

# PROCESS INTEGRATION OF ADSORPTION ENHANCED REFORMING FOR USE IN CONJUNCTION WITH FUEL CELL

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## Summary

Intelligent Energy has developed an adsorption enhanced reformer (AER) for the H<sub>2</sub> generation for use in conjunction with fuel cells in the small sizes (3 to 13 kW). The AER has an efficiency of around 80% on lower-heating value (LHV) basis and operates at a lower temperature (~ 500°C) than the steam methane reformer (SMR). In this work, a preliminary engineering design has been conducted to further improve the developed process. It is shown through engineering calculation that the process efficiency can be further improved by heat integration.

## Keywords

Hydrogen production, Adsorption enhanced reforming, Modeling, Process integration

## Introduction

As reducing the demand on fossil resources has been a public concern, hydrogen, being a potential carrier of clean energy, is now an important topic that may lead into a new era of energy research. Among various industrial techniques, steam reforming of hydrocarbons accounts for about 50% of the hydrogen produced over the world. In the United States, 95% of the hydrogen production is made through steam methane reforming (SMR)<sup>1</sup>. Recently, steam reforming of biomass derived hydrocarbons (e.g., bio-ethanol) has caught lots of attention because it is a potentially carbon neutral, sustainable and viable route for hydrogen production, and will play an important role in the U.S. transition to a hydrogen economy<sup>2</sup>.

Conventional hydrogen generation by SMR, employing a high temperature reformer (~ 800°C), a water gas shift reactor (~ 300°C) and multiple pressure swing adsorbers (PSAs), operates at an efficiency of around 65 to 67% based on lower heating value (LHV) of feed and product. This conventional SMR system is not very easy to scale down cost-effectively for supplying 35 to 150 slpm H<sub>2</sub> (to produce 3 to 13 kW electricity). Intelligent Energy has developed an adsorption enhanced reformer (AER) for the H<sub>2</sub> generation for use in conjunction with fuel cells in the

small sizes (3 to 13 kW)<sup>2</sup>. This AER has an efficiency of around 80% on the LHV basis and operates at a lower temperature (~ 500°C) than the SMR. The AER employs a carbon dioxide capturing material with the reforming catalyst which removes the CO<sub>2</sub> from the products to enhance the forward reforming and water-gas-shift (WGS) reactions such that H<sub>2</sub> is produced in one step with little CO and CO<sub>2</sub> impurities, thus avoiding the WGS unit and PSA. The H<sub>2</sub> content in the product is over 98%, the balance being unconverted methane.

Thermodynamic analyses conducted by the authors show that AER is advantageous over SMR not only in terms of hydrogen yield and purity but also in carbon suppression<sup>4,5</sup>. Studies by other groups also show promising results of AER<sup>6,7</sup>. To further improve the overall efficiency of the process developed by Intelligent Energy, a systematic engineering study of the AER combined with fuel cell is conducted. It is demonstrated by engineering calculations that the process efficiency can be potentially around 90% by heat integration of various process units.

## Process Integration

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This section presents the overview process of the high-efficiency hydrogen generation for fuel cells to be used in distributed power generation. The integration of various process units will be carried out targeting a better yield of H<sub>2</sub> to generate electricity.

In this combined AER and fuel cell power generation process, several AER beds are used alternatively to allow adsorbent regeneration. The feed streams (ethanol and water) are mixed with a specified ratio and are pumped to 5 bar. The mixture is then vaporized in E-101. The reactants are sent to the AER (R-101/A) where hydrogen is produced while CO<sub>2</sub> is adsorbed at 500°C. The gas mixture from the reformer contains CH<sub>4</sub>, H<sub>2</sub>O, H<sub>2</sub> and trace amount of CO and CO<sub>2</sub>. The overall reaction-adsorption in the reformer is endothermic even though the adsorption of CO<sub>2</sub> is exothermic ( $\Delta H = -20$  kJ/mol). The reformat is cooled down in E-102 and the condensed water is knocked out in V-101. The gas (primarily H<sub>2</sub> and CH<sub>4</sub>) enters the fuel cell (R-102). Note that CH<sub>4</sub> is not consumed in the fuel cell. Moreover, unlike CO, CH<sub>4</sub> is not a poison for the fuel. All the CH<sub>4</sub> and part of the unreacted H<sub>2</sub> from the anode of the fuel cell will be combined with air preheated in E-103 to generate heat in R-103. The preheating is important as the quality of heat is improved. The cathode off gas (primarily N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O) is preheated in E-102 and is used as a sweep gas for the removal of CO<sub>2</sub> from another AER (R-101/B). The exhaust is discharged to atmosphere after heat recovery through E-106.

