The parametric study of a novel methanol steam reforming system combining Pd membrane purification and purification retentate combustion

Yaodong Zhou1, Lintao Wang, Bicai Deng, Qiyu Li and Zhimin Lin
Shanghai Marine Diesel Engine Research Institute. No. 400 Niudun Road, Pudong Area, Shanghai, China

1Corresponding author’s e-mail: zydjshm@163.com

Abstract. A hydrogen production process combining methanol steam reforming, Pd membrane purification and purification retentate combustion is proposed and simulated by Aspen plus. The influence of key components’ performance like the methanol conversion rate and hydrogen recovery rate on the methanol consumption is calculated and analyzed. Simulation results show that the overall methanol consumption only reduces by 0.8% when the methanol conversion rate or hydrogen recovery rate increases by 5 percent point. The main benefit is the CO2 emission reduction.

1. Introduction
Hydrogen is one of the most ideal energy. Hydrogen has a high heat value, and the only combustion product is water, which is very friendly to the environment. As a result, hydrogen is regarded as one of the most promising energy in the future. The production, storage, transportation technology of hydrogen have become the focus of attention in the 21st century.

Methanol steam reforming [1] is one of the commonly used technologies for hydrogen production at present. Compared with other chemical hydrogen production technologies, methanol steam reforming has the advantages of high efficiency, low emission, low reaction temperature (250~280°C [2]), easily acquired reactants and less impurity [3].

The products of methanol steam reforming mainly include H2, CO2 and CO. Because CO is harmful to the catalyst of PEMFC, the products must be purified before enter the PEMFC. The most commonly used technologies for hydrogen purification are PSA [4] and membrane separation. PSA equipment is relatively large, which is more compatible for chemical industry. Besides, constrained with adsorption equilibrium and phase equilibrium, the purity of hydrogen is limited. As a result, the PSA technology is not suitable for small and medium size hydrogen production equipment for PEMFCs.

Pd and Pd alloy have the unique selective permeability for hydrogen [5]. Non-hydrogen gas cannot pass the membrane theoretically. Therefore, the ultra-high purity of hydrogen can be acquired. Besides, the Pd membrane equipment is relatively small, which is very suitable for small and medium sized mobile device. Pd membrane-based purification modules have been applied in many hydrogen production systems of hydrocarbon reforming [6]. It should be noticed that the operation temperature for Pd membrane is very restricted, which is usually higher than 300°C [7]. The hydrogen recovery rate is the primary assessment indicator for Pd membrane, which is affected by the pressure,
temperature, membrane thickness [8], and some other factors [9]. Therefore, there is still part of the hydrogen cannot pass the membrane, which can be recovered and reused.

The heat of the whole system can be supplied by purification retentate combustion. However, the heat value of the purification retentate may be not enough in some cases. Therefore, some methanol needs to be added as fuel.

The feedstock of the methanol reforming system includes methanol and water. For a limited space such as on board, the feedstock amount can be carried is restricted. Therefore, the specific methanol consumption per unit weight of hydrogen is one of the most important indicators in this case. Methanol acts as reactant of reforming and fuel of burner in the process. Hence, the overall methanol consumption is the sum of these two kinds of methanol consumption.

The methanol consumption of reforming mainly depends on the methanol conversion rate and also the hydrogen recovery rate. The methanol consumption of burning depends on the supplemental heat needed, which is affected by the heat value of the purification retentate. And the heat value of purification retentate mainly depends on the hydrogen recovery rate, but also slightly affected by the methanol conversion rate.

As stated in previous research, methanol conversion rate and hydrogen recovery rate are both affected by many operating conditions, such as temperature, pressure, composition and so on. However, methanol conversion rate can also be improved by improving the catalyst activity [10] or optimizing the reactor design [11-12]. And hydrogen recovery rate can be improved by optimizing the Pd membrane-based separator design [13-14]. All the measures have a cost, which should be considered in a practical system. Therefore, the focus of this paper is just the methanol conversion rate and the hydrogen recovery rate themselves. And this paper will provide a unique insight about the advantages of increasing the methanol conversion rate and the hydrogen recovery rate.

2. The novel process of methanol reforming
The process of methanol reforming in this paper is shown as Figure 1. The methanol is mixed with water, heated evaporated and fed to the reformer. In the reformer, the methanol-water vapor is converted into hydrogen-rich gas mixture. This reformate gas is further heated to the operation temperature of Pd membrane and then processed in the gas purification unit based on Pd membrane. The major fraction of hydrogen passes through the membrane and can be fed to the Fuel Cell directly. The rest of the reformate is burned with pure oxygen in the burner, under the addition of methanol as fuel, to provide the required heat for the reforming process. The exhaust gas of the burner heat the reformate gas to the operation temperature of the membrane and then discharged after proper handling.

Figure 1. The process of the methanol reforming system.
3. The modelling process by Aspen Plus

The process of methanol reforming in Figure 1 is modeled by Aspen Plus V8.4 [15]. The Stoichiometry Reactor (Rstoic) is selected as the reformer, where the methanol conversion rate and the CO selectivity can be assigned in order to perform the sensitivity analysis. The Separator (Sep) is selected to simulate the purification unit based on Pd membrane, where the hydrogen recovery rate can be assigned. The Rstoic with check of Generate combustion reactions in the Combustion page is selected to simulate the burner.

