International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 0442

HYDROGEN PRODUCITON CHARACERISTICS FROM METHANOL AUTOTHERMAL REFORMING IN SPRAYS

Wei-Hsin Chen [1, 2, *], Yu-Qi Su [1], Bo-Jhih Lin [1]

1 Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan
2 Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 701, Taiwan

*E-mail of the corresponding author: weihsinchen@gmail.com; chenwh@mail.ncku.edu.tw

ABSTRACT

The aim of this study is to perform autothermal reforming (ATR) of methanol by sprays via the h-BN Pt catalyst with cold start for the hydrogen production. The present works mainly focus on the effects of operating conditions on hydrogen production and methanol conversion. Meanwhile, the comparison between ATR and partial oxidation of methanol (POM) are also carried out. The results of POM indicate that the highest H_2 and CO concentrations are obtained at O_2/C (molar ratio of air and methanol) = 0.7, and the CH_3OH conversion can reach 100%. In the ATR process, the methanol conversion reaches 60% under O_2/C ratio =0.7 with S/C (molar ratio of steam and methanol) = 1.5. At S/C =0.5, the CH_3OH conversion increases with increasing the O_2/C ratio and is up to 100%, and the H_2 yield is higher than that of POM. The highest H_2 yield from ATR is 1.697 mol (mol CH_3OH)-1 occurs at S/C =0.5 and O_2/C=0.7.

Keywords: Autothermal reforming (ATR), Sprays, Platinum (Pt) catalysts, Hydrogen production

1. INTRODUCTION

Hydrogen extraction technologies from methanol include thermochemical reactions like methanol decomposition (MD), steam reforming (SR), partial oxidation of methanol (POM), and autothermal reforming (ATR). MD, an endothermic reaction, is a direct decomposition of methanol to produce hydrogen and carbon monoxide without the need for other additives however, coke easily forms on the catalyst surface during the reaction [1]. SR, also an endothermic reaction, adds steam to the reaction. It has better hydrogen production but requires heat addition as well [2]. POM involves oxygen addition during the reaction since oxygen can help methanol to partially burn and ignite the reaction quickly. It is an exothermic reaction so, it does not require the consumption of heat [3]. ATR of methanol proceeds with steam and oxygen, like a combination of SR and POM [4], and improves the shortcomings of both parties. POM has a relatively low hydrogen yield and SR needs relatively high energy consumption, but with ATR, these shortcomings are addressed at the same time

MD is expressed as

$$\mathrm{CH_3OH \rightleftharpoons 2H_2 + CO,\ \ \Delta H^0_{298} = 90.5\ \ kJ\ \ mol^{-1}} \quad (1)$$

SR is expressed as

$$\mathrm{CH_3OH} + H_2\mathrm{O} \rightleftharpoons \mathrm{3H_2 + CO_2,\ \ \Delta H^0_{298} = 49.5\ \ kJ\ \ mol^{-1}} \quad (2)$$

POM is expressed as

$$\mathrm{CH_3OH + 0.5O_2 \rightleftharpoons 2H_2 + CO_2,\ \ \Delta H^0_{298} = -192.3\ \ kJ\ \ mol^{-1}} \quad (3)$$

ATR is expressed as

$$\mathrm{CH_3OH + (1-n)}H_2\mathrm{O + 0.5nO_2 \rightleftharpoons (3-n)H_2 + CO_2,\ \ \Delta H^0_{298} = -192.3\ \ kJ\ \ mol^{-1}} \quad (4)$$

In ATR reaction, methanol reacts with steam like SR, a strong endothermic reaction, and adding oxygen like POM, an exothermic reaction that balances the energy consumed by the endothermic reaction [5, 6], along with change in O_2/C ratio that helps to determine whether thermo-neutral or exothermic to ease the problem on energy consumption and speeds up the reaction as well [7].

Selection and peer-review under responsibility of the scientific committee of the 11th Int. Conf. on Applied Energy (ICAE2019).

Recently, the review of the literature indicates that sprays are being used on POM, wherein a nozzle is used in the reactor, gas is added while injecting methanol, and a high-speed gas is flushed out of the nozzle together with methanol [8]. During the process, methanol is broken up into numerous fine particles, and reacts better with the catalyst resulting to faster response time and increased performance of POM by 30%. Therefore, sprays can also be fully integrated into the ATR system, effectively improving the performance of ATR. This study aims to use ATR on sprays to determine if there will be better hydrogen yield. The catalyst to be used is Pt/Al_2O_3, in which 0.2 wt% of precious metal Pt is added. The advantages of using Pt is that it can react at normal temperatures, eliminating the preheating part of the experiment, and the Pt content is also lower therefore, cost is saved. In the literature review, most of the ATR uses Cu-based catalysts, but since Cu has poor stability at temperatures above 300 °C, it is commonly used as a substrate to combine different chemicals and produce new varieties of catalysts to improve stability [9, 10]. However, this study will use Pt/Al_2O_3 catalyst to explore its suitability for ATR. In addition, the experiment will analyze the performance of ATR by altering steam to methanol molar ratio and oxygen to methanol molar ratio.

