Adsorption enhanced steam reforming of methanol for hydrogen generation in conjunction with fuel cell: Process design and reactor dynamics

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ABSTRACT

This work focuses on a preliminary investigation of hydrogen generation using adsorption enhanced reforming (AER) of methanol in packed-bed reactors. A process design of AER in conjunction with proton exchange membrane fuel cell (PEMFC) is conducted using Honeywell UniSim® Design software. A time-dependent model based on detailed reaction kinetics from the literature is developed to describe the reactor dynamics during both reforming and regeneration steps. It is shown that AER of methanol has a potential to efficiently generate hydrogen in portable fuel cell applications. Implications for ongoing experimental studies are discussed.

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1. Introduction

The dramatic increase in energy consumption has motivated a significant research in efficient utilization of fuels (Song, 2002). The ever-increasing public concern of climate change has led the US government to propose more stringent energy bills to regulate CO2 emissions from the use of fossil fuels, e.g., The American Clean Energy and Security Act of 2009 (Waxman and Markey, 2009). Addressing the issues of energy efficiency and emission reduction will have a great impact on the US economy and environment. Proton Exchange Membrane Fuel Cell (PEMFC) powered on hydrogen could be one of the solutions to power generation in residential, commercial and transportation applications in that it delivers high-density power with not only a higher efficiency, but also a lower greenhouse gas emission as compared to the combustion engine based route (Ahmed and Krumpelt, 2000; Stevens et al., 2007; Reijers et al., 2006; Duraiswamy et al., 2010). On the feedstock side, methanol as the feed to the fuel processor offers several advantages over batteries to provide flexible and durable short-term backup power solutions to telecommunications, highway and railroad safety, and building safety as well.

The wide commercialization of PEMFC power generators requires a reliable on-site hydrogen supply from compact and efficient fuel processors fed on hydrocarbons preferably including renewable resources (Song, 2002; Das and Veziroglu, 2001). On the process technology side, conventional steam reforming may not be a competitive fuel processor due to multiple units and low thermal efficiency (Spath and Mann, 2001). A new adsorption enhanced reforming (AER) method, originated by Sircar and coworkers (Carvill et al., 1996; Hufton et al., 1999) and further developed by several groups around the world (Ding and Alpay, 2000; Stevens et al., 2007; Reijers et al., 2006; Duraiswamy et al., 2010), has shown a great potential to reduce reformer size and to improve process efficiency. Thermodynamic analysis made by the authors also confirms that CO2 adsorption enhances hydrogen yield and purity and suppresses carbon formation (Li, 2008, 2009). On the feedstock side, methanol as the feed to the fuel processor offers several advantages in portable fuel cell applications. First of all, it is a liquid at room temperature and therefore is easily portable. Secondly, mature technologies are available for massive production from syngas. Lastly, it can be steam reformed into hydrogen at relatively low temperatures (250–360 °C). Therefore, AER of methanol has a great potential in compact fuel cell power generators, especially for portable applications.

The authors’ collaborative effort has recently developed a bench-scale AER-based hydrogen generator (Duraiswamy et al., 2010). It has four beds operated alternately at a lower temperature (500 °C) than conventional steam methane reforming (850 °C). It employs potassium-promoted hydrotalcites as the carbon dioxide capturing material and ceria supported rhodium as the reforming catalyst. The removal of CO2 from the product favors the reforming and the WGS reactions so that H2 is
produced in one step with little CO and CO₂ impurities. The adsorbent is regenerated using either steam or PEMFC cathode off-gas. Continuous production of near fuel-cell grade hydrogen has been successfully demonstrated using methane, ethanol and LPG, which may potentially reduce or even eliminate the need of methanation. When pulsing feed and steam purge are employed in the AER process, the H₂/CH₄ ratio in the product stream is as high as 125 while the carbon dioxide and carbon monoxide are on the ppm level. The hydrogen yield in the product gas is about 66% while the overall yield accounting for the regeneration exhaust is around 92%.

This work aims to investigate the potential of AER of methanol for a single-step hydrogen generation, which has not been reported before. The computational studies consist of a preliminary process design as well as a computational study of reformer dynamics during reforming and regeneration steps. Implications for ongoing experimental studies are discussed.

2. Process design of AER in conjunction with PEMFC

A simplified diagram of the AER system is shown in Fig. 1. The AER reactor has multiple reaction beds and is in cyclic operation using several manifolds and solenoid valves (not shown in Fig. 1) to control the flow directions through each bed, which is packed with both the catalyst and the adsorbent. At any particular time only one bed is producing H₂ using forward flow while the others are being regenerated using reverse flow. A similar experimental system for AER of methane, ethanol and LPG around 500 °C can be found in our previous work (Duraiswamy et al., 2010).

