Experimental investigation of Methane Partial Oxidation for Hydrogen Production

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Manuscript received December 12, 2017; accepted January 18,2018. Paper no. JEMT-1712-1051

The thermal partial oxidation process of methane was investigated experimentally. Thermodynamic calculations and kinetic simulation were performed to determine the practical operating conditions. Experimentally, a porous material-based reactor was built to perform the partial oxidation process. Al2O3 granular with different size selected as porous structures and installed in the reaction zone. Physical parameters include diameter of the rector is considered for other experimental test. As the result the temperature profiles along the reactor central axis and concentration profiles of CO and H2 were measured. Also the effects of equivalence air ratio on the reforming process were investigated. Different equivalence air ratio 1.5 and 2 was considered to perform the partial oxidation process.

keywords: *methane reforming, hydrogen, partial Oxidation, porous media, combustion.*

http://dx.doi.org/10.22109/jemt.2018.110940.1051

1. INTRODUCTION

Fuel cells are considered to be the green power sources for the 21st century, and may make the "hydrogen economy" reality. Solid oxide fuel cell is a technology that H2 as well as CO can be utilized as fuel. Thus, synthesis gas (syngas), which can be produced from hydrocarbon fuels, can be directly utilized in such high temperature fuel cells. The syngas can be produced from natural gas, by steam reforming, catalytic or thermal partial oxidation (POX) and auto-thermal oxidation [1]. Compared with the other reforming technologies partial oxidation process has several advantageous. There is no need for external heat sources and additional feeds like water as in steam reforming. Moreover, the process is catalyst free and thus catalyst deactivation problems are completely out of consideration. It has a good dynamic response, a very simple system design and can be applied to almost all hydrocarbons [1]. The process of partial oxidation is considered in porous media rector. Gas mixture combustion in porous media is substantially different from free flame homogeneous oxidation. In the free flame propagation, the dominant mechanism for heat transfer is the convection of hot combustion products. Due to poor heat transfer properties of gas mixture, combustion occurs inside a thin layer of reaction. This leads to a poor upstream heat transfer. A solid porous material placed in the combustion media can transfer the total heat more by radiation and thermal conductivity resulting from the thermal properties of the solid matrix (thermal conductivity and thermal radiation) [2]. Therefore, the upstream flame enthalpy is partially transferred through radiation and conduction, improving the stability of oxidation. Fig. 1 displays the variations in temperature of gas and porous solid along the flame length.

In this paper, the thermal partial oxidation process of methane in an inert porous reactor is studied experimentally. The objective of this paper is to find the best performance of reactor for optimum hydrogen production.

In numerical model for comparing to experimental results the kinetic and thermodynamic data sets GRI Mech. 3.0 were used. In the experimental part, tabular reactor with different diameters, based on porous media, was built. In the diverging conical section the reaction front (oxidation zone) is stabilized. An insulation layer was used in order to reach near adiabatic conditions. Temperature profiles along the reactor central axis and concentration profiles of CO, H2, CO2, and CH4 were measured in three sections. Different sizes of granule for Al2O3 as porous structures were installed in the reaction zone. The effects of mas flow rate of fuel and equivalence ratio on the reforming process were investigated.

2. RELEVANT LITERATURE

Numerous experimental and numerical studies have been conducted on hydrogen production in porous media. In discussing hydrogen production in porous media, the literature revolves around the effects of reactor design, structure of porous media material, equivalence ratio, flow rate and partial oxidation in porous media. Using the Péclet number, the incomplete heat

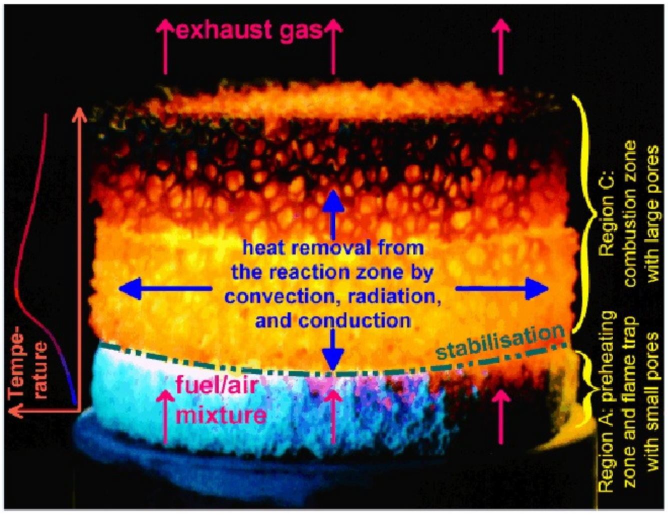

Fig. 1. Variations in temperature of gas and porous solid along the flame length [3]

