EFFECT OF FUEL SPRAY DROPLET SIZE ON THE CHARACTERISTICS OF HYDROGEN PRODUCTION BY A METHANOL REFORMER WITH THERMAL MANAGEMENT

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ABSTRACT

This study investigated the effect of fuel spray droplet size on hydrogen produced by a methanol reformer. The experimental parameters included methanol supply rate, Sauter mean diameter (SMD) of methanol spray, O_2/C (Oxygen/Carbon) ratio and S/C (Steam/Carbon) ratio. The investigation involved the study of cold start transient response of the reformer and the characteristics of the hydrogen production with attention paid on reducing the time taken for the reformer to commence producing hydrogen from cold start.

Partial oxidation reforming was first employed to determine the optimum cold start parameters for this system. A purpose-made twin-fluid nozzle was applied, which allowed varying of the assisting air flow rates to regulate the fuel spray droplet size with the objective of investigating the effect of the droplet size on the cold start performance of the reformer. From the experiments, it was shown that under low methanol supply rate coupled with an appropriate fuel spray droplet size, the catalyst could quickly attain its reaction temperature with a short cold start duration. In comparison, the effect of spray droplet size was less evident with high methanol supply rate from cold start. Further, it was demonstrated that the thermal management method of external heating significantly improved hydrogen yield under different S/C ratios, with the maximum yield of 89% achieved with an S/C ratio of 2.0.

Keywords: methanol reformer, fuel spray droplet size, cold start, hydrogen, thermal management

INTRODUCTION

In the face of increasing energy shortage, continual deterioration of the ecology, the world has risen to the attention of problems of energy and environment. As a result, there is a concerted effort to improve and develop techniques of producing clean energy. Future energy sources include water, wind, bio-energy, solar energy, hydrogen and nuclear energy. Amongst them, hydrogen energy as used in fuel cells is not naturally restrictive due to its abundance and its high desirability for its noise-free, non-polluting and high efficiency characteristics. It is therefore unsurprising that fuel cells are widely accepted as the new technology of the 21st century. Chu et al. [1] recently published a book classifying hydrogen production techniques into five types. The first was the reforming of hydrogen using fossil fuel; the second was water gas shifting; the third, bio-hydrogen production, followed by hydrogen production from bio-fuels. The first method was thought to be the most commercially relevant in this stage.

Emonts et al. [2] developed a methanol-steam reformer that could generate an equivalent of 50kW (LHV) of hydrogen. By applying heating at the catalyst combustion unit, they demonstrated 100% methanol conversion under the low load condition. An increase in operating temperature of 260°C to 280°C also showed obvious improvement in methanol conversion, although for temperatures up to 300°C, there were no further improvements. With the methanol reformer, Wiese et al. [3] investigated the reformer's performance in static, dynamic and transient conditions. The reported that the reformer started hydrogen production in ten minutes after ignition, and that the response of the fuel supply system had a significant effect on the dynamic reaction of the reformer. In view of this, they recommended that fuel should be injected to enhance the response performance. Loffler et al. [4] developed a reforming unit equipped with a pre-reformer for producing oxidation heat for heating up the catalyst to operating temperature rapidly. Steam reforming was adopted and it was found that the system had considerably high thermal efficiency and produced high purity of hydrogen. Choi and Stenger [5] used a $Cu-ZnO/Al_2O_3$ catalyst with methanol as fuel to investigate the effect of adding water on the characteristics of hydrogen production. Without adding water, the conversion efficiency of methanol was as high as 100%. With the addition of water, the hydrogen concentration was much higher and the CO concentration was much lower. Höhlein et al. [6] manufactured a methanol-steam reforming system consisting of a reformer, a catalytic burner and a gas processing unit. Although the reforming system did not meet the requirements for cold start, they found that the CO concentration had a close relationship with the heating pattern and the temperature variation of the reformer under the operating temperatures of 240°C, 260°C and 280°C. Chan et al. [7] developed a combined reforming system for using onboard a high temperature PEMFC vehicle. This reformer was shown to attain 100% conversion efficiency for operating temperature of 200°C with a

