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An investigation of reaction progression through the catalyst bed in methanol autothermal reformation

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Abstract

This study investigates autothermal reforming of fuel cell-grade methanol as a method for producing hydrogen for transportation applications. A previous study on the effects of oxygen-to-carbon ratio on ATR reactor performance showed that the optimum of $O_2/CH_3OH=0.30$ found in the experimental tests is 30% higher than the theoretical optimum of 0.23. In this study, the influence of catalyst bed length is investigated to give insight into the reaction progression through the catalyst bed in methanol autothermal reformation. The effect of reaction progression through the catalyst bed is experimentally investigated in relation to reactor output parameters of fuel conversion, temperature profile, and reactor efficiency. The results from this study serve as a baseline for future research of autothermal reforming of hydrocarbon fuels as a method for producing hydrogen.

Keywords: Autothermal reforming; Reaction progression; Methanol; Efficiency of ATR; Fuel conversion

1. Introduction

Hydrogen is an increasingly attractive fuel and, as a result, research on novel pathways for hydrogen production is necessary to meet future hydrogen demand. Even though hydrogen is the most plentiful element on the planet, there is no natural source, aside from trace amounts contained in natural gas reserves. As such, hydrogen must be produced from primary sources through any of a variety of processes including reforming of hydrocarbon fuels, electrolysis, thermal decomposition of water, and thermal processing. There are currently three main methods for reforming hydrogen fuels into a hydrogen-rich gas: steam reforming (SR), partial oxidation reforming (POX), and autothermal reforming (ATR) [1, 2].

As shown in Eq. (1), steam reformation is an endothermic reaction, requiring an additional source of heat. In contrast to steam reformation, partial oxidation reformation is an exothermic reaction. By combining the SR and POX reactions, the excess heat generated in the partial oxidation step can be used to fuel the energy-deficient steam reformation step. This combined reaction is referred to as autothermal reformation and can be made thermoneutral by controlling the O_2/CH_3OH ratio.

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2, \quad \Delta H^0_{298K} = +49 kJ/mol \tag{1}$$

$$CH_3OH + 0.5O_2 \rightarrow 2H_2 + CO_2, \quad \Delta H^0_{298K} = -192 kJ/mol \tag{2}$$

$$4CH_3OH + 3H_2O + 0.5O_2 \rightarrow 11H_2 + 4CO_2, \quad \Delta H^0_{298K} = 0 kJ/mol \tag{3}$$

ATR has the advantages of both steam reforming and partial oxidation in that it has potentially high efficiencies and adequate response to dynamic loads. Ideally, the heat generated from the exothermic POX

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reaction is used for rapid start up and supplying the heat needed for the endothermic SR reaction during operation. ATR is also capable of reforming multiple fuels, a necessary characteristic if alternative feedstocks of methanol are to be reformed. Methanol produced from coal or biomass may contain higher hydrocarbons. At a paper/pulp mill under investigation for methanol production from waste streams, it was found that small amounts of hydrocarbons (pinenes) and other species exist in the methanol fuel produced. These compounds tend to overwhelm any hydrogen producing catalyst site until they are fully oxidized [3].

For a theoretical calculation, the optimal temperature to reform gasoline into hydrogen is around 400°C [4]. However, in recent studies of gasoline and diesel autothermal reformation, temperatures of 600-800°C have been used [5, 6]. Fuel conversion of greater than 97% can be obtained at temperatures in excess of 800°C [7, 8]. High temperatures require expensive materials and longer start-up times for an automotive scale reformer. Methanol is a very attractive fuel for hydrogen production. Because it is an oxygenated fuel, it requires lower heating temperatures for effective reformation [4]. Ethanol and higher weight alcohols generally have longer carbon chains and therefore require higher temperatures and more energy to break the carbon-to-carbon bonds. Some lighter compounds like methane also require relatively high temperatures. Methanol can be reformed at relatively low temperatures around 250°C. Fuel conversions of greater than 90% are possible at temperatures just above 250°C [9]. Based on thermodynamic equilibrium, when the reaction temperature decreases lower CO concentration can be achieved [10, 11]. This lower temperature means less reformate clean up and, therefore, a smaller and less complicated fuel processing system.