combustion of liquid and gas hydrocarbon fuels took place in the inert base reformer of a porous medium [4]. Babkin investigated the incomplete combustion of methane in two porous media with different thermal conductivity and radiation properties, including silicon carbide foam and aluminum oxide AL2O3 [5]. In an experiment using the stability parameter of Peclet number, Pedersen et al. examined the rich combustion of methanol, methane, octane and gasoline inside an inert porous medium in a quartz or porcelain tube where hydrogen production could possibly take place [6,7]. Furthermore, they employed various types of porous media with different properties including aluminum oxide foam and aluminum oxide grains. This experiment also used solid granules of aluminum oxide and silicon carbide foam in different sizes. Hsu et al. found that the heat transfer rate and radiation coefficients significantly affect the prediction of gas and solid phase temperature in porous media [8]. To achieve correct results in the numerical simulation, it is essential to apply the porous media properties based on accurate empirical data. Howell et al. characterized porous media with several properties such as effective conductivity, permeability coefficients and vanishing coefficient based on empirical tests [9]. Miguel et al. investigated numerically methane thermal partial oxidation (TPOX) within a small scale inert porous media based reactor in order to explore the operating conditions and possible procedures for maximizing the reforming efficiency and minimizing the soot formation [10]. Han et al. optimized detailed reaction mechanism for methane combustion for methane partial oxidation, based on experimental results from a flow reactor. So that the optimized mechanism can predict CO and H2 production more accurately in methane partial oxidation [11]. Using several experiments and numerical results, Pan et al. obtained the effective conductivity of porous media for a few types of ceramics [12]. Malico and Pereira explored the effect of radiation properties of porous media on the function of cylindrical porous torches in a two-dimensional scenario [13]. They found that temperature distribution is strongly dependent on radiation parameters, particularly scattering phase function. Regardless of the radiation, the results will be in good agreement with the available experimental data. In other empirical studies on incomplete combustion in porous media, Al-Hamamre et al. examined the effects of different parameters such as inlet speed (heat load), equivalence ratio and porous material (thermal conductivity and specific heat of porous material). In this research, the output products from the reactor were cooled by an exchanger and then directed as dry gas into the gas chromatograph or gas analyzer system [14]. The product compositions were analyzed for H2, CO, CO2, N2, O2, CH4 and C2H2. Zhdanok conducted several tests for different porous materials, and geometries of porous media [15].

3. POROUS MEDIA COMBUSTION

It is essential to provide a few definitions prior to exploring the combustion in a porous medium. A porous medium is composed of a heterogeneous system made of solid matrix with empty space filled by fluids. It contains a number of pores between a few phase particles inside a duct or control volume. Porous media are characterized by certain parameters constituting the properties of porous material. Oxidation in porous media can be classified into two stationary and non-stationary. The former can be achieved through stabilizing the flame inside the porous media at a specific zone. On the other hand, the combustion wave in the non-stationary mode travels alternatively forward and backward in a porous solid matrix.

4. FUEL-AIR RATIO AND EQUIVALENCE RATION

The mass ratio of fuel to air is called fuel-air ratio represented by FA.

$$FA = \frac{m_f}{m_a} \quad \textbf{(1)}$$

m_f and m_a are the mass of fuel and mass of air, respectively.

Air-fuel ratio plays a crucial role in the quality of combustion. Combustion will not occur if the air-fuel ratio is too large or too small. In between the two boundaries, however, this ratio should be selected depending on the condition until the highest efficiency is achieved.

5. EXPERIMENTAL APPARATUS

Experiments on partial oxidation were conducted using the setup schematically is shown in Fig. 2. The apparatus consisted of a combustion tube filled with a porous medium, fuel and air supply system, temperature measurement system.

For experimental tests, combustion tube with three internal diameters (Fig. 3), wall thickness of 2 mm were made of quartz. Also for investigating the effect of the length of the tubes were made in three size of length. The inner surface of the combustion tube was covered with a 2mm layer of ceramic paper insulation. Also to prevent heat losses and achieve quasi-uniform temperature profiles, additional 20mm thick high-temperature insulation was applied on the external diameter of the reactor. The packed bed of 1, 3 and 5 mm solid Al2O3 spheres were used as a porous medium having a different porosity (Fig. 4). The combustible mixtures of methane with air were prepared by a continuous flow method where the fuel and air flows were metered using a set of mass flow controllers. To ensure uniform gas composition the reactants were premixed in a mixing chamber. The outlet gas of the reactor after passing through the gas cooling system was gathered into a reservoir tank to make a possible for testing sample. In the exhaust, the online oxygen, CO, CO2 and methane analyzers were used with measurement instruments. Fig. 5 shows the test set up for experimental investigation.