hydrogen production rate of 400L/(h-kg catalyst). It was also demonstrated that with a CO concentration of under 0.2% (S/C ratio of 1.2 to 2), the combined fuel cell and methanol reformer could improve the efficiency, and thereby simplifying the system. Wild and Verhaak [8] studied the effect of substrates, namely pellet, foam and heat exchanger type, on catalysts. The latter resulted in the best catalyst performance, whilst the pellet substrate produced the slowest loss of catalyst activity. Using a small-scale methanol reformer, Horng [9] revealed that it took 220 seconds from cold start to commence hydrogen production and that steady production was achieved after four to five minutes. By varying the operating parameters of a methanol reformer, Horng et al. [10] reported the shortest cold start with a heating power of 240W when the heating temperature was set at 100^oC, the methanol supply rate was 25.5cc/min and the air flow rate was 70L/min. The time taken to stable hydrogen production was approximately 3 minutes. Horny et al. [11] designed and manufactured a small scale methanol reformer for investigating the effect of composition and fabrication process of a catalyst for autothermal reforming. The main design consideration was the scaling down of the main body to a diameter of 0.25 to 0.4mm and with a substrate composition of Cu/Zn=4/1. The substrate was made up of Cu-Zn beads aligned to form micro-channels. In the performance study, it was shown that the catalyst reached operating temperature when autothermal reforming was at 250^oC. Under optimum operating parameter settings, this system produced a hydrogen selectivity of 60% and carbon dioxide selectivity of 98% when methanol conversion efficiency was 35%. Takeda et al. [12] combined pre-heating by oxidation with steam reforming on a methanol reformer and with additional heating arrangement on assisting the vaporization of the liquid fuel to facilitate the response of the catalyst. Chan et al. [13] studied the transient response of an autothermal methanol reformer. By applying varying square-waved loading patterns, they successfully predicted the transient response characteristics and revealed that sudden surge in fuel supply resulted in a significant increase in CO concentration. In contrast, sudden decrease in fuel supply caused an evident reduction in methanol conversion efficiency. Horng et al. [14] developed a small-scale methanol reformer to carry out a parametric study of the heating power, pre-heating temperature, methanol supply rate and steady mode shifting temperature, in relation to the temperature rise of the reformer from cold start and hydrogen production characteristics. They demonstrated that increasing the heating power increased the outlet temperature of the catalyst whilst decreasing the heating power resulted in rapid rise of the catalyst outlet temperature. This phenomenon was more evident under high methanol supply rate. It was also shown that a high steady mode shifting temperature led to a rapid rise in catalyst outlet temperature. However, when the shifting temperature was too high, the hydrogen production response was not always the quickest. Seo et al. [15] developed a reformer unit capable of generating 2kW. Preferential oxidation of CO was carried out by a catalyst made up of Pt combined with Ru, of which the overall reaction temperature was regulated by a heat exchange unit and a combustion unit. Qi et al. [16] reviewed and compiled existing thermodynamic analyses and energy management studies on fuel professor devices. They also assessed various fuel types containing hydrogen and reported methanol as theoretically the best fuel in terms of reforming efficiency. Huang and Su et al. [17] reformed methanol-water liquid with three catalysts, namely, $CuO-ZnO-Al_2O_3$, $CuO-ZnO-Al_2O_3$-Pt-Rh and Pt-Rh. The $CuO-ZnO-Al_2O_3$ catalyst was found to produce the best hydrogen production for temperatures under 320^oC. At temperatures higher than this, the other two catalysts were more superior.

From the above review, it is clear that methanol reformers with low reaction temperature are most suitable for use onboard vehicles. The collective concern for international researchers on the reforming process is the cold start performance of the reformers, which currently has not been reported to meet the requirements for actual application on vehicles. This paper investigates the effect of fuel spray droplet size on the cold start performance and hydrogen production characteristics of a reformer equipped with thermal management devices.