In order for a fuel processor utilizing ATR to be effective, it is necessary to understand the reforming system and know the correct operating parameters to obtain peak efficiency. There is a discrepancy between theoretical calculations and experimental results as to what the optimum operating conditions are. This paper presents experimental data of the methanol ATR system that suggests how the ATR reforming reaction progresses through a monolithic catalyst bed.

2. Experimental facility and approach

The preexisting steam-reforming infrastructure included a liquid pumping subsystem, a three-phase vaporizer and superheat subsystem, a condensing subsystem, a gas analyzer, and control switches that are controlled by computer. Fig. 1 displays a simplified schematic of the ATR system employed for experimental research, which consists of the previously mentioned infrastructure and an air supply subsystem and the catalyst housing subsystem. The ATR hardware is controlled by a closed loop control program. The same program is also responsible for collecting and recording data from open loop instrumentation, which simply sends input signals to the computer via a data acquisition board. The elements of the system under active closed loop control are the fuel/water pump, the cartridge and band heaters, and the air mass flow controllers. The open loop signals come from a gas analyzer, a digital scale, and three different circuit voltages [2, 12, 13]. A monolithic catalyst was selected and specially manufactured such that various catalyst placements were possible. A commercial Sud-chemie noble metal based catalyst of proprietary formulation as shown in Fig. 2 was used with a cordierite ceramic substrate in this study. This monolithic washcoated catalyst was used with a substrate cut into cylindrical geometry. The cell wall thickness was approximately 0.11 mm and the distance between cell centers was 1.04 mm. In order to test how the ATR reaction progresses through a monolithic catalyst bed, the catalyst bed length was varied from 0.635 cm to 3.81 cm by stacking 0.635 cm length catalyst slices. To establish a baseline, a single, uniform monolithic catalyst of 3.81 cm length was tested to observe the effects of the discontinuity between stacked catalyst sections.

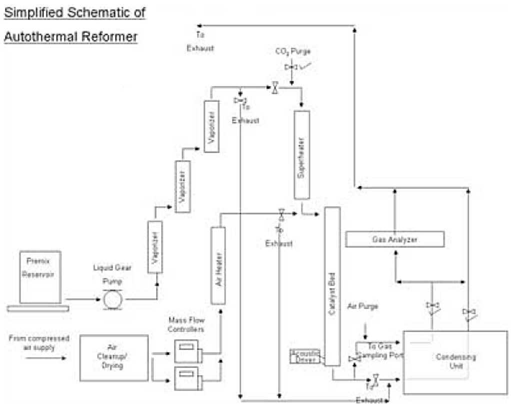

Fig. 1. Simplified schematic of autothermal reforming system.

Fig. 2. Six, 0.635 cm catalyst pieces stacked next to a 3.81 cm catalyst piece.

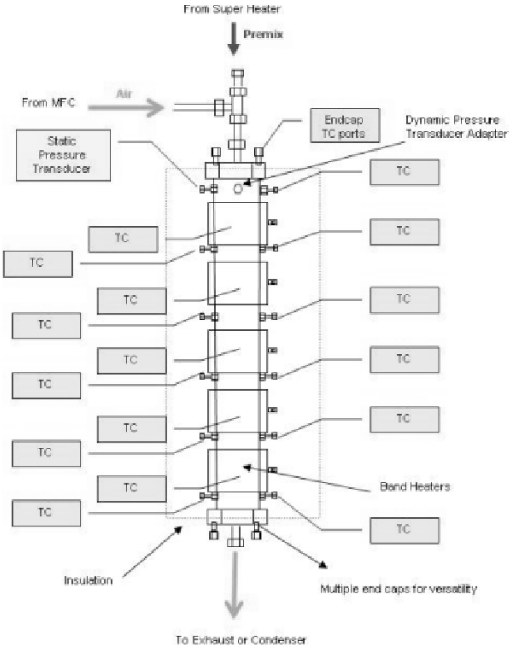

Fig. 3. Schematic of ATR reactor.

