

Absorption-enhanced methanol steam reforming for low-temperature hydrogen production with carbon capture

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ABSTRACT

Methanol is an ideal medium for hydrogen storage and transportation, and is expected to play a crucial role for the low carbon energy system in the foreseeable future. However, hydrogen derivation from methanol (via steam reforming) is faced by critical barriers including high reaction temperature (e.g., 250-300°C) and low methanol conversion (65% at < 200°C), and hydrogen purification process is usually indispensable for deriving high-purity H₂. We propose a new method of H₂ absorption-enhanced methanol steam reforming to tackle such challenges. The effectiveness of the method is further verified by a prototype reactor sequentially filled with bulk catalyst (CuO/ZnO/Al₂O₃) and bulk hydrogen absorbent (LaNi_{4.3}Al_{0.7} alloy), tested at 200°C and 1 bar conditions. As H₂ is absorbed by the alloy, both the reforming reaction and water-gas shift reaction are shifted forward, effectively enhancing the conversion of methanol. High-purity H₂ is derived by regenerating the alloy under inert gas purge at 200°C, 700 mL min⁻¹. During the 10 min reaction step, the H₂ can be nearly completely separated. Furthermore, high purity hydrogen (~85% molar concentration) can be obtained in the regeneration step. Simulations considering the catalytic reaction kinetics further demonstrate the intensification effect of the absorption-enhanced method with different number of cycles and H₂ separation ratios. Major advantages of the new method, including low reaction temperature, high-purity H₂, non-precious material and membrane-less design, indicate great potentials for commercial applications. The remarkably reduced temperature also opens up wide possibilities of integrating with solar thermal energy and industrial waste heat for sustainable H₂ production with significantly reduced CO₂ footprint at the same time.

Keywords: Hydrogen; methanol; absorption-enhanced reforming; CO₂ capture; low-temperature.

NONMENCLATURE

Abbreviations

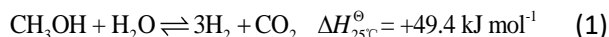
MSR	Methanol Steam Reforming
AE-MSR	Absorption-enhanced Methanol Steam Reforming
LHSV	Liquid Hourly Space Velocity
PSA	Pressure Swing Adsorption
S/C	Molar ratio of steam to CH ₃ OH

Symbols

r_R	Reaction rate of MSR
k	Rate constant of MSR
P_i	Partial pressure of component i
F_i^{out}	Outlet flow rate of component i
$F_{\text{CH}_3\text{OH}}^{\text{in}}$	Inlet flow rate of methanol
$F_{\text{H}_2\text{-ad}}$	Molar flow rate of H ₂ absorbed
F_{H_2}	Molar flow rate of H ₂ generated by the MSR

1. INTRODUCTION

Hydrogen is considered as one of the most desirable alternatives to traditional fossil fuels in the future sustainable energy system, mainly due to its high energy density, cleanliness, and wide range of applications [1, 2]. Large-scale application and deployment of hydrogen are limited by the difficulty and high cost of the storage and transportation process [3, 4]. The ease of producing hydrogen from methanol steam reforming (MSR) provides a feasible scheme for the storage and distribution of hydrogen by way of a stable liquid under ambient conditions [5]. Meanwhile, the methanol hydrogen production process is an essential step in the future carbon-neutral energy cycle and has an important role to play in accelerating the transition to decarbonization [6]. However, hydrogen derivation from methanol (via steam reforming, Eq. (1)) faces the critical barriers including high reaction temperature (e.g., 250-300°C) and low methanol conversion (65% at < 200°C), and hydrogen purification process is usually indispensable for deriving high-purity H₂.



Faced with these issues, intensification of methanol reforming processes, such as separation-enhanced MSR based on Le Chatelier's principle, has become an attractive approach to enhance the reaction conversion, produce high-purity H_2 and CO_2 -rich gas stream [7-10]. Separating H_2 is better than separating CO_2 in the MSR process as H_2 makes up majority of the product which could significantly improve the reaction conversion [11]. Some researchers have proposed methods of selective removal of H_2 through membrane reactors, which allows direct access to ultra-high-purity hydrogen and reduces the conversion temperature of methanol to 200-250°C [12, 13]. However, the high energy consumption required for sufficient hydrogen permeation rates [14], the vulnerability of membrane materials [15], and the high costs [14] make it difficult to apply membrane reactors to practical applications.