EXPERIMENTAL SET-UP AND METHOD

A purpose-designed reforming unit was designed and fabricated with ancillary systems including fuel and gas supply units, temperature control system. The catalyst of the reforming unit was a honeycombed metallic substrate with Pt and Cu-ZnO/Al_2O_3. The fuel supply system composed of a fuel pump, pressure gauge, flow meters and a twin fluid nozzle, whilst the gas supply system consisted a pressure gauge, flow meters, and a single and a multi-hole nozzle. The temperature control system included glow plugs, a temperature regulator and a temperature recording system. Each glow plug provided a heating power of 120W, with the four plugs contributing a total of 480W to the gas mixture through the catalyst. K-type thermocouples were installed at the customary locations of the inlet and outlet of the catalyst and a further three were used on the catalyst to detect the internal and external wall temperatures. Temperature feedback was provided by the thermocouple at the outlet of the catalyst for regulating the temperature. Thermal management was applied in the form of a stainless steel gas jacket enclosing the catalyst main body with the purpose of recycling heat. Gas analysis was carried out with an Agilent 6850 GC, a condenser, a pump and a gas sampling bag. The experimental

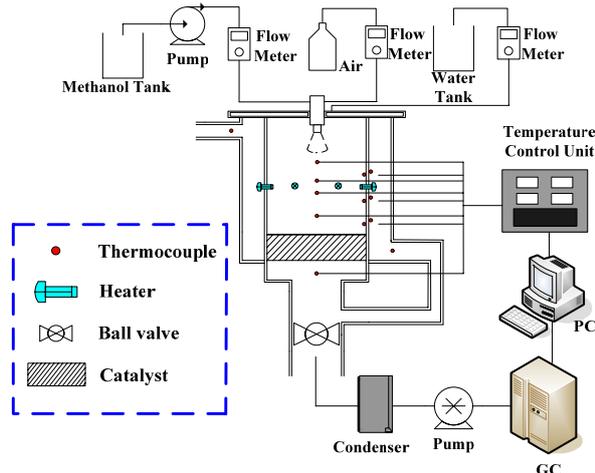set-up is shown in Figure 1, with the catalyst specifications listed in Table 1.

Figure 1 Experimental set-up

Table 1 Reformer Specifications

Main body	
Reactor	120mm-OD, 82mm-ID stainless steel
Height	600mm
Nozzles	Methanol, water, air
Heaters	120W×4 （POX）
	500W×3 （ATR）
Power sources for	12VDC （POX）
heaters	220VAC （ATR）
Catalyst	
Substrate	Stainless steel
Diameter	76mm
Length	30mm
Composition	Pt and Cu-ZnO/Al$_2$O$_3$
Cell density	230 cells/in^2 (3.6×10^5 cells/m^2)

The main methods adopted herein were partial oxidation and autothermal reforming. A twin-fluid nozzle was used to vary the assisting air flow rates for controlling the fuel spray droplet size. The main test parameters were the S/C ratio, the O$_2$/C ratio and the Sauter mean diameter (SMD) of the methanol spray.

In the first stage of the experiments, partial oxidation was used for reforming from cold start and the optimum parameter settings were determined. In the second stage, the twin fluid nozzle was applied to vary air flow rates for altering the methanol spray droplet size. At the start of the tests, the gas analyzer was armed in readiness as the data recorder was activated. The heating system was then switched on and air was supplied. After turning on the glow plugs for 10 seconds to pre-heat the air, methanol was injected and at the same time, the gas sampling pump commenced collection in 60 seconds intervals and transferred the samples into the gas analyzer for analyzing the composition. This analyzing process continued until gas production

was steady. The next test was started only after the thermocouples showed temperatures to have returned to room temperature.

To study the effect of thermal management, the same set up was used. The main operating parameters were the S/C ratio and the O$_2$/C ratio. Once the reformer stabilized to steady hydrogen production, the gas produced was sampled by the gas analyzer for its composition.