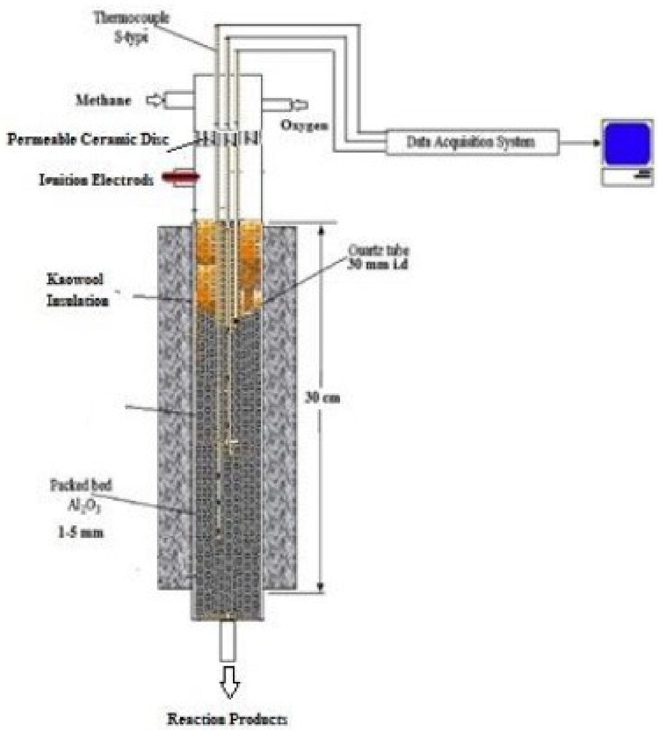

Fig. 2. Schematic of the Set up

Fig. 3. Quartz tubes as combustion reactor with different length and diameter

Fig. 4. Packed bed of 1, 3 and 5 mm solid Al2O3

6. RESULTS AND DISCUSSION

As noted earlier, this paper attempted to make an experimental test set for partial oxidation of methane for a tubular reactor filled with porous material. With an emphasis on higher hydrogen production, this study focused on the effects of porous media, including structural properties of materials such as particle diameter as well as physical changes in the reactor such as diameter of the reactor, and finally the equivalence ratio of fuel and air, and inlet flow rate of fuel and oxygen.

Fig. 5. Experimental set up for partial oxidation of methane

A. Temperature distribution

In Fig.6 the modeling and experimental result of the temperature distribution inside of rector is shown. The model shows the results in different section. In experimental test as explained 3 thermometer were installed for measuring the temperature at different length of reactor. It should be mentioned that the test results are for the flow rate for methane and Oxygen at 100 lit/hour. The equivalence ratio in this model is fixed ($\varphi = 2$).

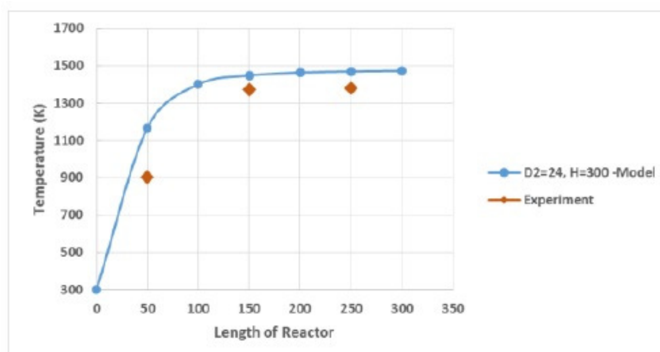

Fig. 6. Variation of temperature distribution in rector, $Q_{methane} = 100 lit/hour$, $Q_{Oxygen} = 100 lit/hour$ $\varphi = 2$

