

UNMIXED REFORMING: AN ADVANCED STEAM REFORMING PROCESS

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ABSTRACT

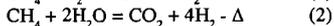
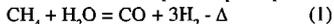
Unmixed Reforming is a novel steam reforming process to convert fossil fuels to hydrogen. It has been developed mainly for small scale generation of hydrogen. The target application is electric power generation in buildings and automobiles using fuel cells. The Unmixed Reforming process has been demonstrated in a packed bed reactor using diesel fuel and natural gas as the feedstock. The average purity of hydrogen in the product stream was around 70%, with the balance being primarily methane, carbon monoxide and carbon dioxide. In Unmixed Reforming, the catalyst is not deactivated by coke or sulfur. The coke is burnt off during a regeneration step. A significant portion of the sulfur is rejected as sulfur dioxide. The process has been simulated by performing chemical equilibrium calculations in different zones of the catalyst bed.

INTRODUCTION

There has been considerable increase in interest in fuel cells due to their higher efficiencies and environmental friendliness. Low temperature fuel cells are being considered for electric power generation in commercial and residential buildings and automobile applications. The low temperature fuel cells require a continuous supply of high-purity hydrogen.

Steam reforming is the most economical means of converting fossil fuels to hydrogen at large scales. Natural gas is principally used as the fossil fuel.

Using methane as an example, the principal reactions in the steam reformer are as follows:



The reforming reactions are highly endothermic and hence require that additional fuel be combusted to supply heat. Both the reforming reactions are equilibrium limited. The methane conversion is maximized by carrying out the reforming reactions at temperatures between 750 to 850°C. In the conventional steam reforming processor long tubes packed with catalyst are used to heat the reactants up to the required temperature. The tubes are contained in a gas-fired furnace.

The limitations of conventional steam reforming at small scales are two-fold—cost of reformer and efficiency (Adris et al., 1996). First consider the cost. The metal tubes are heated in a fired furnace. The metal wall of the tubes reaches temperatures of 900°C and the flue-gas reaches temperatures in excess of 1000°C. The tubes are made of high alloy nickel-chromium steel. The tubes are expensive and account for a large portion of the reformer cost. Second, the efficiency of reformer decreases at small scales due to heat transfer limitations and parasitic heat losses. The transfer of heat from the combustion products to the reactants is an inherently inefficient process, and in any practical system, especially for smaller scales, it is not possible to transfer all of the energy released by combustion into the process being heated.

If small scale hydrogen production is to be practical, the issues of cost and efficiency should be addressed. The Unmixed Reforming (UMR) process was developed to address these issues. UMR, like conventional reforming, can be used to generate hydrogen from a variety of liquid and gaseous fuels such as natural gas, landfill gas, propane, methanol, gasoline, diesel fuel, JP-8, etc.

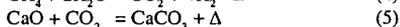
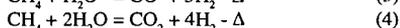
PROCESS DESCRIPTION

UMR relies on an EER-patented process (Lyon, 1996) known as Unmixed Combustion (UMC) to heat the packed bed. In the UMC process the combustion is carried out by alternately cycling air and fuel over a metal, in this case nickel, placed in a packed bed reactor. The metal is dispersed on a high surface area catalyst support. When air is passing over the bed, the nickel oxidizes to form nickel oxide in an highly exothermic reaction. Most of the heat is deposited on the ceramic matrix since there are no gaseous products for this oxidation reaction. The subsequent and separate introduction of a fuel will release additional energy while reducing the nickel oxide back to metallic nickel. The heat thus generated in-situ is then available for the endothermic steam reforming reactions. Nickel was chosen as the metal for UMC, since it is the most common catalyst for the steam reforming reactions. The UMR process was improved by introducing a carbon dioxide acceptor (e.g. calcium oxide) into the catalyst bed.