RESULTS AND DISCUSSION
-Test of the Reformer Performance

Figure 2 shows the effect of O$_2$/C ratio on H$_2$ concentration and catalyst outlet temperature under four different methanol supply rates. It is evident from the figure that optimum H$_2$ concentration was produced for an O$_2$/C ratio of between 0.23 and 0.34. When the O$_2$/C was too low, H$_2$ was not effectively improved due to lack of oxidation and therefore the low operating temperature. As a consequence, carbon particles may form. In contrast, overly high O$_2$/C ratio will result in high operating temperature, which may be damaging to the catalyst and may lead to the undesirable effect of the oxidation of H$_2$. In view of this, the outlet temperature was regulated to be within 450°C.
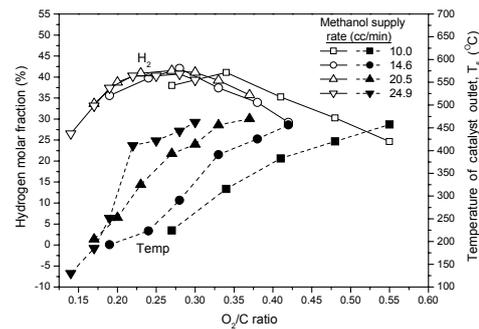

Figure 2 Hydrogen concentration and catalyst outlet temperature under varying methanol supply rates and O$_2$/C ratios
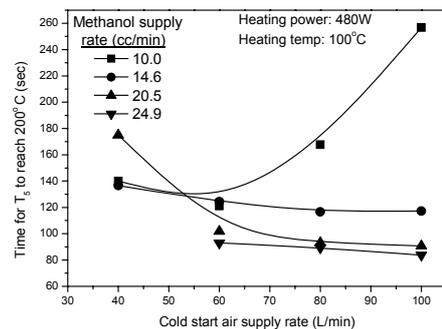

Figure 3 Time taken for the catalyst outlet temperature to reach 200°C under varying methanol supply rates and cold start air supply rates

Figure 3 shows the effect of air intake rate on the time taken for the catalyst outlet temperature (T$_5$) to reach 200°C under four different methanol supply rates. With the lowest methanol supply rate of 10.0

cc/min and a cold start air intake rate of 40 L/min, the time required is approximately 140 seconds. This reduces to 121 seconds when the air supply rate is increased to 60 L/min. However, with even higher air intake rates of 80L/min and 100L/min, the response after cold start becomes slower, up to 257 seconds for the 100L/min case. This could be due to the overly lean fuel-air mixture, leading to incomplete combustion of methanol and therefore too little oxidation heat. With the other three higher methanol supply rates, the air intake rate rises after cold start and therefore reduces the time taken for the catalyst outlet temperature to reach 200°C. The shortest time of 84 seconds is achieved under a fuel supply rate of 24.9cc/min coupled with an air intake rate of 100L/min.

Table 2 Air-to-fuel ratio under different methanol supply rates and air flow rates*

Methanol supply rate (cc/min)	Air supply rate (NL/min)			
	40	60	80	100
10.0	5.94	8.91	11.88	14.85
14.6	4.08	6.12	8.16	10.20
20.5	2.89	4.34	5.79	7.24
24.9	2.38	3.58	4.77	5.96

*Stoichiometric air-to-fuel ratio of methanol: 6.435

From Table 2, it is evident from the relationship of the A/F ratio and the cold start air intake rate when the methanol supply rate is 10cc/min with a corresponding cold start air intake rate between 40 and 60L/min, the A/F ratio is maintained between 5.94 and 8.91, leading to rapid catalyst response. When the air intake rate rises to 80L/min, the A/F ratio is 11.88, which further rises to 14.85 when the air intake rate increases to 100L/min, far exceeding the theoretical A/F ratio. The consequence is poor oxidation. For the higher methanol supply rate of 20.5cc/min and 24.9cc/min, an air intake rate of 100L/min results in an A/F ratio of 5.96 and therefore the shortest time to achieve the required catalyst outlet temperature.

From the series of tests, it transpires that an appropriate A/F ratio can optimise cold start effects for every methanol supply rate and air intake rate. Optimum cold start condition also means less energy wastage during cold start.