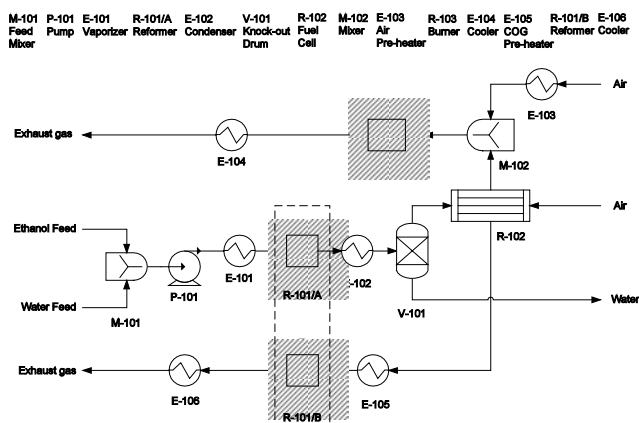


Figure 1. PFD of adsorption enhanced reforming based hydrogen generator in conjunction with fuel cells for distributed power generation (before heat integration).

Even though the target is to improve the yield of hydrogen, it does not imply that it should be close to 100% for two reasons. One reason is that the required amount of CO<sub>2</sub> adsorbent and reactor size would be huge. The other reason is that no adequate heat might be generated downstream of the reformer to cover the heat demand of units E-101, E-103, E-105 and R-101/A. Based on these considerations, one preliminary process is designed as follows. The feed has a steam/ethanol ratio of 4/1. The

yield of hydrogen in the AER is 88%. Both CO and CO<sub>2</sub> in the reformat are less than 10 ppm (based on equilibrium calculation) due to substantial CO<sub>2</sub> adsorption. About 95% of the H<sub>2</sub> is consumed in the fuel cell to generate electricity. The rest of H<sub>2</sub> and all the CH<sub>4</sub> are burnt to supply heat.

With such a design, the heat generated by CH<sub>4</sub>/H<sub>2</sub> combustion, reformat condensation, and CO<sub>2</sub> adsorption is able to cover the heat requirement of feed vaporization, reforming, preheating before combustion, and CO<sub>2</sub> desorption with a minimum temperature of 20°C (see Figure 2 for the composite heat curves of all the streams). The detailed heat integration will be presented in a full-length paper. This design has an overall hydrogen yield of 84%. If calculated on LHV basis, the AER efficiency is 95%. In a real process, the efficiency may be lower due to un-modeled loss of hydrogen (e.g., hydrogen trapped in the bed) in the engineering calculation.

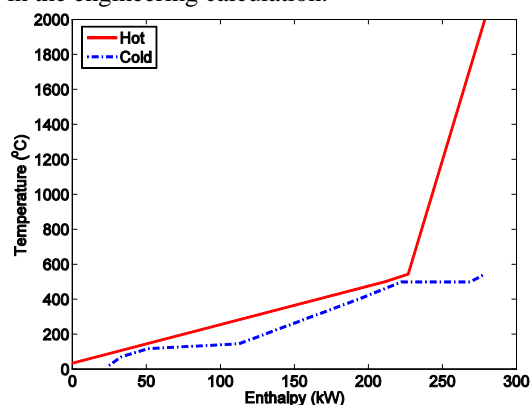


Figure 2. Composite heat curves for the proposed design (normalized based on ethanol flow rate of 1 kmol/hr).

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