2. MATERIALS AND METHODS

2.1 Reaction system

The entire system for ATR of methanol could be divided into four different sections, including the feeding unit, reaction unit, product gas treatment unit and gas analysis unit. The feeding unit includes a syringe pump (Chemyx Fusion 200) and electric two flow rate controllers (KD-4000), control the flow rate of methanol and water using the syringe pump and control the flow rate of air and nitrogen using flow rate controllers, the gas flow rate value was displayed on the controller readout (Brooks 5850E), and the two streams of air and N_2 were mixed in a gas mixer. In the reaction unit, a quartz tube and a concentric tube have nozzle were installed, the characteristics about nozzle of concentric tube is using high-speed gas to Spray methanol and water, the quartz tube was wrapped with refractory wool to minimize heat loss from the ATR. The K-type thermocouple was placed in the catalyst bed to measure the reaction temperature. Install a layer of glass beads 1.5 cm high below the catalyst bed to adjust the height of the catalyst bed in the tube. In order to remove moisture in the product gas, a condenser (YIHDER, BL710) and a dryer were included in the gas treatment unit. The gas analysis unit includes a gas analyzer (GA, Fuji ZRJF5Y23-AERYR-YKLYYCY-A) and a gas chromatograph (GC, SRI 8610C) to measure carbon dioxide, carbon monoxide, methane, and hydrogen gas concentrations.

Methanol conversion is calculated by:

$$\mathrm{CH_3OH\ conversion\ (\%)} = \left(\frac{\dot{n}_{CO_2,out} + \dot{n}_{CO,out} + \dot{n}_{CH_4,out}}{\dot{n}_{CH_3OH,in}}\right) \times 100 \qquad (5)$$

The H_2 concentration will be converted to molar flow rate and calculation of hydrogen yield:

$$\mathrm{H_2\ yield\ (mol/mol\ CH_3OH)} = \left(\frac{\dot{n}_{H_2}}{\dot{n}_{CH_3OH}}\right) \qquad (6)$$

2.2 Experimental procedure

In the operating conditions, it was mainly divided into two parts, ATR and pom. The parts of ATR were the steam to methanol molar ratio (S/C), the oxygen to methanol molar ratio (O_2/C) and the gas hourly space velocity (GHSV), part of the pom had a molar ratio of oxygen to methanol (O_2/C). In the ATR section, methanol and water were first mixed into a 100 ml syringe in a ratio of S/C ratios of 0, 0.5, 1 and 1.5, and injected at a flow rate of 1 cm^3/min (at room temperature), the flow rates of air and nitrogen would be adjusted according to O_2/C ratios of 0.5, 0.6, 0.7, 0.8 and GHSV=10000h^{-1}, respectively. Therefore, the air and nitrogen with a flow rate of 3805ml / min were adjusted according to the above O_2/C ratio. In the pom section, the methanol flow rate was fixed at 1 cm^3/min, the O_2/C ratio was 0.5, 0.6, 0.7, 0.8 and the GHSV was fixed at 10,000h^{-1}.

3. RESULTS AND DISCUSSION

3.1 Performances of POM at various O_2/C

Fig. 1 shows temporal distributions of CH_3OH conversion and temperature from POM reaction under the operation conditions of O_2/C=0.5-0.8 and GHSV=10000 h^{-1}. The results find that the interval of CH_3OH conversion and temperature are on 89 to 100 percent and 437 °C to 658 °C, respectively. The whole experiment takes 15 min from room temperature to steady state temperature, and then maintaining stable temperature until the finish of experiment. From this observation, the h-BN-Pt/Al_2O_3 catalyst demonstrates very good performance to trigger at cold start. In **Fig. 1a** and **Fig. 1b**, the CH_3OH conversion and temperature increase along with the increase of O_2/C ratio, and it is mainly attributed to the increasing of oxygen concentration can enhance the exothermal reaction during POM to increase and reaction temperature. As shown in **Fig. 1a**, the methanol conversion is achieve 100% when the O_2/C ratio is as higher as 0.7.