-Effect of Methanol Spray Particle Size

Figure 4 shows the measured methanol spray droplet diameter for a methanol supply rate of 10.0 to 24.9cc/min and an air intake rate of between 3 and 12L/min. It is clear from the figure that methanol spray droplet size decreases with increasing assisting air intake rate but graduates when the air

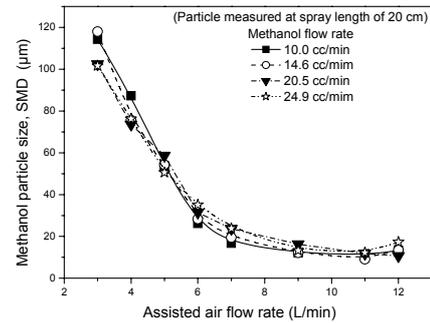intake rate exceeds 7L/min and stabilises at approximately 20µm at 9L/min.

Figure 4 Methanol particle size under varying assisted air flow rates and methanol flow rates (measured at 20cm from nozzle outlet)
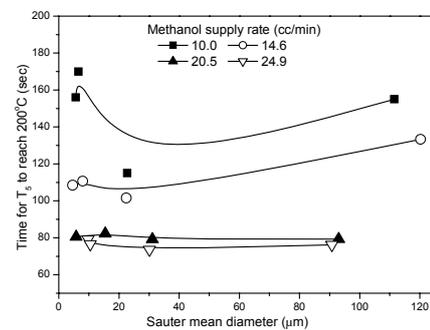

Figure 5 Time taken for the catalyst outlet temperature to reach 200°C under varying methanol supply rates and Sauter mean diameters

Figure 5 shows the effect of methanol spray droplet size on the time taken for the catalyst outlet temperature to reach 200°C under different methanol supply rates. At the lowest tested methanol supply rate of 10cc/min, an SMD value of 22.7µm requires 115 seconds for the catalyst outlet temperature to reach 200°C. This reduces to 101 seconds with a higher methanol supply rate of 14.6cc/min with an SMD size of 22.4µm. It is therefore clear that rapid catalyst reaction temperature is achieved with an SMD size of 22µm under low methanol supply rates of 10.0cc/min and 14.6cc/min, and not due to decreasing SMD size. The reasons could be that the large flow rate of air for smaller SMD leads to a longer spray penetration length to cool down the catalyst as they hit the catalyst surface. Alternatively, the high speed of the fuel spray may leave some fuel droplets passing the catalyst unburnt. The consequences are inefficiency fuel conversion and slow catalyst temperature rise. Further, it can be seen that with the higher methanol supply rates of 20.5cc/min and 24.9cc/min, the effect of SMD on cold start response is less distinct. In this case, the heat dissipation per unit time is higher, which increases the internal temperature of the catalyst. The higher fuel supply rates thus avoid the

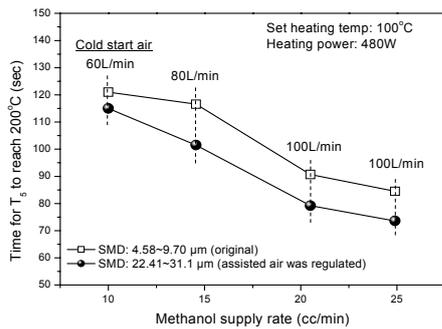two aforementioned problems encountered due to lower supply rates.

Figure 6 Time taken for catalyst outlet to reach 200°C under optimum Sauter mean diameter and varying methanol supply rates

Figure 6 shows the time taken for the catalyst outlet temperature to reach 200°C using the best methanol spray droplet size. The existing twin fluid nozzle for the assisting air intake rate was not modified and flow rates were varied according to the O_2/C ratio. It is noted that this set-up may result in excessive assisting air causing cooling problems due to long fuel penetration length. From the figure, it is evident that when the methanol supply rate is 10.0cc/min, if the assisting air intake rate were adjusted optimally, the time taken for the catalyst to respond could clearly be improved. At a higher methanol supply rate of 24.9cc/min, the time taken for the catalyst outlet temperature to reach 200°C is 73 seconds. Although this is the shortest time taken for all tested methanol supply rates, it is not far off from that with the 20.5cc/min setting. The reason for this is the use of two nozzles for air intake, one of which was a twin fluid nozzle for providing an appropriate air to atomize the fuel spray, and the other for purely supplying air. This set-up provides a balance between lowering the size of the methanol spray droplets and reducing the penetration length, and therefore a rapid cold start response.