In this process, premixed methanol and water based on a specified steam/carbon (or S/C) ratio are vaporized and mixed with AOG (anode off-gas from the PEMFC, primarily H₂) before entering one of the beds in the AER reactor. H₂ is produced and collected at the exit of the bed while CO₂ is adsorbed on the adsorbent. It has been reported that alumina adsorbs water (Li et al., 2009). Therefore, the steam contained in the COG may displace the CO₂ on the adsorbent and be released later during the next reforming step, subsidizing the overall steam demand. The produced H₂ is sent to the anode of the PEMFC. The unconsumed AOG gases are recycled to the AER. At the cathode of the PEMFC, the air partially depleted in oxygen is sent to the AER to regenerate the other beds.

Because of the cyclic operation of AER, part of the H₂ produced in the reaction bed inevitably exits the AER through the COG exhaust when the flow is reversed. The percentage is estimated to be around 25% based on our experimental studies on methane (Duraiswamy et al., 2010); it might be reduced by optimizing the pulsing period in the hydrocarbon feed or by reducing intraparticle diffusion effect in the catalyst particle. The COG exhaust, which contains N₂, O₂, H₂, CO₂ and trace amount of CO, is sent to a catalytic combustor where heat is generated. The heat is used to supply the endothermic reforming reaction (CH₃OH + H₂O = CO₂ + 3H₂, ΔH°₂₉₈ K = 49.2 kJ/mol) as well as the vaporization of the methanol/water premix.

The material and energy balances of AER of methanol in conjunction with PEMFC are analyzed using UniSim Design from Honeywell. The simulation diagram is shown in Fig. 2. The fluid package for process simulation is SRK. For design purposes, focus is on the quasi-steady-state and the dynamic transitions between different beds are not considered. The multiple reaction beds are simulated as a single block connected by several inlet and outlet streams. In the engineering solver, the AER reformer is simulated using a conversion reactor (CRV-100) and two component splitters (X-100 and X-101). The temperature of the reformer is maintained at 250 °C. Stream COG1 from the component splitter X-100 represents the fraction of COG water vapor which is trapped in the bed during the regeneration step and is released in the subsequent reforming step (the value might vary depending on the adsorption capability of water by the adsorbent). It is also assumed that a small fraction (about 1%) of O₂ in the COG during the regeneration step is consumed in the subsequent reforming. In CRV-100, it is assumed that all CH₃OH is converted to CO₂ and H₂ (This assumption is reasonable if the S/C ratio is large enough). In X-101, only 75% of H₂ produced in the bed goes to the product gas while the rest to the COG exhaust. The flow rate of air to the PEMFC is about 5 times the one of H₂. About 90%
of H₂ is consumed in the anode of the PEMFC to generate electricity while the rest is recycled to the reformer as AOG. The catalytic combustor is simulated using a Gibbs reactor (GBR-100). The duty of the heat exchanger (E-101) after the catalytic combustor, Q₁₀₁, is set to be the one of the reformer (or the sum of Q₁₀₁ₐ, Q₁₀₁ₐ, and Q₁₀₁ₐ). The combustion exhaust will then be sent to heat exchanger E-100 to vaporize the methanol/water premix.

In order for the designed system to be thermally sustainable, the heat supplied by the catalytic combustor should be adequate to cover the demand of the reformer and the vaporizer with a minimum approach temperature (e.g., 20 °C). The simulation indicates that this requirement can always be satisfied if 25% of the produced hydrogen is available in the catalytic combustor. Fig. 3 shows the heat curves in the vaporizer at different S/C ratios in both the reformer and the vaporizer, assuming that the heat generation in the catalytic combustor and the heat removal by the reformer and the vaporizer occur in sequence. In a real situation, because of the coupling of the combustor and reformer, heat generation and removal occur simultaneously, and therefore, the highest gas temperature in the combustor would be around 380 °C but not 650 °C. In this sense, it may still be called a low-temperature process. It is shown that the change in the S/C ratio in the feed does not have a significant effect on the heat requirement of the reformer. However, the duty of the vaporizer is quite different. As the S/C ratio in the feed increases, the duty of
the vaporizer increases and the approach temperature decreases. As a result, the required heat transfer area is larger. A small \( S/C \) ratio is desired from a view point of heat transfer. A large \( S/C \) ratio, however, is preferred to improve \( \text{CH}_3\text{OH} \) conversion and reduce \( \text{CO} \) in the product gas. It was pointed out by thermodynamic analysis (Faungnawakij et al., 2006) that the optimal region for steam methanol reforming without \( \text{CO}_2 \) adsorption (in terms of maximizing hydrogen production and minimizing carbon monoxide formation) is 100–300 \(^{\circ}\text{C} \) and \( S/C \geq 1.5 \).