Fig. 3 shows a schematic of the ATR reactor. The catalyst housing in the reactor is where the actual reforming reaction took place. Since the reactor was required to withstand temperatures of up to 800 °C, the reactor housing was made of a 3.81 cm nominal diameter stainless steel pipe that was threaded at both ends. The reactor was 30.48 cm long, much longer than the monolithic catalyst to allow for variable positioning of the catalyst as well as for testing various enhancement methods. External heating was applied to the ATR reactor by using five nozzle bend heaters, each with a 120 V, 400 W rating. In a similar fashion as the superheater, a highly conductive aluminum

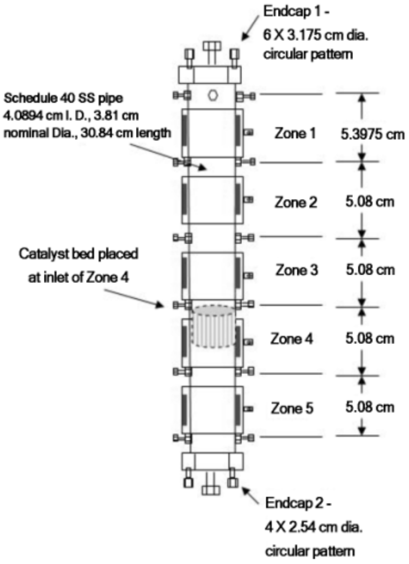

Fig. 4. Schematic of zones and some important dimensions of the ATR reactor.

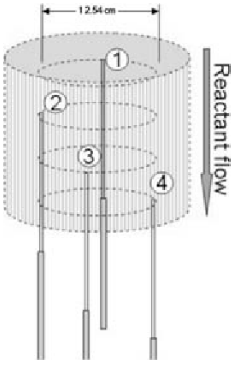

Fig. 5. Schematic of axial thermocouple placement within monolithic catalyst.

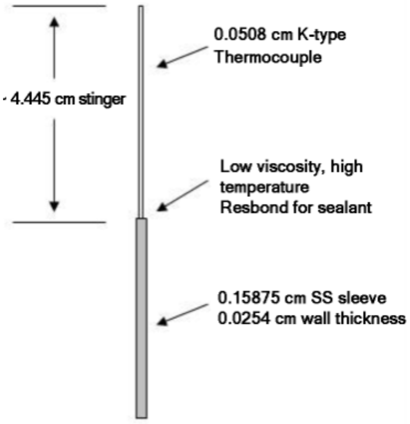

Fig. 6. Schematic of manufactured axial thermocouple.

tape was wrapped around the exterior of the pipe to evenly increase the temperature distribution throughout the reactor.

For the methanol ATR experiments, the catalyst bed was positioned such that the beginning of the catalyst bed was at the inlet of Zone 4 of the reactor, as seen in Fig. 4. Zone 4 was selected to allow upstream mixing of the reactants in the reactor. For most of the experimental runs, the end cap was used for measuring catalyst bed temperature, as seen in Fig. 5. It was positioned at the bottom of the reactor so as to avoid disruption of the reactant flow upstream of the catalyst bed. The thermocouple stinger that protruded from the stainless steel tube, as seen in Fig. 6, was 4.445 cm long such that it could penetrate the full 3.81 cm catalyst section.

To compensate for variability in data, three replications at each operating point were performed. To ensure that unknown effects did not misrepresent the data, the test runs were randomized by catalyst arrangement and then by O_2/CH_3OH. The random order minimized effects that were unaccounted for such as catalyst degradation. The error at each operating point was determined by multiplying the standard deviation of the mean by the t-interval at 95% confidence. This represents the bounds of the mean for which all randomly collected data points should fall with 95% confidence.

Conversion of fuel is a basic indicator of reactor performance. It gives a general idea of the efficiency of the reactor. Percent conversion (%C) of methanol to a hydrogen-rich gas is given in Eq. (4), with methanol input and output on a mass basis.

$$\%C = \left(\frac{CH_3OH_{input} - CH_3OH_{output}}{CH_3OH_{input}} \right) \times 100 \tag{4}$$

In this study, reactor efficiency is defined as hydrogen power output divided by fuel power input, as displayed in Eq. (5). Hydrogen and fuel power are based on the lower heating value (LHV) of the hydrogen and fuel respectively and their molar flow rates.