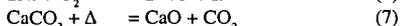
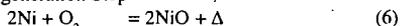
The three steps of the UMR process are shown in Figure 1. The figure portrays the progress of the reaction starting at the left of the figure and moving toward the right. The three steps are referred to as the reforming step, the air regeneration step and the fuel regeneration step. During the reforming step, fuel and steam react over the catalyst to produce hydrogen through conventional steam reforming chemistry. The calcium oxide is converted to calcium carbonate as it captures some of the carbon dioxide formed during the reforming reactions. This shifts the reforming reactions to higher conversions, thus improving the purity of the hydrogen product stream. During the next process step, air is passed through the packed-bed reactor to oxidize the catalyst. The heat released by the oxidation reaction raises the temperature of the bed. This decomposes the calcium carbonate to produce calcium oxide, while releasing carbon dioxide into a vent gas stream. In the final process step, fuel is introduced to the packed bed, reducing the oxide form of the catalyst back to its elemental form and further increasing the temperature.

The primary reactions that are occurring in the reactor are as follows:

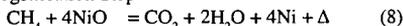
Reforming Step



Air Regeneration Step



Fuel Regeneration Step



The carbon dioxide acceptor material, calcium oxide, serves three functions in the process. First it provides additional "thermal mass" to transfer sensible heat from the regeneration step to the reforming step of the process. Second, the adsorption of carbon dioxide by the calcium oxide to produce calcium carbonate is an exothermic chemical reaction that also delivers energy to the reforming reactions in the form of chemical potential energy. During the air regeneration step, heat released by oxidation of nickel is largely absorbed by the process of decomposing the calcium carbonate to calcium oxide, and this substantially moderates the temperature rise of the packed bed. Much of the enthalpy of nickel oxidation is thereby stored as chemical potential energy in the calcium oxide. That chemical potential energy is subsequently released during the reforming process when calcium oxide is converted back to calcium carbonate. This method of using the interconversion between calcium oxide and calcium carbonate to supply heat to the reforming process, is a far more efficient means of transferring energy to the reforming process even than relying solely on the sensible heat stored in the ceramic catalyst support matrix. Furthermore, reducing the temperature rise during regeneration reduces parasitic heat losses from the reactor and promotes process efficiency. Finally, the presence of the solid-phase acceptor material improves the reaction equilibrium for reactions (1) and (2). By removing carbon dioxide from the products of the steam reforming process, equilibrium is shifted toward greater hydrogen production, reduced carbon monoxide and carbon dioxide concentrations, and increased fuel conversion.

Catalyst poisoning by carbon formation during reforming is not a problem, since any carbon formed is burnt off during the air regeneration step. UMR is also tolerant of fuel sulfur, which makes it a more robust process than conventional steam reforming. In conventional steam reforming sulfur must be removed from the feedstock fuel before it sees the catalyst, otherwise the catalyst is deactivated by the formation of nickel sulfide. In UMR, on the other hand, sulfur reacts with both nickel and calcium oxide during the reforming step, but is rejected as sulfur dioxide during the air regeneration step.

MATERIALS AND METHODS

The UMR process was studied in pilot scale and bench scale experimental systems. A simple schematic of the pilot scale system that was used to perform the experiments is shown in Figure 2. The pilot scale system consists of a dual packed bed reactor system. Switching valves are used to deliver steam and fuel, air and finally fuel to the packed bed for the three steps of the UMR process. The reactors are packed with a blended mixture of the catalyst and the carbon dioxide sorbent. The catalyst is Nickel supported on calcium aluminate and the carbon dioxide sorbent is dolomite. The particle sizes for the catalyst and dolomite are around 1 to 7 mm. A back pressure regulator is used to set the pressure in the reactor which in the reforming step is to 2-7 bar. The pressure during the regeneration step is around 1-2 bar. The reformat (reformer product) stream was analyzed using online infrared gas analyzers. The readings from the online analyzers were verified using gas chro-

matography with a thermal conductivity detector. The system was designed to produce 100 standard liters per minute of hydrogen, which is sufficient to generate 10kW of electricity using a Proton Exchange Membrane fuel cell. The bench scale system consisted of a single packed bed reactor.