In contrast to membranes, materials for hydrogen storage, such as metal alloys, might indicate a potentially different way of hydrogen separation [16, 17]. H_2 in the gas mixture can be absorbed by metal alloys through hydride reaction and released by decreasing the partial pressure of H_2 or increasing the temperature. Rare-earth alloys are considered promising materials for hydrogen separation due to their superior thermodynamic properties, outstanding stability and kinetic properties [18, 19]. Theoretically, H_2 absorption separation can realize the same function as membrane separation.

In this work, a new method of H_2 absorption-enhanced methanol steam reforming (AE-MSR) is proposed to tackle the challenges above. The effectiveness of the method is verified by a prototype reactor sequentially filled with bulk catalyst ($\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$) and bulk hydrogen absorbent ($\text{LaNi}_{4.3}\text{Al}_{0.7}$ alloy), tested at 200°C and 1 bar conditions. Based on experiments, comparison of the methanol conversion rate of the new method with that of the traditional MSR is carried out by simulations under various number of cycles and H_2 separation ratios. The superiority of the new method compared to traditional MSR is demonstrated by experiments and simulations.

2. METHOD DESCRIPTION AND EXPERIMENTAL

2.1 Method description

The schematic of the AE-MSR method based on hydrogen absorbent is displayed in Fig. 1. The reactor is filled sequentially with MSR catalyst and H_2 absorbent in the form of alternating packed beds for MSR reaction and separation of H_2 , respectively. When the absorbent is saturated, the absorbent can be regenerated isothermally by reducing the H_2 partial pressure. H_2 and

CO_2 are separated and flow out at different phases of operation, so that high-purity H_2 can be produced and CO_2 can be captured directly.

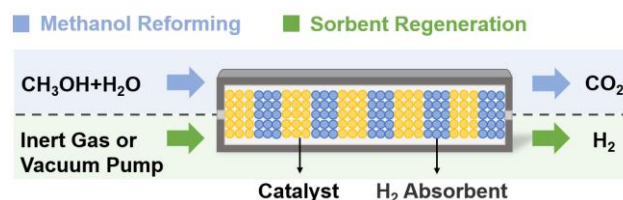


Fig.1 Schematic of the AE-MSR reactor based on H_2 absorbent.

2.2 Materials

The catalyst used in the MSR was a commercial catalyst of CNZ-1 type from Southwest Institute of Chemical Co., Ltd. with the composition of $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$. The catalyst was crushed into 0.25-0.60 mm particles for the experiments. $\text{LaNi}_{4.3}\text{Al}_{0.7}$ alloy in reference [21] was used as the H_2 absorbent to achieve the product directly separation.

Before the reaction, the fresh catalyst was reduced under the ambience of 15% H_2 and 85% helium at 230°C for 2 h with 200 mL min^{-1} flow rate. In addition, the H_2 absorbent was activated and maintained in an atmosphere of pure hydrogen at 100°C and 3 bar for 30 min.

2.3 MSR and AE-MSR experiment

The AE-MSR experiments were carried out in a fixed-bed reactor, as shown in Fig. 2. The reactor contained 1 g of catalyst and 150 g of H_2 absorbent in the form of a sectional packed bed. The amounts of catalyst and H_2 absorbent were determined based on material properties, reaction temperature, liquid hourly space velocity (LHSV) of feed and cycling strategy parameters. When the bed temperature was stable at 200°C, an aqueous methanol solution with a specific molar ratio of steam to CH_3OH (S/C) was pumped into the steam generator by a high-pressure pump and then entered the reactor. The compositions of gases passing through the reactor were analyzed by mass spectrometer (Omnistar GSD 320) after condensation of unreacted methanol and steam. When the $\text{LaNi}_{4.3}\text{Al}_{0.7}$ alloy reached the maximum H_2 absorption capacity, the reaction was stopped and H_2 absorbent was regenerated for reuse by reducing the partial pressure of H_2 with 700 mL min^{-1} of helium at 200°C. It should be noted that the purge with helium is a requirement for mass spectrometry measurements and in practice water vapor purge or vacuum pumping can be used to obtain a pure regenerative gas stream directly. The gas components in the regeneration step were still passed into the mass spectrometer for detection. During