$$\eta = \frac{H_2 \ \left(kW_t\right)}{Fuel \ \left(kW_t\right)} \tag{5}$$

The molar flow rate of methanol is known from the flow rate of premix fuel; this value is multiplied by the LHV of methanol to obtain the fuel power input. Calculating hydrogen power output relies on various assumptions. Hydrogen power output was based on dry product gas concentration measurements made with the gas analyzer, as well as the molar flow rate of methanol fuel and the measured conversion. The gas analyzer measures concentrations of H_2, CO, CO_2, and CH_4. Assuming 100% conversion of oxidant, a reasonable assumption, and that all methanol and water are condensed out of the product gas in the two stage condensing unit, the only other component in the effluent is nitrogen. This component concentration, added to the other four gaseous component concentrations of H_2, CO, CO_2, and CH_4, should add to 100% for the dry product gas. The quantity of nitrogen input is always proportional to the O_2/ CH_3OH by a factor of 3.76, since that is the ratio of N_2 to O_2 in air. Therefore, it is possible to quantify the molar flow rate of hydrogen by simply balancing the nitrogen in the products and reactants. The molar flow rate of hydrogen is then multiplied by the LHV of hydrogen to obtain the hydrogen power output. This technique was used to calculate the efficiency of the ATR reactor for each experimental run.

3. Results and discussion

The stacked catalyst performed in a very similar manner as the solid catalyst, as evidenced in Fig. 7 which shows the reactor efficiency as a function of O_2/CH_3OH for both catalyst configurations. For the most part, reactor efficiencies are nearly identical between the solid catalyst bed and the stacked catalyst bed. The most notable difference is at O_2/CH_3OH =0.20 when light-off occurs [13]. At the light-off point, the catalyst bed may undergo extreme temperature fluctuations due to an unsteady reaction and concomitantly varying conversion and efficiency. At O_2/CH_3OH =0.20, the mean efficiency of the solid catalyst bed is 20% higher than that of the stacked catalyst bed. This indicates that the discontinuities between the stacked catalyst pieces could be a contributing factor to the instability of the reaction, which results in a decrease of reactor efficiency.

After comparing seven different catalyst configurations, catalyst bed lengths from 1×0.635 cm to 6×0.635 cm and 3.81 cm length, it is apparent that the catalyst bed length has little or no effect on conversion or reactor efficiency as shown in Figs. 9-10. In order to help characterize reactor operating parameters, space velocity is used as a measure of how fast reactants are fed through a reactor relative to the volume of catalyst inside the reactor. Gas hourly space velocity (GHSV) is given in Eq. (6), where $\dot{V}$ represents gas volumetric flow rate and $\dot{V}$ represents catalyst bed volume.

$$\mathrm{GHSV} = \frac{\sum \dot{V}_{reactants}}{V_{catalyst}} \qquad (6)$$

Fig. 10 shows that there is no significant difference in fuel conversion over the range of corresponding GHSV from 9,700 to 58,100 h^{-1}. Above the light-off point, catalyst bed temperatures remained above 550°C and fuel conversion was approximately 99.5% for all catalyst configurations and O_2/CH_3OH.

In order to find the upper limit of GHSV for ATR with the selected catalyst, preliminary testing was performed with a catalyst bed of 0.635 cm length and 3.81 cm diameter at varying reactant flow rates. Stoichiometry was held constant at S/C=1.5, O_2/CH_3OH =0.23. The highest GHSV of 140,000 h^{-1} was obtained at a premix flow rate of 21.8 ml/min, and air flow rate of 9.0 SLPM. Reactant flow rates were limited to this level due to the capacity of the air MFC and excess heat in the reactor exhaust which caused downstream valves to malfunction. In the preliminary stages of the ATR operation, two tests were performed, one at an inlet temperature of 350°C and

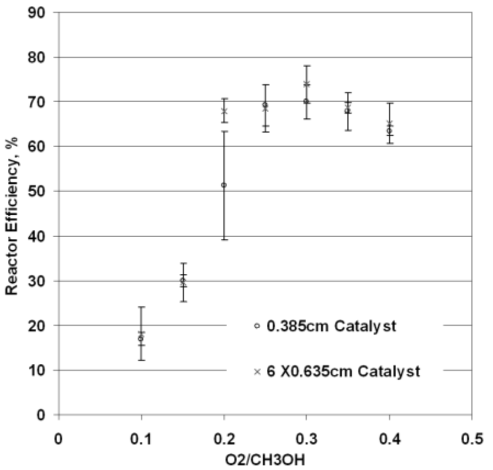

Fig. 7. Comparing 3.81 cm catalyst to six stacked catalyst pieces, equivalent to 3.81 cm.

