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Experimental study on the performance of oxidative dry reforming from simulated biogas

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Abstract

This study was to investigate the CO₂ reforming under isothermal condition. The fuel conversion efficiency and hydrogen-rich gas production were enhanced via the oxidative dry reforming (ODR) from simulated biogas (50%-CH₄+50%-CO₂). This paper covers two subjects. The first was to investigate the CO₂ conversion characteristics under various feeding molar ratios (e.g. H₂/CO₂ and O₂/CH₄ molar ratio). In the second, the whole performance index of the reformer was investigated. The experimental results demonstrate that the CO₂ reduction capacity of methane is superior to that of hydrogen. This effect is clearer under higher reaction temperatures. The ODR reaction experiment results indicate that adding appropriate amounts of oxidants can increase the methane conversion and reforming efficiency. But, the excessive oxidizes could reduce the CO₂ conversion efficiency. Additionally, at high DR/ODR reaction temperatures, reverse water-gas shifting (RWGS) side reactions become significant, which can reduce CO₂ to CO efficiently, thereby improving the CO₂ conversion efficiency. Overall, the optimal methane conversion efficiency can reach 100% in ODR reaction (O₂/CH₄ molar ratio=0.5). The CO₂ conversion efficiency is based on DR reactions (CO₂/CH₄ molar ratio=1) reaching between 57% and 95%.

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Keywords: Oxidative dry reforming; Biogas; Reverse water-gas shifting; Methanation; Hydrogen-rich syngas production

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1. Introduction

International energy development goals can be divided roughly into short-term, mid-term, and long-term goals. Short-term goals focus on increasing effective energy use, such as using waste heat, recycling waste electricity, and reducing carbon emissions. Mid-term goals involve increasing renewable energy ratios, such as industrialized solar energy, renewable energy, wind energy, clean coal technology, and biomass energy. Long-term goals include hydrogen energy, ocean energy, and carbon dioxide capture/storage (CCS). Applying CO₂ reforming to reduce and convert CO₂ satisfies the energy development requirements of each stage. Additionally, biogas (CH₄+CO₂ mixture) and industrial emission sources are extensive. Thus, using this reforming technology to process biogas appropriately enables efficient energy saving and carbon reduction. And they are not only a low-carbon fuel, but also a valuable source of alternative energy. Recently published papers related to energy policy and sustainable energy indicated that several countries are promoting low-carbon energy from biogas [1,2]. The composition of biogas is complex, including CO₂, CH₄, H₂, CO, H₂O, NH₃, H₂S, HCs, and N₂ [3], which were determined by waste sources and environmental conditions. Biogas would be a promising source of alternative energy if properly managed. Dry reforming (DR) is a suitable approach for fuel processing to produce hydrogen. The other CO₂-rich gas reforming method were reverse water-gas shifting (RWGS) and methanation. The process are shown in equations (1), (2) and (3).

Dry reforming:



Reverse water-gas shifting:



CO₂ methnation:



As a whole, CO₂-rich gas reforming is an endothermic reaction and carbon-rich reaction. In addition, the carbon dioxide molecule has a double-bond structure, and bond breaking is difficult. In the oxidative dry reforming (ODR) case, the O₂ also adsorbs on the active site of catalyst surface and then preferentially reacts with carbon atoms onto the active site. Therefore, carbon does not accumulate on the surface of the catalyst during the reforming reaction. From the literature results [4-6], the reforming performance was affect by feeding molar ratio, especially in oxidises. Consequently, this study focused on a reforming parameter selection for oxidative dry reforming in isothermal condition.

2. Experimental set-up and method

The experimental apparatus included a reforming unit, data acquisition system, reactant supply system, gas sampling/analyzing system. The equipment with isothermal heating used furnaces to simulate the conditions of waste heat environments and perform DR, ODR, RWGS, and methanation reactions, as shown in Figure 1. The reforming unit consisted of the catalyst reaction bed and reactant preheating zone. Catalyst was made of noble metal (Pt-Ru base), coated over the alumina-ceria washcoat (Al₂O₃) on ceramic sphere (Al₂O₃). In order to know the reaction temperature in the reforming reaction, the catalytic

reaction temperature were measured in the downstream of the catalyst bed. A gas chromatographer (Agilent GC-6850) and a real-time gas analyzer were used for determining the gas species in the products.