The operation condition of the model is listed in Table 1.

| The given parameter                              | Unit | Value |
|--------------------------------------------------|------|-------|
| Reforming temperature                            | ℃    | 260   |
| Reforming pressure                               | MPa  | 2.5   |
| Operation temperature of purification unit       | ℃    | 400   |
| Mass ratio of methanol and water                 |      | 1:1   |
| The final exhaust temperature of burner          | ℃    | ≥310  |
| Output flux of pure hydrogen                     | Kg/h | 1.0   |

In this model, the methanol conversion rate (MCR) is defined as the ratio of the converted methanol flux to the total input methanol flux of the reformer, which can be expressed by:

\[
MCR = \frac{m_{\text{CH}_2\text{OH}-\text{converted}}}{m_{\text{CH}_2\text{OH}-\text{input}}} = \frac{m_{\text{CO}\text{-product}}+m_{\text{CO}_2\text{-product}}}{m_{\text{CH}_2\text{OH}-\text{input}}}
\]  

(1)

The hydrogen recovery rate (HRR) is defined as the ratio of the recovered hydrogen flux to the total hydrogen flux in the reformate.

\[
HRR = \frac{m_{\text{H}_2-\text{recovered}}}{m_{\text{H}_2-\text{total}}}
\]  

(2)

Besides, CO selectivity is defined as follow:

\[
S_{\text{CO}} = \frac{m_{\text{CO}\text{-product}}}{m_{\text{CO}\text{-product}}+m_{\text{CO}_2\text{-product}}}
\]  

(3)

4. Results and discussion

The influence of MCR and HRR on the methanol reforming system is discussed in this section. And only the influence of MCR or HRR itself is focused. This discussion should be useful when someone is determining the value of MCR and HRR in the designing stage.

4.1. The influence of hydrogen recovery rate

In this section, the methanol conversion rate is set as 90% and the CO selectivity is fixed as 4.44%. All the other parameters are assumed unchanged under the variation of HRR. The hydrogen recovery rate affects the hydrogen amount in the purification retentate, which has a great influence on the burner design. The influence of HRR on the composition of purification retentate is shown in Figure 2. And the influence of HRR on the main parameters of the burner is shown in Table 2.

As shown in Table 2, when HRR is less than 80%, the exhaust temperature is very high and much energy is wasted. This is because that hydrogen amount in the purification retentate is excess for combustion. On the contrary, when HRR is higher than 80%, the hydrogen amount in the purification retentate is not enough for combustion and additional methanol acting as fuel is needed to compensate the heat demand. In this situation, the exhaust temperature can be controlled by adjusting the methanol fuel flux. Therefore, much less energy will be wasted, as shown in Figure 3.

Besides, it can be seen that the combustion temperature and oxygen flux decrease as the hydrogen recovery rate increases, which is more apparent when HRR is less than 80%. However, the result of CO₂ emission is a little different. The downtrend is almost linear, with no clear turning point at 80%, as shown in Figure 3. To be specific, the CO₂ emission reduces by average 5.4% as HRR increases by 5 percent point even if it is higher than 80%. The CO₂ emission reduction comes largely from the
reforming side as shown in Figure 4. This is because that when HRR increases, the methanol consumption of reforming is decreased, which leads to the reduction of CO₂ production from reforming.

![Figure 2. The influence of hydrogen recovery rate on the composition of purification retentate.](image1)

![Figure 3. The influence of hydrogen recovery rate on the exhaust.](image2)

Table 2. The influence of hydrogen recovery rate on the burner.

| HRR (%) | Exhaust temp. (°C) | Exhaust heat (kW) | Combustion temp. (°C) | Oxygen flux (kmol·h⁻¹) | CO₂ emission (kmol·h⁻¹) |
|---------|--------------------|-------------------|-----------------------|-------------------------|--------------------------|
| 70      | 811                | 13.15             | 2221                  | 0.167                   | 0.266                    |
| 75      | 505                | 8.77              | 2058                  | 0.137                   | 0.249                    |
| 80      | 310                | 6.43              | 1955                  | 0.117                   | 0.233                    |
| 85      | 310                | 5.95              | 1932                  | 0.113                   | 0.219                    |
| 90      | 310                | 5.57              | 1914                  | 0.111                   | 0.207                    |
| 95      | 310                | 5.25              | 1893                  | 0.108                   | 0.196                    |

The variation of methanol consumption regarding hydrogen recovery rate is shown in Figure 5. As shown in Figure 5, the total methanol flux decreases as the hydrogen recovery rate increases. And when HRR is higher than 80%, the overall methanol consumption decreases very slightly. To be specific, the overall methanol consumption only reduces by average 0.8% as HRR increases by 5 percent point. The reason is that although the methanol flux of reforming decreases obviously as the recovery rate increases, the methanol consumption of burning will increase in order to meet the heat demand as the hydrogen amount in the purification retentate decreases. Therefore, the overall methanol consumption changes little when HRR is higher than 80%.