Profiles of POM reaction with different O_2/C ratios to produce H_2 are shown in **Fig. 2**. The H_2 yield of is about 1.2-1.3 (mol/mol CH_3OH). The H_2 yield increases with increasing of O_2/C, but it is decrease at the O_2/C ratio = 0.8. In **Fig. 1a**, CH_3OH conversion is 100% when the O_2/C ratio at 0.7. The addition oxygen (higher O_2/C ration) will not enhance the H_2 production. The decreasing of H_2 yield is mainly attributed to the methanol combustion reaction [11], tending dramatically with increasing of O_2/C ratio. Because of the combustion, the H_2 turns water, and the H_2 yield is further decreased.

3.2 Effect of S/C rations on ATR

In the investigations of autothermal reforming, the S/C ratio and O_2/C ratio are the crucial operating conditions. For this reason, the three-axis distribution diagrams of methanol conversion, reaction temperature, and H_2 yield are inspected under the operating conditions of S/C and O_2/C ratio in **Fig. 3**. The methanol conversion and reaction temperature are in the range of 35-100% and 225-658 °C, respectively. **Fig. 3a** and **Fig. 3b** show the methanol conversion and reaction temperature have similar trends. These observations are owning to that the reaction temperature is effected from the exothermic reaction during autothermal reforming. According to **Fig. 3b**, it is discovered that the reaction temperature is decreased with increasing the S/C ratio. This is mainly due to the endothermic reaction of steam reforming is more dramatic, when the proportion of water increase in the experiments. Therefore, the process of the experiment should apply more heat for ATR of methanol to avoid the incomplete reaction. On the other hand, the exothermic reaction of ATR of methanol can be assisted by increasing the O_2/C ratio.

In **Fig. 3c,** it is found that the highest hydrogen yield is observed at the operation of S/C=0.5 and O_2/C=0.7. At higher O_2/C ratio (O_2/C=0.8), the hydrogen yield is decreased from the methanol combustion. Additionally, once the reaction temperature is too low, the ATR of methanol cannot complete reaction, resulting in the decreasing of the hydrogen productivity.

4. CONCLUSIONS

The h-BN-Pt/Al_2O_3 catalyst has been employed to trigger POM (partial oxidation of methanol) and ATR in this study. The experiments suggest that ATR can be triggered at room temperature with h-BN-Pt/Al_2O_3 catalyst by sprays. If S/C ratio is too high and O_2/C ratio is too low, the reaction will become incomplete. On the contrary, if S/C ratio is too low and O_2/C ratio is too high, reaction will be dominated by methanol combustion. When the methanol conversion reaches 100%, the hydrogen yield from ATR is higher than POM by sprays over cold start. The trend of methanol conversion and reaction temperature is similar, indicating that the performance of the reaction is inseparable from the reaction temperature.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Ministry of Science and Technology (MOST 108-2221-E-006-127-MY3), Taiwan, R.O.C, for this study.

REFERENCE

[1] Wei P, Xia W, Li JZ, Long H, Chen J, Li T, et al. Single-phase Ni3Sn alloy alkali-leached for hydrogen production from methanol decomposition. Renewable Energy. 2015;78:357-63.
[2] Zheng T, Zhou W, Yu W, Ke Y, Liu Y, Liu R, et al. Methanol steam reforming performance optimisation of cylindrical microreactor for hydrogen production utilising error backpropagation and genetic algorithm. Chemical Engineering Journal. 2019;357:641-54.
[3] Chen W-H, Shen C-T. Partial oxidation of methanol over a Pt/Al2O3 catalyst enhanced by sprays. Energy. 2016;106:1-12.
[4] Sepehri S, Rezaei M, Wang Y, Younesi A, Arandiyan H. The evaluation of autothermal methane reforming for hydrogen production over Ni/CeO2 catalysts. International Journal of Hydrogen Energy. 2018;43:22340-6.
[5] Richards N, Needels J, Erickson P. Autothermal-reformation enhancement using a stratified-catalyst technique. International Journal of Hydrogen Energy. 2017;42:25914-23.
[6] Luneau M, Gianotti E, Meunier FC, Mirodatos C, Puzenat E, Schuurman Y, et al. Deactivation mechanism of Ni supported on Mg-Al spinel during autothermal reforming of model biogas. Applied Catalysis B: Environmental. 2017;203:289-99.
[7] Chen W-H, Lin B-J. Hydrogen production and thermal behavior of methanol autothermal reforming and steam reforming triggered by microwave heating. International Journal of Hydrogen Energy. 2013;38:9973-83.
[8] Chen W-H, Guo Y-Z. Hydrogen production characteristics of methanol partial oxidation under sprays with ultra-low Pt and Pd contents in catalysts. Fuel. 2018;222:599-609.
[9] Jampa S, Jamieson AM, Chaisuwan T, Luengnaruemitchai A, Wongkasemjit S. Achievement of hydrogen production from autothermal steam reforming of methanol over Cu-loaded mesoporous CeO2 and Cu-loaded mesoporous CeO2–ZrO2