The effect of fuel spray characteristics on gas compositions during steady catalyst temperature is studied in this section. Figure 7 shows the effect of SMD on the gas concentrations for a methanol supply rate of 14.6cc/min and an O_2/C ratio of 0.28. It is evident from the figure that the H_2 concentration increases and peaks whilst the CO concentration shows a decreasing trend with increasing SMD value. The rise of the H_2 concentration may be due to decreasing assisting air intake rate as the SMD value increases. Reduced air flow rate would result in shorter spray penetration length and therefore less risk of the fuel spray cooling the catalyst as it hits the walls. If the SMD value were to be increased further, both the H_2 and CO concentration begin to descend, with the (H_2+CO) concentration tending to the trend of the H_2 concentration.
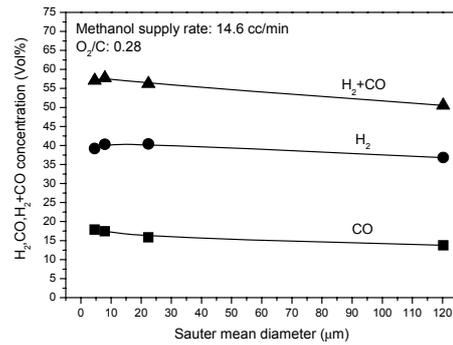

Figure 7 Effect of Sauter mean diameter of methanol on gas concentrations during steady reforming for a methanol supply rate of 14.6cc/min
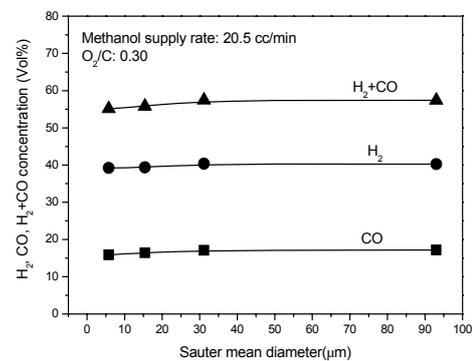

Figure 8 Effect of Sauter mean diameter of methanol on gas concentrations during steady reforming for a methanol supply rate of 20.5cc/min

Figure 8 shows the effect of SMD size on the gas concentrations for a methanol supply rate of 20.5cc/min and an O_2/C ratio of 0.30. With the smallest SMD of approximately 5.75μm, the H_2 concentration is approximately 39.22%. When the SMD is increased to 93.02μm, the corresponding H_2 concentration is marginally improved to 40.24%. Overall, the CO concentration ranges from 15.90% to 17.17%. The (H_2+CO) concentration displays similar trend to the H_2 concentration. It is therefore clear that at high methanol supply rate, the effect of SMD on the H_2 concentration is less distinct, with the H_2 concentration in the range of 39.22% and 40.24%. During steady state response, the SMD affects the H_2 concentration only at low methanol supply rates and not at high methanol rates.

-Effect of Thermal Management
Figure 9 shows the effect of S/C ratio on the produced gas compositions during steady state response using different thermal management methods. The methanol supply rate is 20.5 cc/min, the O_2/C ratio is 0.40 and the S/C ratio is in the range 0 to 2.5. The thermal management methods included heat recycling and external heating, with the original system as baseline. From the figure, it is

evident that with the original system, the H_2 concentration reduces from 38.1% to 31.0% whilst the CO concentration decreases from 13.6% to 9.4% as the S/C ratio increases from 0 (i.e. partial oxidation) to 2.5. Changes in the CO_2 concentration are, however, less distinct. The reducing of the H_2 concentration with increasing S/C ratio may be attributed to the latent heat of water, which has the effect of lowing the temperature of the catalyst bed and therefore the conversion efficiency of methanol.