![Figure 4. The influence of hydrogen recovery rate on the CO₂ emission.](image3)
4.2. The influence of methanol conversion rate

In this section, the hydrogen recovery rate is set as 85% and the CO selectivity is fixed as 4.44%. All the other parameters are assumed unchanged under the variation of MCR. The methanol conversion rate doesn’t affect the hydrogen amount in the purification retentate, but the methanol amount instead. The influence of methanol conversion rate on the composition of purification retentate is shown in Figure 6. Likewise, the methanol conversion rate has an influence on the burner parameters, as shown in Table 3.

As can be seen from Table 3, when MCR is higher than 85%, the exhaust temperature can be controlled by adjusting the methanol fuel flux. The influence of MCR on the burner is similar with HRR. It should be noted that MCR also has a relatively large influence on the CO2 emission. The CO2 emission reduces by average 5.1% as MCR increases by 5 percent point when it is higher than 85%, as shown in Figure 7. Different with HRR’s case, the CO2 reduction comes completely from the burning side, as shown in Figure 8. Because the H2, CO2 and CO production is fixed when HRR is fixed, as shown in Figure 6. The increase of MCR just means less methanol consumption of reforming is needed, which leads to the reduction of reaction heat needed. As a result, less fuel is needed and the CO2 emission from burning is reduced.
### Table 3. The influence of methanol conversion rate on the burner.

| MCR (%) | Exhaust temp. (℃) | Exhaust heat (kW) | Combustion temp. (℃) | Oxygen flux (kmol·h⁻¹) | CO₂ emission (kmol·h⁻¹) |
|---------|-------------------|-------------------|----------------------|------------------------|------------------------|
| 75      | 706               | 11.68             | 2105                 | 0.161                  | 0.263                  |
| 80      | 476               | 8.41              | 2001                 | 0.134                  | 0.247                  |
| 85      | 310               | 6.42              | 1931                 | 0.118                  | 0.233                  |
| 90      | 310               | 5.95              | 1932                 | 0.113                  | 0.219                  |
| 95      | 310               | 5.60              | 1934                 | 0.111                  | 0.208                  |
| 100     | 310               | 5.34              | 1936                 | 0.108                  | 0.198                  |

The influence of MCR on the methanol consumption is shown in Figure 9. As can be seen from Figure 9, the influence of MCR on the methanol consumption is also similar with HRR. When MCR is higher than 85%, methanol needs to be added as fuel to meet the heat demand. In this case, the overall methanol consumption only reduces average 0.8% as MCR increases by 5 percent point. The reason is the same as explained in Section 4.1.

**Figure 8.** The influence of methanol conversion rate on the CO₂ emission.

**Figure 9.** The influence of methanol conversion rate on the methanol consumption.

### 4.3. The influence mechanism of methanol consumption

It’s clearer to explain the influence mechanism of methanol consumption from the energy balance perspective. The overall methanol consumption contains two parts: the reforming part and the combustion part. From the energy balance perspective, the input energy of the system is the heat value of all the methanol. The output energy is the heat value of the output hydrogen and the heat of the burner exhaust. In this paper, the output hydrogen flux is fixed. Therefore, the overall methanol consumption mainly depends on the heat of the burner exhaust. Two scenarios will be discussed:

a) When the heat value of the purification retentate is too high, which means there is no need to add methanol as fuel, then the burner exhaust heat will be excessive. And the overall methanol consumption will get higher as MCR or HRR decreases. In this scenario, much energy is wasted.

b) When the heat value of the purification retentate is not enough to meet the heat demand of the system, there is a need to add methanol as fuel. In this case, the temperature of the burner exhaust can be controlled by adjusting the methanol fuel flux. Then the heat of the exhaust changes little as MCR or HRR varies. Therefore, the overall methanol consumption changes little in this scenario.
5. Conclusions
A novel hydrogen production process combining methanol steam reforming, Pd membrane purification and purification retentate combustion is proposed and modeled by Aspen plus in this paper. The influence of key component indicators such as methanol conversion rate and hydrogen recovery rate on the process is analyzed. Also, the influence mechanism of methanol consumption is discussed. Main conclusions are drawn as following:

a) The methanol consumption can be reduced by increasing MCR or HRR. But it should be noticed that under the circumstance of adding methanol as fuel, the methanol consumption can only be reduced by 0.8% when MCR or HRR are increased by 5 percent point.

b) From the perspective of energy balance, the overall methanol consumption is mainly affected by the exhaust heat. As long as MCR and HRR are high enough, the heat value of the purification retentate will be not enough to meet the heat demand of the system, then there is a need to add methanol as fuel. In this case, the temperature of the burner exhaust can be controlled by adjusting the methanol fuel flux. Then the overall methanol consumption will not change much.

c) Usually, MCR is higher than 90% and HRR is higher than 80% in practice. In this case, there is a need to add methanol as fuel, which means the impact of increasing MCR or HRR on the methanol consumption cutdown is very limited. The primary benefit is to reduce the CO₂ emission. The CO₂ emission can still be reduced by about 5.1% or 5.4% when MCR or HRR is increased by 5 percent point, respectively.

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