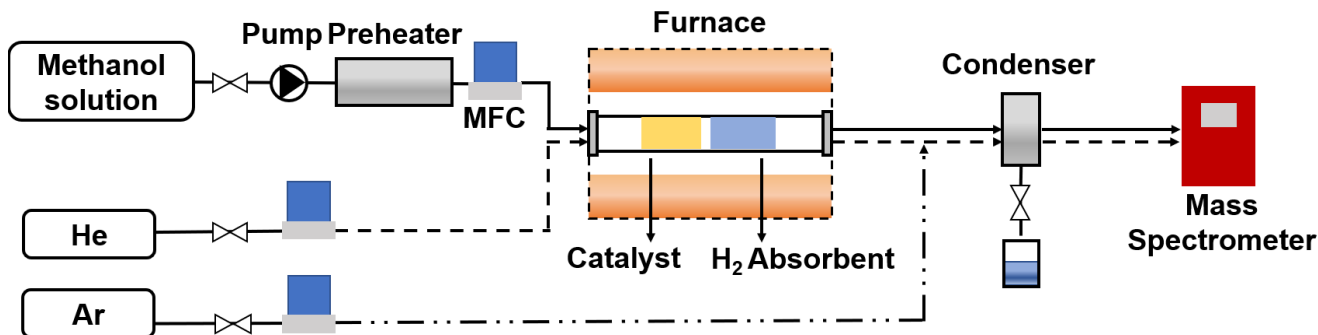


Fig. 2 A schematic of the experimental system.

the experiment, Argon as standard gas was mixed into the gas path from the reactor outlet and used to calculate the flow rate of other components.

A traditional MSR experiment at 200°C, 1 bar and LHSV of 0.5-2 mL $g_{cat}^{-1} h^{-1}$ was carried out in the same experimental system as a comparison, in which only 1 g of catalyst was loaded in the reactor.

It should be noted that, as shown in Fig. 1, the catalyst and H₂ absorbent in the reactor are packed in multiple sections to achieve the intensification effect. However, in order to analyze the effect of each improvement, only one section was filled in the reactor in the actual experiment. By circulating the outlet components into the reactor inlet, the effect of multi-stage absorption enhancement was equivalently achieved.

Methanol conversion rate was calculated using the following equation:

$$X_{CH_3OH} = \frac{F_{CO_2}^{out} + F_{CO}^{out} + F_{CH_4}^{out}}{F_{CH_3OH}^{in}} \times 100\% \quad (2)$$

where F_i^{out} is the outlet flow rate of component i , $F_{CH_3OH}^{in}$ is the inlet flow rate of methanol.

3. PROCESS SIMULATION

On the basis of the experiments, AE-MSR method were simulated in a plug flow reactor system (Fig. 3 (a)) and the absorption-enhanced systems (Fig. 3 (b)) with different numbers ($n = 2,3,4$) of cycles (i.e., a combination of a plug flow reactor and a H₂ separator) using Aspen Plus software. The kinetic equation for the