catalysts. International Journal of Hydrogen Energy. 2017;42:15073-84.
[10] Iruretagoyena D, Hellgardt K, Chadwick D. Towards autothermal hydrogen production by sorption-enhanced water gas shift and methanol reforming: A thermodynamic analysis. International Journal of Hydrogen Energy. 2018;43:4211-22.
[11] Yang J, Liu Y, Deng J, Xie S, Hou Z, Zhao X, et al. PtxCo/meso-MnOy: Highly efficient catalysts for low-temperature methanol combustion. Catalysis Today. 2019;332:168-76.

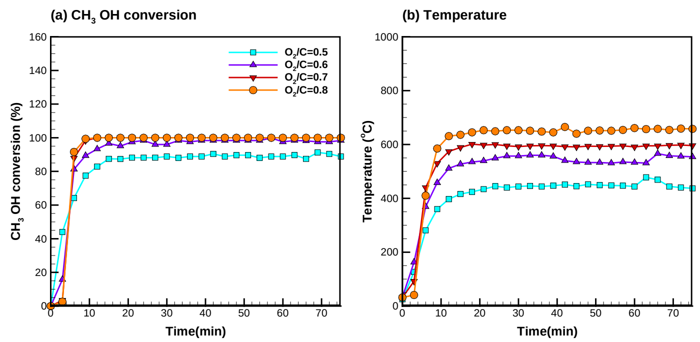

Fig. 1. Temporal distributions of (a) CH_3OH conversion and (b) Temperature of POM at various O_2/C ratios.

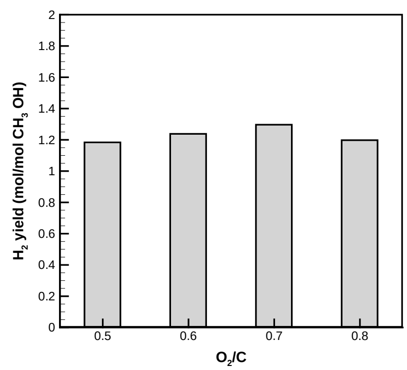

Fig. 2. Profiles of H_2 yield of POM at various O_2/C ratios.

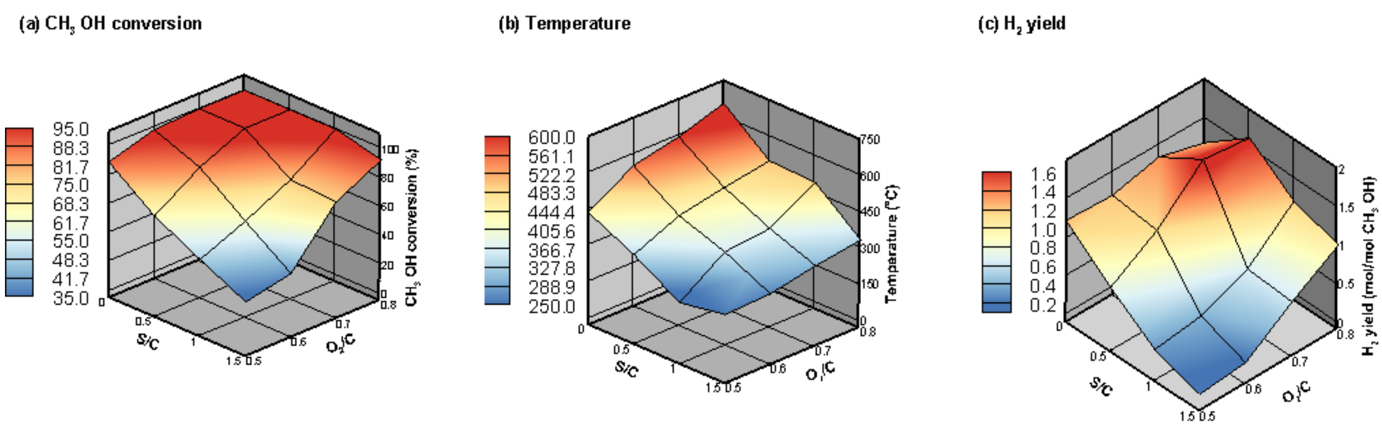

Fig. 3. Three dimensional profile of (a) CH_3OH conversion, (b) Temperature, and (c) H_2 yield of ATR with various S/C ratios and O_2/C ratios.