The UMR process was simulated by modeling the packed bed reactor as a series of equilibrium reactors. The packed bed was divided into five zones. The reforming, air regeneration and fuel regeneration steps were subdivided into twenty, fifteen and five sub-steps respectively. The feed gas stream during each sub-step enters the first zone and reaches thermodynamic chemical equilibrium with the solid phase in the first zone. The gas leaving the first zone enters the second zone and reaches equilibrium with the solid phase in the second zone, and so forth. The equilibrium calculations were performed using a NASA Chemical equilibrium code (McBride and Gordon, 1996). The steam to fuel molar ratio during the reforming step was set to be three. The length of the time steps for the reforming, air regeneration and fuel regeneration steps were assumed to be 300, 225 and 75 seconds respectively. The model adjusts the fuel and steam flow rate during the reforming step to stabilize the maximum temperature during the UMR process to a preset value. A PID algorithm was used to adjust the fuel and steam flow rate. The flow rates for air and fuel during the regeneration steps were kept constant. The model was run for multiple cycles until steady state conditions were obtained.

RESULTS & DISCUSSION

Pilot plant experiments, using diesel fuel, have demonstrated product gas hydrogen concentrations typically averaging 70+ percent and as high as 85 percent under certain conditions, with the balance primarily CH_4 , CO and CO_2 . Figure 3 shows data collected over a one hour period of the pilot plant operation during which the average purity of hydrogen in the reformat stream was maintained at 70%. The reforming step was conducted for 300 seconds. The variation in the gas composition is a result of the cyclic UMR process. At the beginning of the reforming step the hydrogen concentration is low since the NiO in the bed is still being reduced to Ni by fuel. As the reforming step progresses the temperature of the packed bed decreases and as a result the methane concentration in the reformat stream increases and the carbon monoxide concentration decreases.

For low temperature fuel cells the concentration of CO needs to be reduced to 50 ppm, and hence a high H_2 to CO ratio is preferable in the reformat stream. The UMR process was able to generate a hydrogen product gas with an average H_2 to CO molar ratio in excess of 10. Competing technologies such as partial oxidation produce a reformat stream with H_2 to CO molar ratios ranging from less than 2 to about 3, while conventional steam reforming attains a ratio of about 5.

Bench scale experiments using diesel fuel have shown that for typical fuel sulfur concentrations there is no detectable sulfur in the product gases to at least the sub-ppm level. In the bench scale experiments, when sulfur was added to diesel fuel at a concentration of 2000 ppm by weight only 5 ppm H_2S was detected in the product gases. In pilot scale experiments using diesel fuel the sulfur concentration in the reformat stream was around 12 ppm.

Due to the manner in which fuel is oxidized in UMR, the byproduct exhaust gases contain no oxides of nitrogen, and the emissions of carbon monoxide are typically less than 10 ppm. Therefore, relative to conventional reforming, and when compared with most alternative hydrogen production processes, UMR is nearly pollution free.

The predicted UMR dry gas product composition using the theoretical model is shown in Figure 4, when methane is used as the fuel. The figure shows that the temperature of the gas leaving the bed decreases during the reforming step. The carbon monoxide concentration decreases as the temperature decreases. The model predicts that the methane concentration in the product gas is low (< 3%) and that the concentration of hydrogen in the product gas increases during the reforming step.

ACKNOWLEDGEMENTS

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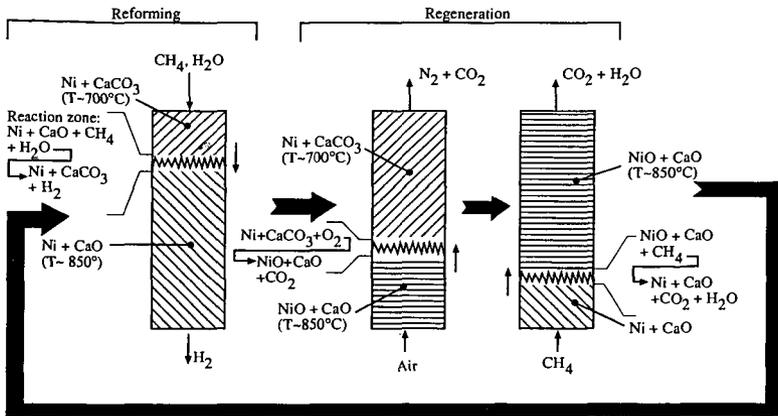


Figure 1. Illustration of the Unmixed Reforming process. The steam reforming of methane (left) produces hydrogen in an endothermic reaction which absorbs some of the sensible heat of the packed bed. Carbon dioxide, produced by the reforming reaction is absorbed by calcium oxide to form calcium carbonate. Once the calcium oxide is all consumed, the reactor must be both chemically and thermally regenerated using the unmixed combustion process as shown in the middle and right-side portions of the figure.