It is worth noting that \( \text{COG} \) contains water vapor which might be available for the reforming step. If part of the steam is adsorbed on the bed during the regeneration step and released later during the reforming step, the \( S/C \) in the reformer should be higher than the \( S/C \) in the feed. Fig. 4 shows the relationship between \( S/C \) in the reformer, \( (S/C)_R \), and \( S/C \) in the feed, \( (S/C)_F \), as well as the fraction of \( \text{COG} \) water that is adsorbed on the bed during regeneration and released for reaction during reforming, \( S_{\text{FCOG}} \). Based on the simulation results, a correlation can be derived as follows:

\[
(S/C)_F = (S/C)_R + 2.19S_{\text{FCOG}}
\]  

Clearly, a better adsorption capability of water by the adsorbent (represented by the value of \( S_{\text{FCOG}} \)) significantly improves the \( S/C \) ratio in the reformer (or subsidizes the demand of water in the feed). However, a complete elimination of water in the feed might be challenging unless a \( \text{CO}_2 \) adsorbent that strongly adsors water is available.

The operating parameters of AER in conjunction of a PEMFC system to deliver about 100 W power are shown in Table 1. The process requires a methanol flow rate of 43 g/h and a feed \( S/C \) between 1 and 2. The \( S/C \) in the reformer is calculated based on an assumption that 10% of \( \text{COG} \) water during the regeneration step is transferred as reactant in the reforming step. Please note that 10% is a rough estimate of \( S_{\text{FCOG}} \) used in the computer simulation while a more accurate value requires experimental studies.

3. Reactor dynamics during reforming and regeneration steps

The AER is a complex dynamic reaction-transport process (Christofides, 2001). It involves flow through packed beds, axial diffusion, reactions (reforming, WGS and combustion), intraparticle diffusion, \( \text{CO}_2 \) adsorption/desorption, heat transfer, and transitions between different states. Because of the inherent complexity (dynamics, nonlinearity, dynamic computational modeling is used to describe the coupled reaction-transport behavior in AER (Ding and Alpay, 2000; Lee et al., 2004; Li and Cai, 2007; Reijers et al., 2009; Xi et al., 2002). It is expected that a coordination between computational modeling and experimental efforts is mutually beneficial for both investigations. The experimental studies help to validate the computational model. The validated model provides a fundamental understanding of the process and guides the design and operation to enhance process performance (Xiu et al., 2003; Harale et al., 2010).

A one dimensional time-dependent partial differential-algebraic equation (PDAE) model, which consists of conservation equations of mass, momentum and energy, is used to describe the evolution of temperature, pressure, gas concentration and \( \text{CO}_2 \) loading in the reformer. The dynamic model consists of Eqs. (2)–(5) listed below:

\[
\frac{\partial (\rho \text{q}_j)}{\partial t} + \frac{\partial (\rho \text{v}_j \text{q}_j)}{\partial z} = \frac{\partial}{\partial z} \left( \frac{\partial \text{q}_j}{\partial z} \right) - \frac{\partial}{\partial z} \left( \frac{\partial \text{q}_j}{\partial z} \right)
\]

\[
0 = \sum_{j=1}^{N} y_j - 1
\]

\[
\frac{\partial \text{q}_{\text{CO}_2}}{\partial t} = k_{\text{ads}}(\text{q}_{\text{ads}} - \text{q}_{\text{CO}_2})
\]

\[
\text{Momentum balance:}
\]

\[
0 = -\frac{\partial P}{\partial z} - \frac{150 \mu (1-\epsilon) \rho_b \epsilon_b \rho_h \epsilon_h \text{v}^2}{\frac{\partial \text{P}}{\partial z}} - 1.75 \rho_b \epsilon_b \rho_h \epsilon_h \text{v}^2
\]

\[
\text{Energy balance:}
\]