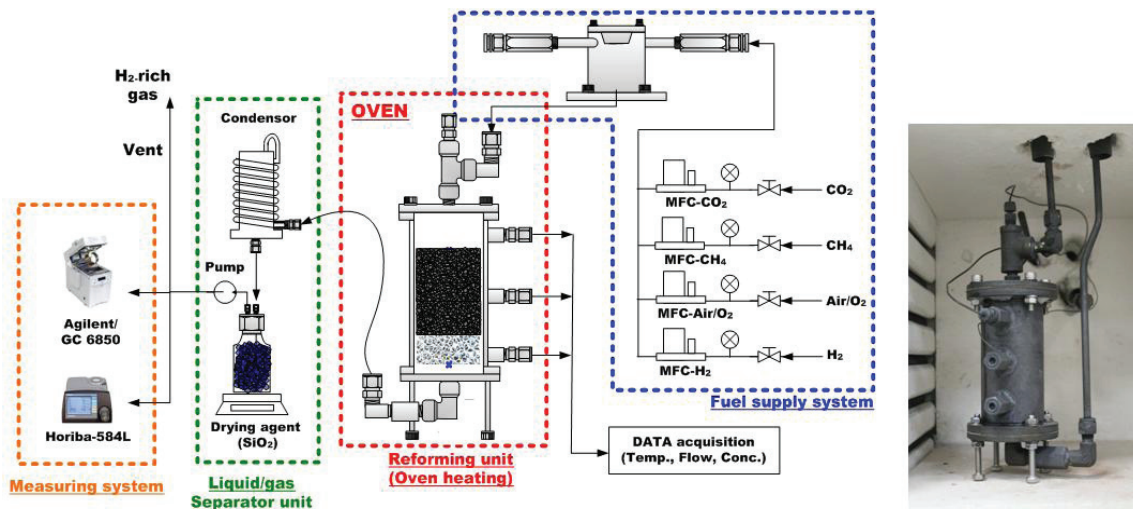


Fig. 1. Schematic of the experimental set-up.

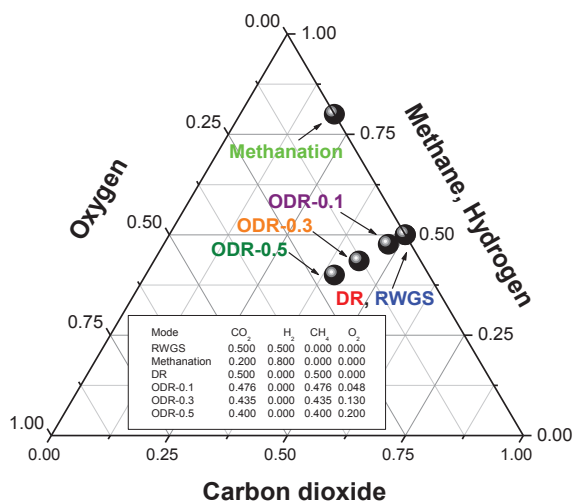


Fig. 2. The location of reforming modes in the O₂-CO₂-CH₄(H₂) ternary diagram.

This study investigated the activity of CO₂-rich gas reforming with catalyst inlet temperatures. CO₂ thermo-chemical reactions must be performed by the reduction reaction. Thus, we also used hydrogen and methane to investigate reduction reactions. Hydrogen reduction methods include RWGS and methanation reactions. DR and ODR reactions are the methane reduction methods. Figure 2 shows the triangular relationship of the CO₂-O₂-CH₄ (H₂) mole fractions in the various reforming methods. In the DR and RWGS reactions, the reducing agents (CH₄ or H₂) were 0.5 of the reactant mole fraction. ODR reactants are DR reactions that match various oxygen fractions (an O₂/CH₄ ratio between 0.1 and 0.5). The results in Figure 2 indicate that the CO₂ in the experimental parameter setting range comprised less than 0.5 of

the total input mole fraction. The mole fraction of the reducing agents (CH₄ and H₂) ranged between 0.4 and 0.8. A suitable amount of oxidants was added to the ODR reactions to contribute to the reforming reactions. The oxygen mole fraction was less than 0.2. The mole fractions of all the reactant types are indicated by their placement in Figure 2.