The CO concentration reduces from 10.5% to 9.1%, a change of 3.5% when the S/C ratio increases from 1.0 to 2.5. With heat recycling, the H_2 concentration is 38.0% when the S/C ratio is 0, but remains between 37.9% and 38.0% even when the S/C ratio is increased to 1.0-1.5. Further increase in S/C ratio to 2.0-2.5, results in a decrease in H_2 concentration from 34.8% to 33.7%, a clear indication that the latent heat has increased too much, which inevitably deteriorates the reforming efficiency. Adding external heating produces the highest H_2 concentration. In this case, the H_2 concentration increases with increasing S/C ratio, peaking at 41.7% when the S/C ratio is 2.0-2.5. The corresponding CO concentration decreases with increasing S/C concentration, reaching 6.5% when the S/C ratio is 2.5.
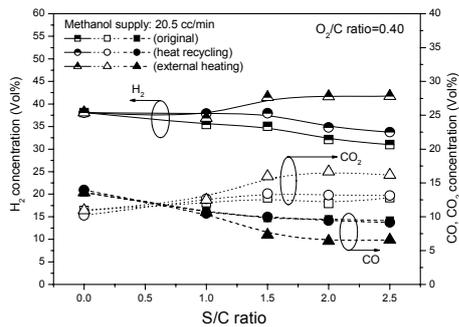

Figure 9 Effect of different operating conditions on thermal efficiency during steady reforming for a methanol supply rate of 20.5cc/min
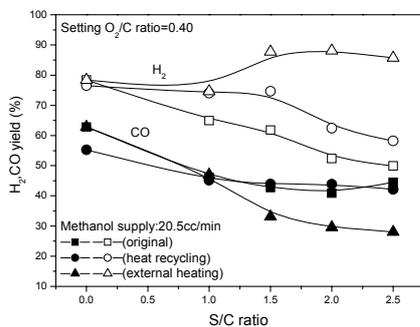

Figure 10 Effect of S/C ratio on the H_2 and CO concentrations for during steady autothermal reforming under a methanol supply rate of 20.5cc/min

Figure 10 shows the effect of S/C ratio on H_2 and CO yield under steady autothermal reforming for a

methanol supply rate of 20.5 cc/min, an O_2/C ratio of 0.40 and an S/C ratio of 0 to 2.5. For both the original and with additional heat recycling cases, the H_2 and CO yield decrease with increasing S/C, but with the latter yielding a higher hydrogen concentration for all S/C ratios by approximately 10%. When the S/C ratio is set to 1.5, the H_2 yield is as high as 74.63%, the highest under the tested operating conditions. The CO yields for these two systems, however, are similar, between 40.8% and 46.1%. The system with additional external heating expectedly has a well-maintained temperature with the H_2 yield increasing with increasing S/C ratio. When the S/C ratio is 2, the H_2 yield is optimum at 88.13% for this fuel supply rate. Further increase in the S/C ratio to 2.5, however, does not further improve the H_2 yield. In fact, there appears to a slight decrease to 85.75%. Under this thermal management method, the CO concentration shows an effective reduction, for example to as low as 28.03% when the S/C ratio is 2.5. To summarise, H_2 yield is much higher with heat recycling than the original system for autothermal reforming although the improvement is less than expected, presumably due to insufficient heat recycling or the cooling down of the main catalyst body by the recycled gas. In light of this, it is recommended that when recycling heat, the recycled gas should not be directed at the walls of the catalyst where the temperature is high to prevent the catalyst from cooling down by the gas. Low operating temperature translates to poor reforming efficiency.
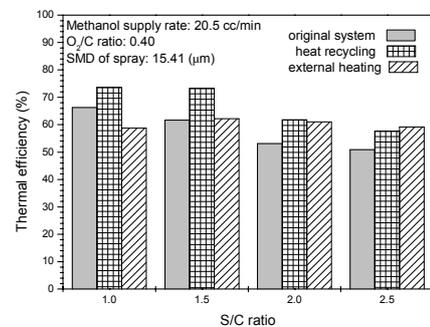

Figure 11 Effect of S/C ratios on thermal efficiency during steady autothermal reforming with a methanol supply of 20.5cc/min