\[
\left( \epsilon_b \sum_{j=1}^{N} (C_p \text{C}_j) + \rho_b C_p \right) \frac{\partial T}{\partial z} \leq \sum_{j=1}^{N} \left( C_p \text{C}_j \right) \frac{\partial T}{\partial z} + \left( k \frac{\partial T}{\partial z} \right)
\]

\[
+ f_{\text{ads}} \rho_b \left( \Delta H_{\text{ads,CO}_2} \frac{\partial \text{q}_{\text{CO}_2}}{\partial z} \right) - \frac{\partial P}{\partial z}
\]

\[
= \frac{4 U}{D_z} (T_w - T) + (1 - f_{\text{ads}}) \rho_b \sum_{i=1}^{3} r_i (-\Delta H_i)
\]

\[
\text{Equation of state:}
\]

\[
C = \frac{P}{RT}
\]

where \( \epsilon_b \) and \( \epsilon_h \) are the bed porosity and total porosity, respectively, \( C \) is the gas concentration, \( y_j \) is the gas mole fraction, \( z \) is the axial location, \( f_{\text{ads}} \) is the mass fraction of the adsorbent in the packed material, \( R_i \) is the generation rate of species \( j \) by surface reactions, \( v \) is the superficial velocity, \( \rho_b \) is the bulk density of the packed material, \( D_z \) is the axial dispersion coefficient, \( q_{\text{ads}} \) is the loading of \( \text{CO}_2 \) on the adsorbent, \( q_{\text{CO}_2} \) is the saturated loading of \( \text{CO}_2 \), \( P \) is the pressure, \( T \) is the temperature, \( \text{d}_p \) is the diameter of the packed material, \( D_z \) is the diameter of the reaction.
tube, $\Delta H_i$ is the enthalpy change of reaction $i$, and $\Delta H_{ads,CO_2}$ is the enthalpy change of CO$_2$ adsorption.

The thermodynamic properties are based on NASA CEA database (Gordon and McBride, 1996). Ideal gas mixing law was used to estimate the mixture properties. The adsorbent is sodium promoted alumina. Its adsorption dynamics on CO$_2$ has been reported by Lee et al. (2007). The kinetics of steam reforming of methanol has been studied by several groups (Jiang et al., 1993a,b; Peppley et al., 1999a,b; Purnama et al., 2004). According to the studies on steam reforming of methanol on Cu/ZnO/Al$_2$O$_3$ catalyst (Peppley et al., 1999a,b), the following reversible reactions occur simultaneously on the surface of the catalyst:

CH$_3$OH + H$_2$O $\rightleftharpoons$ 3H$_2$ + CO$_2$

CO + H$_2$O $\rightleftharpoons$ H$_2$ + CO$_2$

CH$_3$OH $\rightleftharpoons$ 2H$_2$ + CO

and the reaction rates (mol/m$^2$ s) of the three reactions ($r_R$ for reforming, $r_W$ for water gas shift, and $r_D$ for decomposition) are given below:

$$r_R = \frac{k_1 K_{CH_3OH}^* \left( \frac{P_{CH_3OH}}{P_{H_2}} \right) \left( 1 - \frac{P_{CO}}{K_{water} P_{H_2}} \right)}{1 + K_{CH_3OH}^* \left( \frac{P_{CH_3OH}}{P_{H_2}} \right) + K_{CO} P_{H_2} P_{CO} + K_{H_2O}^* \left( \frac{P_{H_2O}}{P_{H_2}} \right) \left( 1 + K_{H_2O} P_{H_2} \right)} C_1 C_2$$

$$r_D = \frac{k_D K_{CH_3OH}^* \left( \frac{P_{CH_3OH}}{P_{H_2}} \right) \left( 1 - \frac{P_{CO}}{K_{water} P_{H_2}} \right)}{1 + K_{CH_3OH}^* \left( \frac{P_{CH_3OH}}{P_{H_2}} \right) + K_{H_2O}^* \left( \frac{P_{H_2O}}{P_{H_2}} \right) \left( 1 + K_{H_2O} P_{H_2} \right)} C_1 C_2$$

$$r_W = \frac{k_W K_{CH_3OH}^* \left( \frac{P_{CO} P_{H_2O}}{P_{H_2}^2} \right) \left( 1 - \frac{P_{CO}}{K_{water} P_{H_2}} \right)}{1 + K_{CH_3OH} \left( \frac{P_{CH_3OH}}{P_{H_2}} \right) + K_{H_2O}^* \left( \frac{P_{H_2O}}{P_{H_2}} \right) \left( 1 + K_{H_2O} P_{H_2} \right)} C_1^2$$