The main composition of simulated biogas, namely 50% CH₄, 50% CO₂, was used for the reactant species setting in this study. Thus, the reforming parameters were set as carbon dioxide feeding rate 3 NL/min, the H₂/CO₂ molar ratio between 1 and 4, the CO₂/CH₄ molar ratio was set as 1, the O₂/CH₄ molar ratio between 0 to 0.5, and the catalyst volume was 92 ml. The effect of reactant feeding ratio on the reforming performance was investigated. The catalyst inlet temperature was set as ranged between 700°C and 1000°C, the operation pressure was set at atmosphere condition.

3. Results and discussion

3.1 Theoretical chemical equilibrium product analysis

Before conducting methane and CO₂ reforming (e.g. DR) reactions, the operational range of the control parameters must be established. However, CO₂ reforming reactions are complex, and the side reactions are extremely diverse. Side reactions include CO₂ decomposition (CD), Boudouard reactions (BR), reverse water-gas shifting, and methanation reactions (MR). In this section, we examine the theoretical chemical equilibrium of the CO₂ reforming reaction, including the reaction enthalpy and reaction constants. This study conducted theoretical analysis based on the minimization of Gibbs free energy. Figure 3 shows the relationship between the reaction temperature and enthalpy of reaction at various CO₂ reforming reaction settings. Equation (4) is the enthalpy of reaction calculation method. Theoretical calculations indicate that CO₂ reforming reactions must be performed at high temperatures (RT ≅ 800°C) to achieve chemical equilibrium. Additionally, these reactions are all endothermic. DR reaction enthalpy values are substantially higher than those of steam reforming (SR). This indicates that external heat sources are required for the CO₂ reforming process to provide the necessary heat for the reaction.

$$\Delta H = \sum_P n_e (\overline{h}_f^0 + \Delta \overline{h})_e - \sum_R n_i (\overline{h}_f^0 + \Delta \overline{h})_i \quad (4)$$

Figure 4 shows the relationship between reaction temperatures and reaction equilibrium constants in various CO₂ reforming reactions. Equations (5), and (6) show the free energy and reaction constant calculation methods. The data in Figure 4 show that during CO₂ conversion, excluding methanation reactions, higher reaction temperatures facilitate spontaneous reactions. This indicates that high-temperature environments are beneficial for reducing CO₂ and CO. Overall, DR, BR, and RWGS are positively correlated with higher reaction temperatures. Additionally, they react spontaneously only at temperatures that exceed 800°C. CD and MR are unlikely to occur at such high temperatures.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (5)$$

$$\ln k = \frac{-\Delta G^0}{R_u T} \quad (6)$$

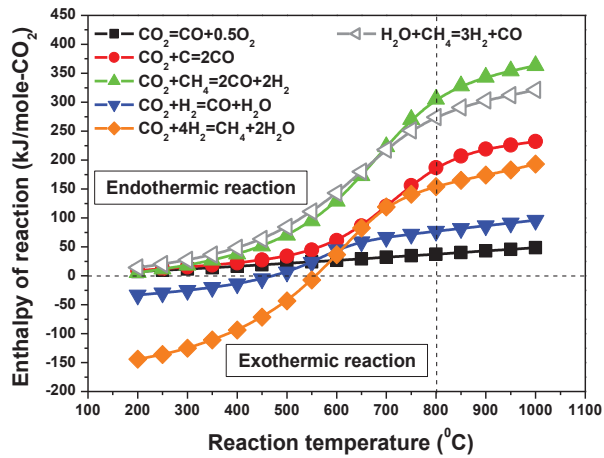


Fig. 3. Relationship between reaction temperature and enthalpy of reaction under various reforming mode.