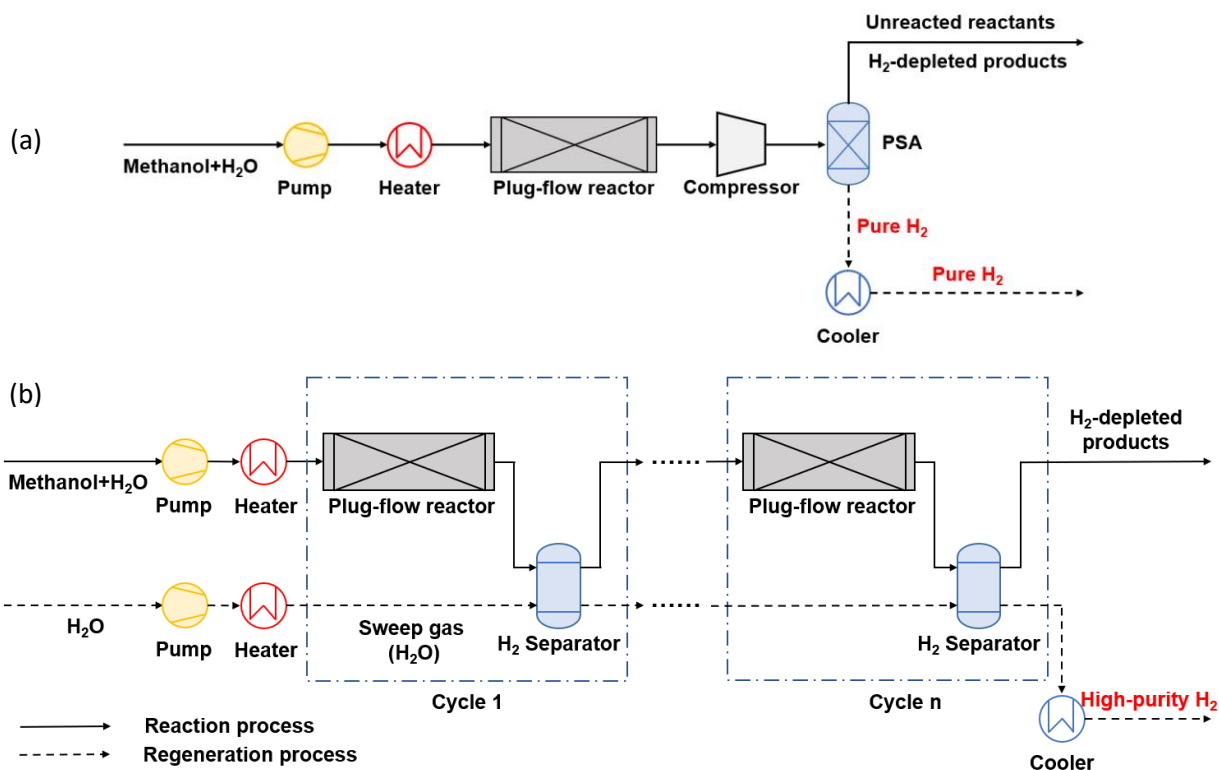


Fig. 3 Block flow diagram for MSR in (a) traditional system and (b) absorption-enhanced systems.

Cu/ZnO/Al₂O₃ catalyst proposed by Jiang et. al [20] was used in the reactor, given as:

$$r_R = kP_{\text{CH}_3\text{OH}}^{0.26} P_{\text{H}_2\text{O}}^{0.03} P_{\text{H}_2}^{-0.2} \quad (3)$$

where r_R is the reaction rate of MSR; k is the rate constant of MSR; P_i represents the partial pressure of component i .

The Peng-Robinson method was chosen for the simulations. A mixture of 1 kmol h⁻¹ of methanol and 1.5 kmol h⁻¹ of water was heated and fed to the reactors. After isothermal and isobaric reactions in each reactor, the H₂ in the product stream was turned into a pure H₂ stream under different routes. In the traditional system, the product stream was passed through one of the commercial H₂ separation technologies, the pressure swing adsorption (PSA) process, to separate H₂ from other components. In addition, in the absorption-enhanced system, the H₂ in the product stream from the reactors was absorbed in the various H₂ separators. Thereafter, in the regeneration process, the H₂ absorbed in the separators was purged out using water vapor as the purge gas. After passing through the condenser, the water was condensed and pure H₂ was obtained. In order to improve the generality of the simulation results, H₂ separation ratio was used to measure the absorption performance of the absorbent, defined as follows:

$$H_2 \text{ separation ratio} = \frac{F_{H_2\text{-ad}}}{F_{H_2}} \quad (4)$$

where $F_{H_2\text{-ad}}$ is the molar flow rate of H₂ absorbed, F_{H_2} is the molar flow rate of H₂ generated by the MSR.

4. RESULTS AND DISCUSSIONS

4.1 Experimental results

To demonstrate the feasibility of the method, experimental investigations were performed with CuO/ZnO/Al₂O₃ catalyst and LaNi_{4.3}Al_{0.7} alloy as H₂ absorbent. In the experiments, the effectiveness of H₂ separation and regeneration was first test at 200°C with a single cycle. Afterwards, the performance of the AE-MSR method was tested in the multiple cycles.

4.1.1 First reaction step and regeneration step

Taking the first cycle as an example, the actual performance of the AE-MSR method was investigated in separating the products. The experimental conditions for the first cycle were 200°C, 1 bar and LHSV = 2 mL g_{cat}⁻¹ h⁻¹.

