the fuel cell for use in fuel processing was evaluated. Finally, heat integration options were explored.

2. Simulation methods

A number of previous studies have simulated fuel processing systems to convert alcohols and hydrocarbons to hydrogen to power a fuel cell [13–16]. Of these simulations, only the work by Ahmed and Krumpelt looks at the potential of CPO for fuel reforming [14]. That work uses stoichiometry and thermodynamics to compare different fuel processing methods (autothermal reforming, steam reforming and catalytic partial oxidation); it does not model the individual fuel processing steps in detail nor does it look at the interplay between those steps. This study focuses on CPO, and in particular how the choice to use CPO as the first step in fuel reforming affects the downstream processing steps. The chemical process simulator, ChemCad, was used to model fuel processing of JP-8 to fuel cell-grade hydrogen.

2.1. Process flowsheet and design basis

Fig. 1 shows the base case process flowsheet for the fuel processing system modeled in this work. In this process, the fuel (JP-8) is vaporized and mixed with air. This combined feed is fed to the catalytic partial oxidation reactor, where the fuel is converted to a stream primarily comprised of syngas (CO and H_2) with some CO_2 and H_2O. The products of the catalytic partial oxidation reactor are mixed with steam, cooled, and fed to a reactor in which the water-gas shift reaction is run. This reactor removes CO from the process stream while producing additional H_2. The third reactor oxidizes the remaining CO to CO_2 to reach a CO concentration of 10 ppm, which would be suitable for a PEMFC.

To simulate JP-8, a mixture of hydrocarbons was assumed. The JP-8 surrogate mixture reported by Sarofim et al. was used [17]. This mixture is composed, by volume, of 10% isooctane, 20% methylcyclohexane, 15% *m*-xylene, 30% *n*-dodecane, 5% tetralin, and 20% *n*-tetradecane, and was developed to closely match the distillation curve and sooting propensity of JP-8. This mixture has a molecular weight of 133.048, and an H/C ratio of 1.91, and can be approximated as $C_{9.57}H_{18.27}$. JP-8 was assumed to be sulfur-free, since sulfur would poison the catalytic partial oxidation reactor. An upstream sulfur-removal process would be needed to achieve the simulated feed, but this process was not modeled in this work.

A primary design variable was the carbon to oxygen (C/O) ratio fed to the CPO reactor. This is defined as the ratio of carbon atoms to oxygen atoms in the feed.

The process was designed to supply a PEM fuel cell with sufficient hydrogen so that it can produce 1 kW of energy. For this power requirement, a H_2 flow rate of ~12–13 standard liters per minute (SLPM) to the fuel cell was required and was the basis for design. This corresponded to a hydrogen molar flow rate of $\sim 0.033\ \mathrm{kmol\,h^{-1}}$. The primary design constraint was to produce this flow rate of H_2 with less than 10 ppm CO. The amount of water in the feed to the PEMFC was not a consideration. To achieve the specified H_2 flow rate and purity, the size of the reactors and the water flow rate were changed.

2.2. Hydrogen yield and process efficiency

The hydrogen yield was calculated from the ratio of hydrogen produced by the process to the total amount of hydrogen fed to the process, both in JP-8 and as water. The equation used is

$$Y_{H_2} = \frac{F_{H_2}}{F_{H_2O_o} + F_{JP\text{-}8_o}} \qquad (1)$$

where Y_{H_2} is the yield of H_2, F_{H_2} is the molar flow rate of H_2 at the exit of the process, $F_{H_2O_o}$ is the molar flow rate of H_2O into the process, and $F_{JP\text{-}8_o}$ is the molar flow rate of H_2 contained in JP-8 that is fed the process.

The fuel processor efficiency was calculated to compare different process conditions. The efficiency was calculated from the ratio of the lower heating value of the hydrogen produced by the process to the lower heating value of the JP-8 fuel fed to the system.