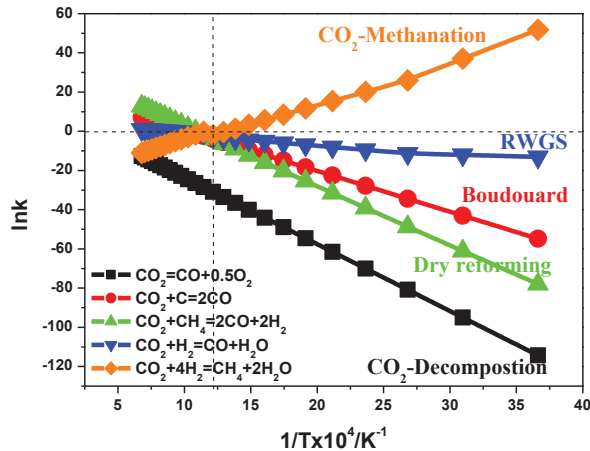


Fig. 4. Relationship between reaction temperature and reaction equilibrium constant under various reforming mode.

3.2 Effect of feeding molar ratio on reforming performance

Figure 5 shows the influence of Pt-Ru/Al₂O₃ catalysts on CO₂ conversion under various catalyst inlet temperature. The control parameters were the reforming reaction mode and catalyst inlet temperature. The CO₂ feed flow rate was set to 3NL/min and the catalyst volume was 92 ml. The reforming methods can be divided into two categories: hydrogenation and methane reforming. In sequential order, our methods were RWGS, methanation, DR, and ODR. The catalyst inlet temperatures equaled the environmental temperatures and ranged between 700°C and 1000°C. The experimental results indicate that higher catalyst inlet temperatures facilitated CO₂ conversion in all reforming reactions. Methanation reactions

increased the reduction opportunities because their H_2/CO_2 ratios are high. Therefore, the CO_2 conversion ranged between 78% and 87%. The CO_2 reforming efficiency of RWGS reactions ranged between 43% and 55%. If reducing reactions are performed using CH_4 , DR provides superior CO_2 conversion efficiency. However, adding oxidants reduces the CO_2 conversion opportunities. Overall, the DR reducing capacity is significantly higher than that of RWGS under the operating parameters. The DR reducing capacity can also exceed that of methanation at high temperatures. Overall trends echo the reaction constant calculation results (as shown in Figure 4). Therefore, methane is better able to reduce CO_2 within the parameter settings compared to hydrogen.

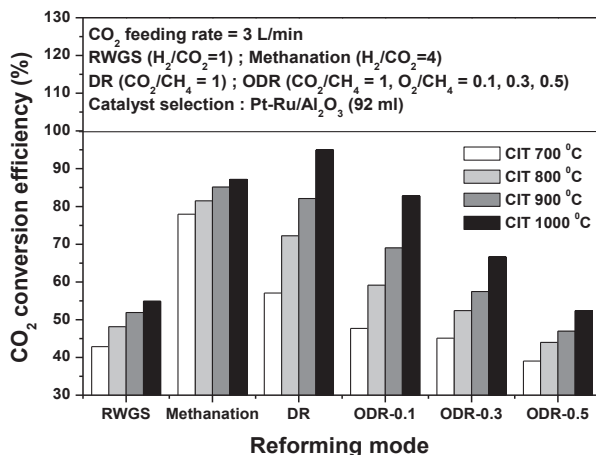


Fig. 5. The CO_2 conversion efficiency of different reforming mode under various catalyst inlet temperature.

Figure 6 shows the relationship between the reformate gas temperature and \ln (CO production) under various reforming reactions. CO_2 conversion effects can be evaluated by the CO yield. Additionally, the Arrhenius equation can be employed to assess the relationship between each reaction and the CO output activation energy. The reformate gas temperature in this section represent the catalyst bed outlet gas temperatures. The catalyst inlet temperatures were controlled between 700°C and 1000°C. Because the CO_2 -rich gas reforming process is an endothermic reaction, the reformate gas temperature is significantly lower than the preheating temperature of the reactant. Furthermore, heat absorption is substantial in DR and ODR reactions. Therefore, the reformate gas temperatures are also lower than those of RWGS and methanation. Theoretical calculations and experimental results prove that the carbon atoms within CH_4 facilitate CO_2 reducing reactions. Thus, this produces more CO compared to hydrogen reducing methods. The hydrogen products created from methane reforming can further perform RWGS reactions with CO_2 . Therefore, using methane for CO_2 conversion is more effective and substantially reduces greenhouse gases. The activation energies of each reaction indicate that DR and ODR-0.1 have higher activation energy. Thus, adding an appropriate amount of hydrogen reduces the activation energy in methane and CO_2 reactions. Furthermore, the activation energy may be less than that of hydrogen reduction (RWGS and methanation) methods.