Fig. 4 shows the profiles for the main gas products (dry basis) coming from AE-MSR reactor during the first cycle. The cycle was divided into 2 steps, namely reaction step (9 min, 25 mL min⁻¹ helium as carrier gas) and regeneration step (40 min, 700 mL min⁻¹ helium purge).

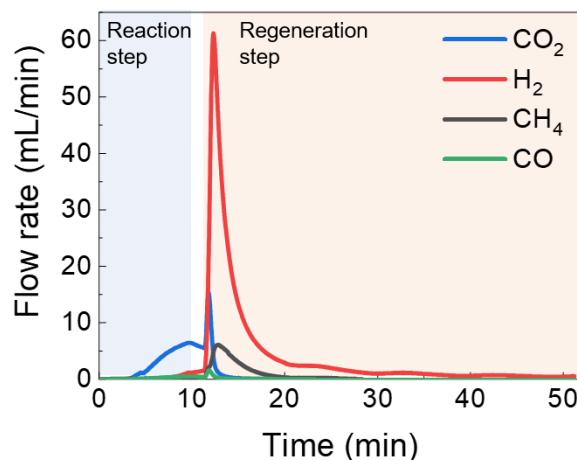


Fig. 4 Flow rate of gas species in the first cycle.

A dwelling period of 2 min was added between the two steps. In the reaction step, H₂ was absorbed by LaNi_{4.3}Al_{0.7} alloy via hydride reaction resulting in a high-purity CO₂ outlet gas stream (84.10%) and low CH₄, CO and H₂ concentrations (4.94%, 4.66% and 6.30%, respectively). During the regeneration step, a H₂-rich gas stream (81.66%) was obtained, with the remaining components being CH₄ (10.62%), CO₂ (6.58%) and a minor amount of CO (1.14%). Among these impurities, CO₂ and CO are the residues resulting from abruptly step transformation, which can be rapidly (~2 min) removed from the reactor by purging and can be eliminated by optimizing the separation strategy. The relatively large amount of methane impurity may be from side reactions. Some studies have shown that LaNi₅-type alloys are able to catalyze the hydrogenation of CO₂ and CO at about 200°C [22, 23]. Pre- or simultaneous separation of CO₂ when separating hydrogen, as in the literature [24], may be able to inhibit the production of methane. After optimizing the regeneration strategy and limiting the methanation side reactions, it is expected to obtain a higher purity H₂ stream.

4.1.2 Multi-cycle AE-MSR tests

AE-MSR were performed in multiple cycles at 200°C, LHSV = 2 mL g_{cat}⁻¹ h⁻¹. Each cycle consists of a reaction step of 10 min and a regeneration step of 40 min to regenerate the H₂ absorbent by 700 mL min⁻¹ helium purging. The outlet gas stream of the previous cycle was passed to the reactor inlet of the next cycle by means of gas blending.

In our experiments, three cycles of absorption enhanced MSR process have been successfully implemented. During the reaction step of each cycle, almost no H₂ flows out of the reactor outlet. A high concentration of H₂ stream was obtained in the regeneration step of each cycle. The flow rate of gas species in the regeneration step of three cycle are shown

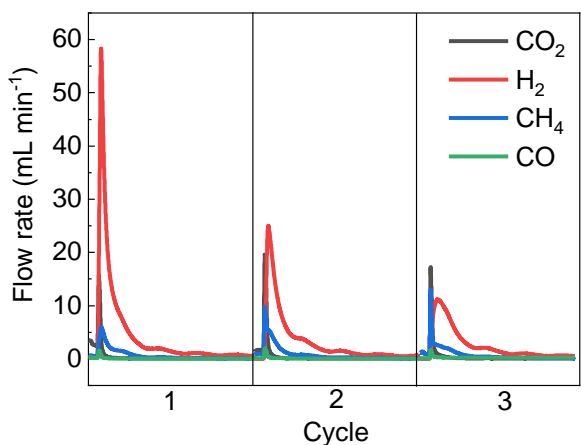


Fig. 5 Flow rate of gas species in the regeneration step of three cycles.

in Fig. 5. As the cycle increases, the total hydrogen production gradually increases. However, due to the decrease in methanol reactants at the inlet of each cycle, the hydrogen increment gradually decreases until the methanol is completely converted. At the same time, it is undeniable that the amount and inhibition of methane increases as the cycle increases. Future research on inhibiting methane production and increasing the hydrogen absorption capacity of the H₂ absorbent may further demonstrate the superiority of the AE-MSR method.