Fig. 5. Dynamics of AER during the reforming step.
where $K_n$ is the adsorption parameter, $k$ is the reaction constant, and $K$ is the equilibrium constant. Therefore, the net generation rate of each species is described as follows:

\[
R_{CO_2} = (r_R + r_W)S_A
\]

\[
R_{CO} = (r_D - r_W)S_A
\]

\[
R_{H_2} = (3r_R + 2r_D + r_W)S_A
\]

\[
R_{CH_3OH} = -(r_D + r_W)S_A
\]

\[
R_{H_2O} = -(r_R + r_W)S_A
\]

where $S_A$ is the specific surface area of the adsorbent (m$^2$/kg cat).

It has been shown that the kinetic parameters could be different if the composition of the catalyst is different (Agarwal et al., 2005).

The reformer dynamics are then simulated by solving Eqs. (2)–(5) using orthogonal collocation on finite elements. The pressure is chosen to be 1 bar and the temperatures of the feed and the wall of the reformer are both maintained at 250°C. The packed bed is composed of 90 wt% adsorbent and 10 wt% catalyst. Moreover, it is assumed that only CO$_2$ is adsorbed. As a preliminary study to show the dynamics, it is assumed that the reformer is initially filled with 50% H$_2$ and 50% H$_2$O, and a methanol/water premix ($S/C=1$) is sent to the reformer at $t=0$. The gas compositions along the reformer at different times during the reforming step are shown in Fig. 5(a)–(d). It is seen that as the reactions proceed, H$_2$ and CO$_2$ are produced. Fractions of CO$_2$ and CO in the gas phase are almost negligible except at the entrance of the reformer because of CO$_2$ adsorption on the surface of the adsorbent. High purity H$_2$ is then collected at the exit of the reactor. However, when more and more CO$_2$ is adsorbed on the surface, un-occupied sites will become fewer. Eventually, CO$_2$ breakthrough will occur and the AER decays to regular steam reforming. Therefore, before CO$_2$ breakthrough occurs, the bed should be regenerated to evacuate sites available for adsorption.

The gas compositions along the reformer at different times during the regeneration step are shown in Fig. 6(a)–(d). The current model does not account for the reactions between oxygen contained in the COG and gases and particles in the bed. It is seen that the CO$_2$ concentration will gradually decrease and the adsorbed CO$_2$ will be desorbed and carried away by the regeneration gases. The simulation also indicates that a full regeneration of...
bed takes a long time (more than 100 times of the space time). Therefore, for practical reasons, it would be desirable to operate the AER between partially clean and partially loading states. This would certainly reduce the effective adsorption capacity of the bed. However, it makes possible continuous hydrogen generation using several beds running simultaneously. It is also seen from Fig. 6 that a fair amount of H₂ will inevitably go to the regeneration exhaust. In practice, because of intraparticle diffusion, the escaping ratio of H₂ would be even greater. Therefore, a direct switch from production to regeneration is not desirable in terms of H₂ yield. The pulsing feeding concept developed in our previous work Duraiswamy et al. (2010) might be used to effectively improve the yield of H₂ in the product gas.

The concentration of CO in H₂ is a very important parameter for PEMFC applications. It should be below 10 ppm to avoid poisoning the anode catalyst of the PEMFC. The current model indicates that when fewer sites are available for CO₂ adsorption during the reforming step, the concentration of CO in the product gas will gradually increase, which suggests that CO₂ adsorption reduces CO formation (see Fig. 7). This conclusion is consistent with our previous thermodynamic analysis (Li, 2008, 2009). However, the CO concentration is still above 10 ppm so a methanation may be necessary for fuel-cell grade H₂ but its load is expected to be smaller than the one using conventional steam reforming. Future work should focus on the development of a more comprehensive cyclic dynamic model and its comparison with ongoing experimental studies. Studies should also be pursued in the areas of H₂O adsorption on the adsorbent (e.g., using thermogravimetric analysis), catalyst preparation (to reduce intraparticle diffusion and CO formation), and process optimization strategies (to enhance H₂ yield and to reduce CO) during the cyclic operation of AER.

4. Conclusions

A preliminary study of AER of methanol in conjunction of PEMFC was done in this work. It was shown that CO₂ adsorption reduces impurities of both CO₂ and CO in the product gas and allows generation of high purity H₂ in a single unit. Methanation may be necessary for fuel-cell grade H₂ but its load is expected to be smaller than the one using conventional steam reforming.

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