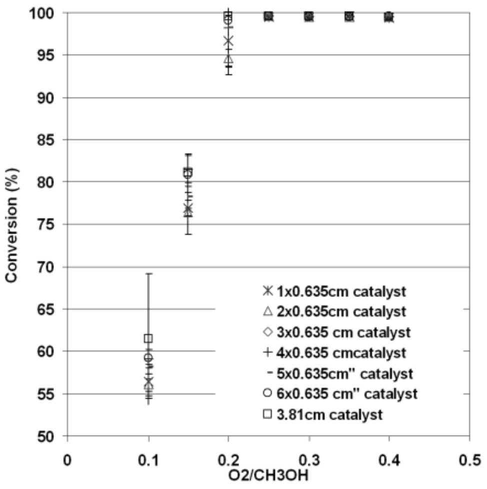

Fig. 8. Fuel conversion for different length of catalysts.

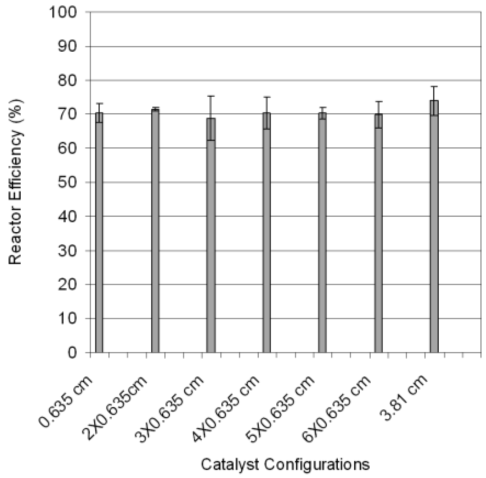

Fig. 9. Reactor efficiency at 7 different catalyst configurations.

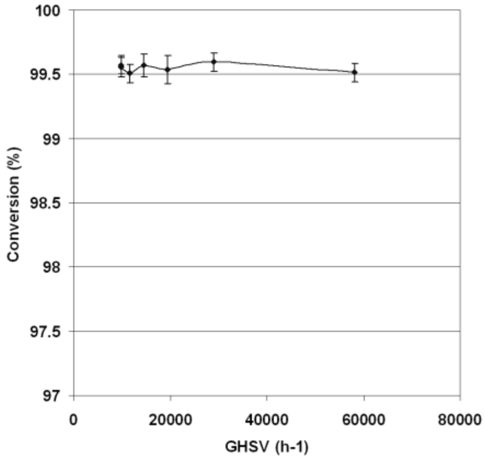

Fig. 10. Fuel conversion at 7 different catalyst configurations, GHSV from 9,700 to 58,100.

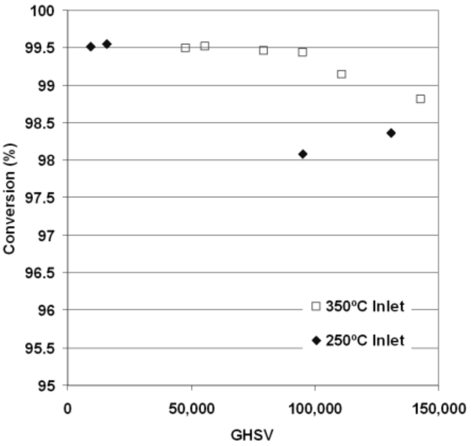

Fig. 11. Fuel conversion as a function of gas hourly space velocity.

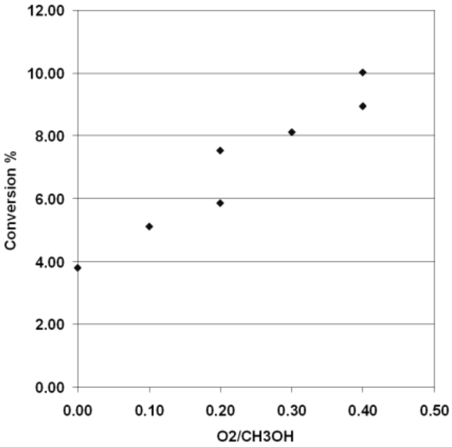

Fig. 13. Fuel conversion with no catalyst.