4.2 Simulation results

Based on the experiments, the influence of key parameters such as the number of cycles and the H₂ separation ratio are studied in simulations.

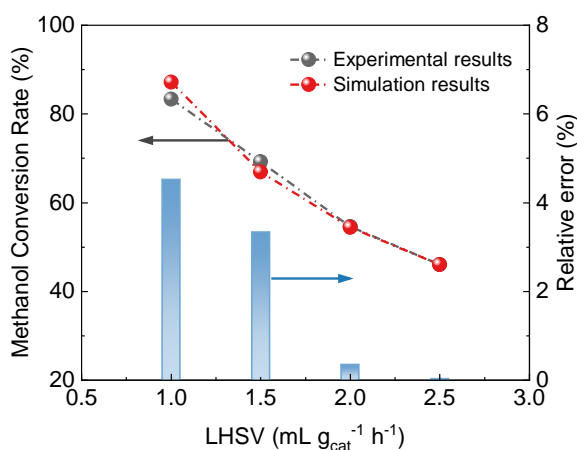


Fig. 6 Model validation of simulation results with experimental results at 200°C and various LHSV.

Firstly, to verify the model system, the methanol conversion rate tested in the traditional reactor was compared to the simulation results. The reaction temperature was set at 200°C and the reaction pressure was set at 1 bar. As shown in Fig. 6, the methanol

conversion rate versus LHSV fits well with the experimental results.

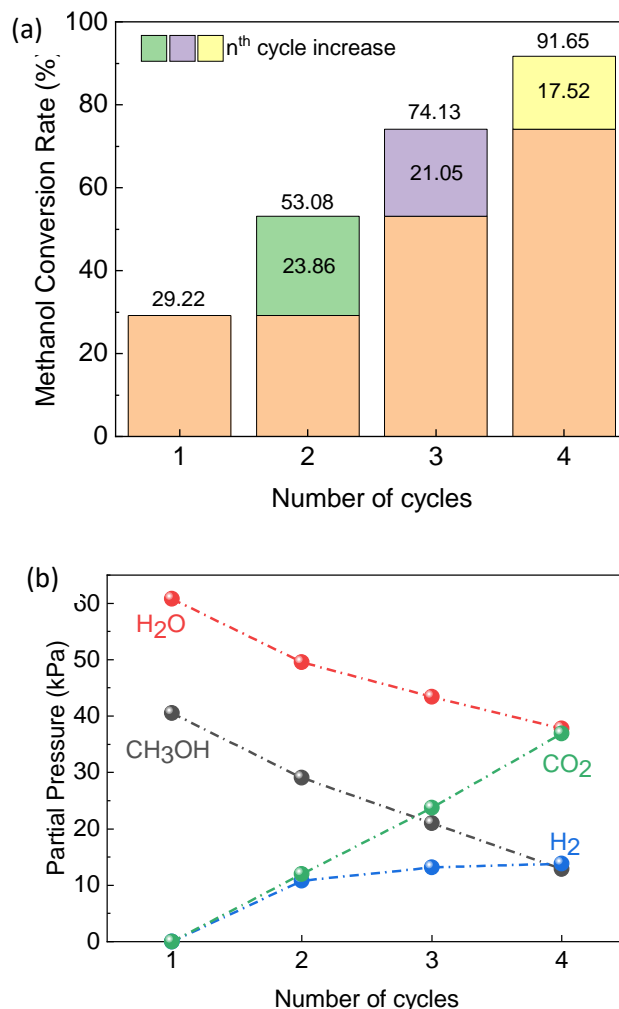


Fig. 7 Comparison of traditional MSR system and AE-MSR system. (a) Variation of methanol conversion rate under different number of cycles. The number above each column represents the methanol conversion rate for that system, and the numbers in the different colored columns represent the incremental methanol conversion rate from the new cycles added to the system. (b) Partial pressure of gas components at the inlet of each cycle.