Figure 7 shows the relationship between the reformate gas temperature and conversion efficiencies under various reforming mode. The reforming parameters are O_2/CH_4 ratios between 0 and 0.5 and catalyst inlet temperatures between 700°C and 1000°C. The solid symbol represents the methane conversion efficiency and the hollow symbol represents the CO_2 conversion efficiency. Higher O_2/CH_4

ratios enable the provision of partial oxidation heat for increasing the reformat gas temperature. Although this increases the methane conversion efficiency, the syngas in the products is oxidized by the introduction of excess oxygen. This oxidizes the CH_4 and CO into CO_2 , reducing the CO_2 conversion efficiency. This is primarily because the partially oxidized reaction constants are significantly higher than those of DR. Thus, CO_2 is not conducive to reducing reactions with methane at high oxygen concentrations. Additionally, the CO_2 conversion efficiency is higher than that of CH_4 in the DR reaction process mainly because of the influence from RWGS side reactions. Hydrogen within the products is used at sufficient reformat gas temperatures to facilitate CO_2 reducing reactions. Overall, the optimum methane conversion efficiency in ODR reactions can reach 100%. CO_2 conversion efficiency is optimal under DR reaction conditions, reaching between 57% and 95%.

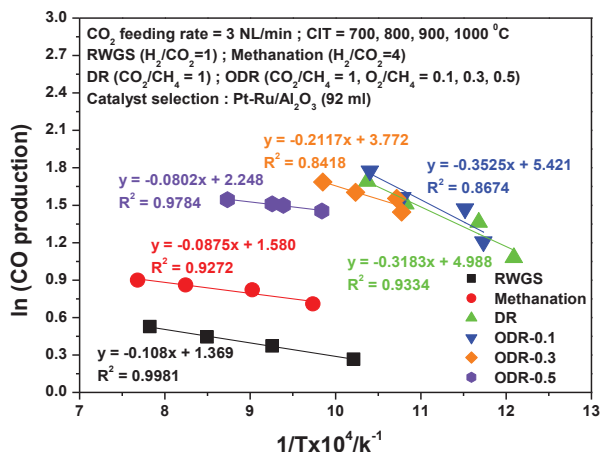


Fig. 6. Relationship between the reformat gas temperature and ln(CO) production under various reforming mode.

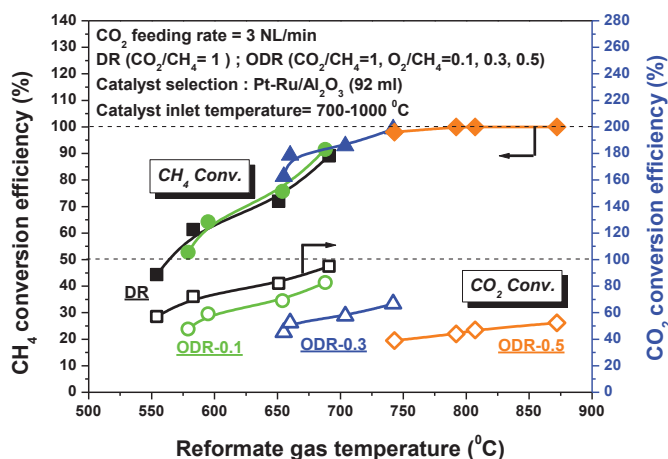


Fig. 7. Relationship between the reformat gas temperature (catalyst outlet temperature) and conversion efficiencies under various reforming mode.