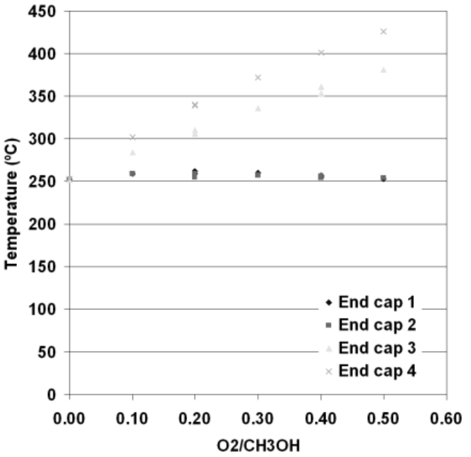

Fig. 12. Blank substrate temperature profile.

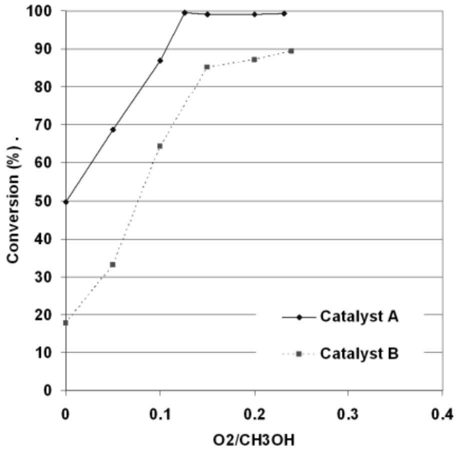

Fig. 14. Comparing catalyst A and catalyst B.

another at 250°C. The results are illustrated in Fig. 11. As expected, the conversion in these preliminary results appears to start diminishing at GHSV upwards of 100,000 h^{-1}.

For investigating the effects of the catalyst, a blank cordierite substrate was tested at identical operating conditions as the methanol ATR experiments. The blank substrate replaced the catalyst-coated substrate, located at the Zone 4 entrance of the reactor. Fig. 12 shows that substrate bed temperatures were much lower than with catalyst present. In this figure, end caps 1-4 represent the axial thermocouples placed through the bottom end cap of the reactor, with 1 being located closest to the substrate inlet and 4 closest to the substrate exit. An O_2/CH_3OH =0.5, where the reactant temperature reached a maximum of 425°C at the exit of the substrate bed, is a 25% higher level than the oxidant levels tested with the catalyst. The fuel conversion measured with the blank substrate is shown in Fig. 13. The highest fuel conversion is approximately 10%, compared to nearly 100% with the catalyst [13]. Furthermore, the gas analyzer readings indicated that there was little or no hydrogen generated; therefore, the efficiency of the non-catalyst system is approximately zero. Catalyst A, which is a proprietary catalyst manufactured specifically for ATR, outperforms catalyst B, made from platinum and palladium and used for the oxidation reaction in a standard automotive catalytic converter. Fig. 14 displays a comparison of the fuel conversion of each catalyst at a reactant inlet temperature of 350°C.

4. Conclusions

Autothermal reformation of fuel cell-grade methanol fuel was investigated for hydrogen production. For experimental results an ATR system was integrated into an existing steam-reforming infrastructure. Data were collected that suggests the upper limit of GHSV for this system is at GHSV above 100,000 h^{-1}. Higher inlet temperatures of the reactants seem to allow for higher conversions at high flow rates as expected by theory. No significant changes in conversion were found by analyzing the stacked catalyst vs. the single monolithic catalyst above the light-off O_2/CH_3OH ratio for the flow rates studied. This implies that the bulk of the oxidation takes place early in the reaction as manifested by high temperatures. Unsteady reaction behavior was manifest near the light-off point for both configurations but especially for the stacked catalyst pieces. This study provides a baseline for future research on ATR of hydrocarbon fuels.

Acknowledgments

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Nomenclature

ATR : Autothermal reforming
CH_3OH : Methanol
GHSV : Gas hourly space velocity
η : Efficiency
LHV : Low heating value
MFC : Mass flow controller
O_2/CH_3OH : Oxygen-to-methanol molecular ratio
POX : Partial oxidation reforming
SLPM : Standard liters per minute
SR : Steam reforming
TC : Thermocouple
V : Volume
x : Air-to-fuel ratio
Y : Fraction of fuel entering reformer

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