Theoretical calculations of methanol conversion rate were performed for systems with different number of cycles at 200°C, LHSV = 4.5 mL g_{cat}⁻¹ h⁻¹ and H₂ separation ratio of 0.7. As shown in Fig. 7 (a), low methanol conversion rate of 29.22% is obtained in the traditional system. With increase of the number of cycles, the methanol conversion rate increases rapidly. Especially in the system with 4 cycles, methanol conversion rate can reach 91.65%. Meanwhile, it can be observed that the methanol conversion rate in each cycle

decreases from 29.22% to 17.52% with the increase of the number of cycles.

To further explore the explanation of the incremental decrease in methanol conversion rate, the partial pressure of each component at the inlet of each cycle was calculated, as shown in Fig. 7 (b). At the inlet of the first cycle, the gas stream contained only reactants and obtained the largest reaction driving force. As the degree of reaction proceeded, the reactant partial pressure decreased and the product (mainly CO₂) partial pressure increased. Although the partial pressure of H₂ in cycles 2, 3 and 4 remained nearly constant under the effect of H₂ separation. According to the kinetic equation, the reaction rate in the cycles still gradually decreased, leading to a decrease in the methanol conversion rate increment in each cycle.

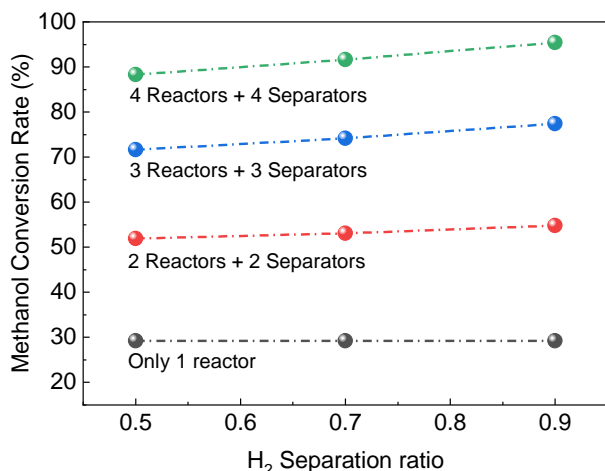


Fig. 8 Correlation between the methanol conversion rate and the H₂ separation ratio.

The H₂ separation ratio was used to indicate the absorption performance, which played an important role in the methanol conversion rate of AE-MSR. The performance of traditional MSR system was independent of the separation ratio and was used as a basis for comparison. As shown in Fig. 8, methanol conversion rate increased as H₂ separation ratio increased. However, little effect on enhancement compared to the number of cycles was found. For example, in the system of 2 cycles, when the H₂ separation ratio increased from 0.5 to 0.9, methanol conversion rate of 51.90% slightly increased to 54.76%. However, much larger enhancement of methanol conversion rate from 88.29% to 95.42% were obtained in the system of 4 cycles.

5. CONCLUSIONS

A method of H₂ absorption-enhanced methanol steam reforming is proposed for the first time to produce high-purity H₂ and capture CO₂ with low energy penalty at low temperatures. The effectiveness of the method is

further verified by a prototype reactor sequentially filled with bulk catalyst (CuO/ZnO/Al₂O₃) and bulk hydrogen absorbent (LaNi_{4.3}Al_{0.7} alloy), tested at 200°C and 1 bar conditions. High-purity H₂ and CO₂-rich streams with concentrations higher than 80%, respectively, are obtained separately in the first cycle. Three cycles of the absorption-enhanced MSR process have been successfully implemented, with high concentrations of hydrogen streams obtained in all regeneration steps and increasing total hydrogen production. Simulation results considering the catalytic reaction kinetics demonstrate that the AE-MSR method is capable of significantly improving the methanol conversion rate. The methanol conversion rate could reach 91.65% in the system with 4 cycles at 200°C, S/C=1.5 and LHSV= 4.5 mL g_{cat}⁻¹ h⁻¹. Major advantages of the new method, including low reaction temperature, high-purity H₂, non-precious material and membrane-less design, indicate great potentials for commercial applications. The reduced reaction temperature also increases possibilities of integrating with solar thermal energy and industrial waste heat for sustainable H₂ production with significantly reduced CO₂ footprint at the same time.

ACKNOWLEDGEMENT

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