In this section, the effectiveness of the proposed thermal management methods on improving reforming efficiency with the optimum SMD is discussed. Figure 11 shows the effect of the thermal management methods on reforming efficiency during steady reforming with the operating conditions of a methanol supply rate of 20.5cc/min, an O_2/C ratio of 0.40, an SMD of 15.41 μm and an S/C ratio of 1 to 2.5. With the original system, it is clear that thermal efficiency decreases with increasing S/C ratio. When S/C is set as 1, the thermal efficiency is 66.24%. With heat recycling, high thermal efficiency

is maintained at around 73.3% for an S/C ratio of between 1 and 1.5, but decreases as the S/C ratio increases to 2, and falling to 57.63% for an S/C ratio of 2.5. Although adding external heating to the original system results in improvements in both the H_2 concentration and H_2 yield, but when considering the additional energy supply, thermal efficiency is maintained at merely 60%, approximately.

-Comparison of Theoretical Equilibrium Calculations and Experimental Results

Figure 12 compares the predicted and experimental gas concentrations of H_2, CO and CO_2 produced during partial oxidation with a methanol supply rate of 20.5cc/min under different operating temperatures. The experimental temperature was taken as the mean of that measured at the catalyst inlet and outlet. It is clear from the figure that hydrogen production begins as the temperature reaches 300°C and peaks and stabilises when the reaction temperature reaches approximately 700°C. The gas concentrations shown in Figure 12 are the maximum stable gas production levels during the reforming process. It is clear that the predictions and the experimental results are in good agreement.
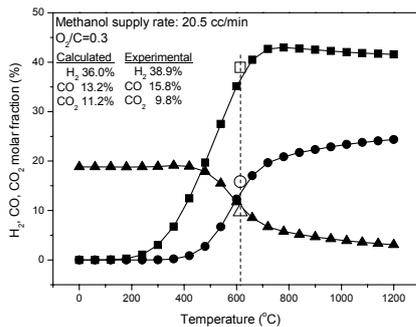

Figure 12 Predicted and experimental gas concentrations for partial oxidation reforming under varying operating temperatures and with a methanol supply rate of 20.5cc/min and an O/C ratio of 0.3

Figure 13 shows the effect of S/C ratio on gas production concentration during autothermal reforming under different operating temperatures. The methanol supply rate is 20.5 cc/min, the O_2/C ratio is 0.4 and the S/C ratio is 1 to 2.5. It is evident from the figure that under this operating condition, the predicted and experimental H_2 and CO_2 concentrations are in good agreement, although the deviation of the CO concentrations is more pronounced.
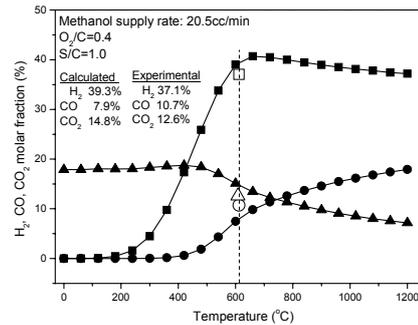

Figure 13 Predicted and experimental gas concentrations for autothermal reforming under a methanol supply rate of 20.5cc/min and an S/C ratio of 1

CONCLUSIONS

The effect of methanol spray droplet size on cold start response and the hydrogen production characteristics by a methanol reformer has been investigated with a twin fluid nozzle. The experiments showed that the SMD of the fuel has significant effects when the methanol supply rate was low. With higher methanol supply rate, the effects were less distinct. In general, smaller SMD resulted in shorter response time from cold start, with the optimum value found to be near 22µm for a low methanol supply rate of 10.0cc/min or 14.6cc/min. During steady state operation, the produced gas concentrations were found to be still affected by spray conditions with low methanol supply rate but less affected with high methanol supply rate. Different thermal management methods were applied to the reforming system. By recycling heat to carry out autothermal reforming, it was revealed that the H_2 yield was increased compared to the original system. The reforming efficiency, however, was not as good as by partial oxidation. The reason was due to either insufficient recycled heat or the cooling down of the catalyst by the recycled gas flow. Applying external heating was shown to improve H_2 yield under different S/C ratios with the highest yield of 88% attained for an S/C ratio of 2.0.

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