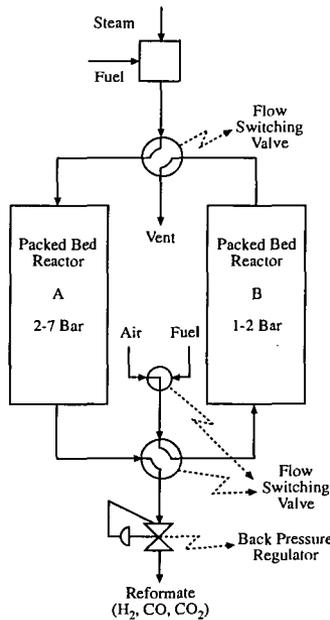


Figure 2. Schematic of experimental system.

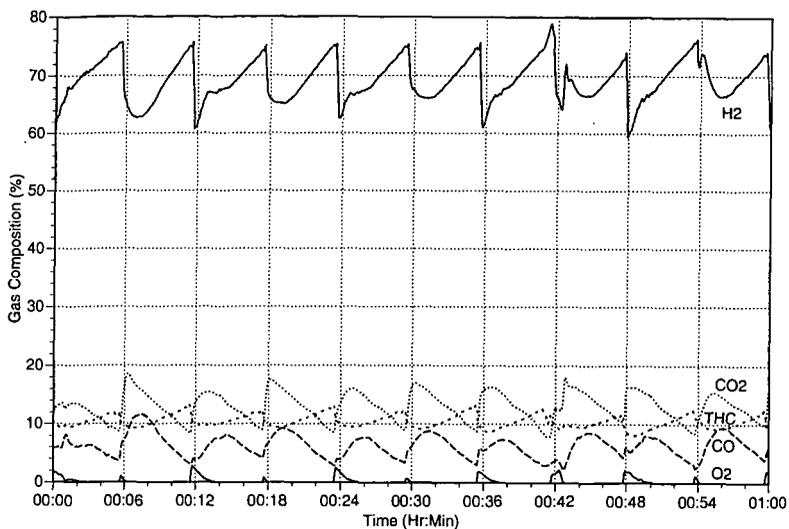


Figure 3. Experimental gas composition data from the Unmixed Reformer (THC - Total Hydro Carbon).

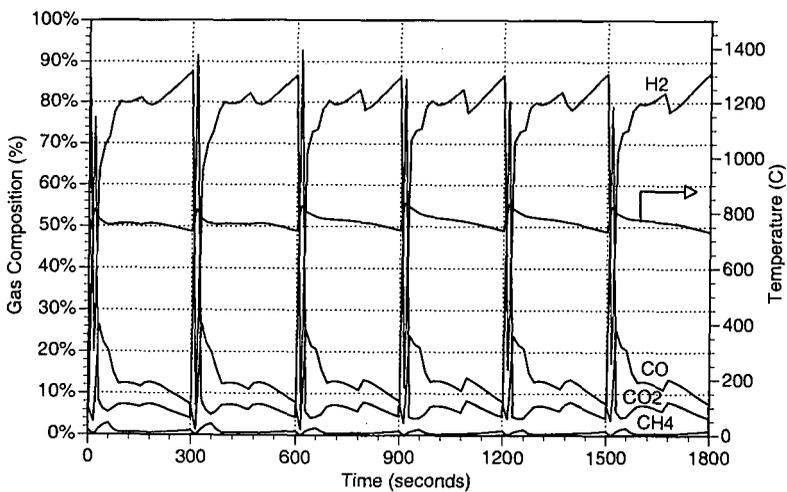


Figure 4. Predicted Unmixed Reformer gas composition using model.