Figures 8 (A) and (B) show the influence of additional oxygen on the H₂ and CO yield and the reforming efficiency under various catalyst inlet temperatures. This study used thermo-chemical

conversion methods. Therefore, with external heat, the CO yield may exceed the theoretical production capacity of CH₄. This experimental results prove that adding an appropriate amount of oxygen at lower temperatures can increase fuel conversion efficiently and improve the H₂ and CO yields. However, at higher temperatures, if the methane is already entirely converted, adding extra oxygen leads to excessive oxidation reactions because of the syngas. This subsequently reduces syngas production, as shown in Figure 8 (A). Overall, if the waste heat cannot be recovered efficiently during the thermo-chemical conversion process, adding appropriate amounts of oxygen is an effective method for increasing syngas production. This method also increases the fuel reforming efficiency, as shown in Figure 8 (B). In summary, adding an appropriate amount of oxidants can increase reformat gas temperature efficiently. This method prevents coking on the catalyst surface, supports the stability of the produced gas, and increases the reforming efficiency. Additionally, at high DR/ODR reaction temperatures, RWGS side reactions become signification, which can reduce CO₂ to CO efficiently, thereby improving the CO₂ conversion efficiency.

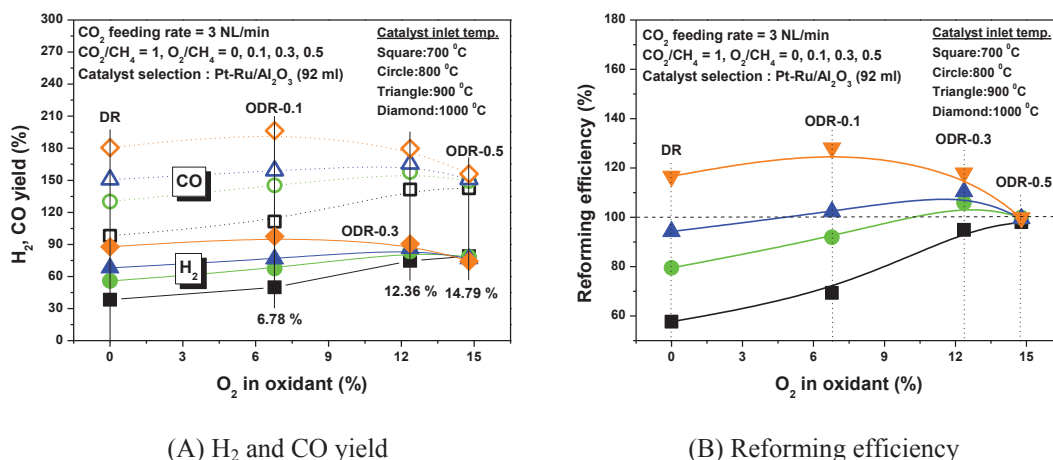


Fig. 8. Effect of O₂ in oxidant on syngas yield and reforming efficiency under various catalyst inlet temperature.

4 Conclusions

In summary, we used experiments to investigate the performance of syngas produced by oxidative dry reforming from simulated biogas (CO₂/CH₄ molar ratio=1). We examined the selection of reforming parameters. The control parameters included the CO₂ feed flow rate, H₂/CO₂ ratio, O₂/CH₄ ratio and catalyst inlet temperature. The experimental results support the following conclusions:

1. Catalyst activity testing indicates that Pt-Ru/Al₂O₃ is more effective for CO₂ reforming. Additionally, the RWGS, methanation, DR, and ODR reforming experiment results indicate that the CO₂ reduction capacity of methane is superior to that of hydrogen. This effect is clearer under higher reaction temperatures.
2. Additionally, the CO₂ conversion efficiency is higher than that of CH₄ in the DR reaction process mainly because of the influence from RWGS side reactions. Hydrogen within the products is used at sufficient reformat gas temperatures to facilitate CO₂ reducing reactions. Overall, the optimal methane conversion efficiency rate can reach 100% in ODR reactions. The CO₂ conversion

efficiency is based on DR reactions reaching between 57% and 95% without adding oxygen.

3. The ODR reaction experiment results indicate that adding appropriate amounts of oxidants can increase reformat gas temperatures efficiently. This subsequently increases the methane conversion and reforming efficiency. However, the syngas in the products is oxidized by introducing excessive oxygen. This oxidizes the methane and CO into CO₂, reducing the CO₂ conversion efficiency.

Acknowledgements

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