B. Effect of the mass flow rate

From various aspects, the mass flow rate affects the thermal incomplete combustion in porous media: stationary time, temperature distribution and heat load. It has been found that high mass flow rate results in a shorter stationary time in the reactor. This implies that the reactant has shorter time to complete the reaction. Furthermore, the high mass flow rate of fuel/air was coupled with a high degree of distribution, covering a heat load higher than low mass flows. However, if the reactor is built for a wide range of fluctuations, such as porous-medium reactors, the effect of stationary time on the degree of conversion will be smaller than the effect of turbulence and heat released in porous structure. It is therefore expected that hydrogen concentrations in high thermal loads be greater than those in low thermal loads, despite shorter stationary time. This is due to the fact that relative heat loss occurs lower in high thermal loads than lower ones. This implies that a small portion of the heat is transferred to preheat the incoming gases toward the upstream flow. Consequently, in the low power scenario, the hydrogen product is low and low temperature is expected in the reactor. Fig.7 displays the model and experimental results of temperature variations at the reactor outlet. Fig.8 displays the mole percentage of hydrogen, while Fig.9 displays the mole percentage of carbon monoxide in the reactor output for different flow rates. The diameter of the reactor is 30 mm, the length is 30 cm and equivalence ratio of 2 for different flow rates. As the figures show at flow rate 50 lit/h we have high difference between the model and the experimental test. It is because the stability of the combustion cannot be controlled and stabilized.

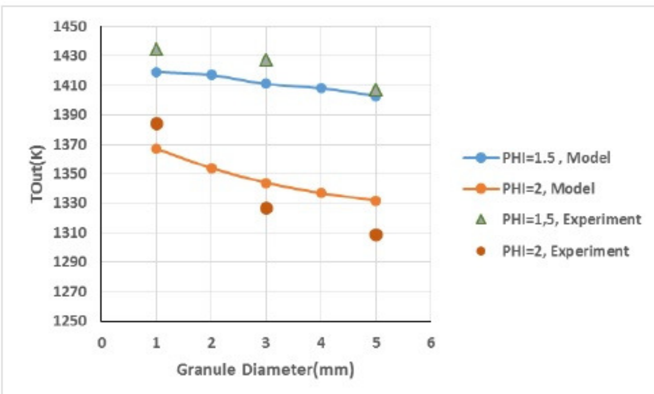

Fig. 7. Temperature variation with fuel flow rate Equivalence ratio 2, D=30mm & L= 30cm

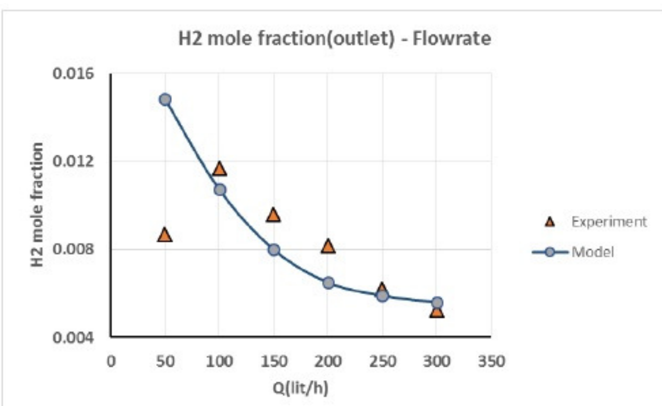

Fig. 8. Hydrogen mole fraction variation with fuel flow rate Equivalence ratio 2, D=30mm & L= 30cm

C. Effect of material diameter in porous matrix

As stated earlier, high rate of heat transfer in porous bodies is not only due to high thermal conductivity, but also due to numerous pores in porous bodies, which increases the heat transfer surface and subsequently the heat transfer. One parameter effective in this process is the diameter of granules in the porous medium.

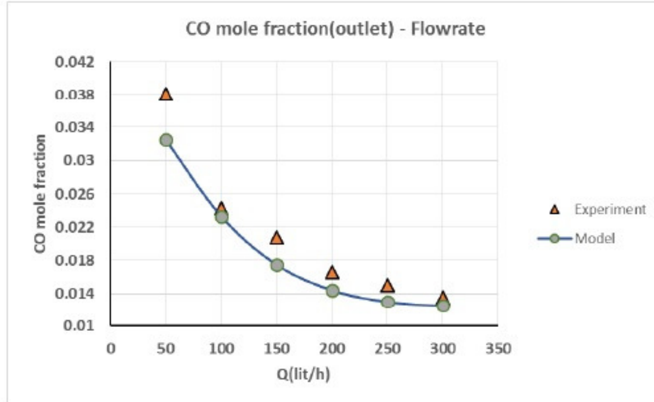

Fig. 9. CO mole fraction variation with fuel flow rate Equivalence ratio 2, D=30mm & L= 30cm

In this modeling, the particle diameter was considered to be between 1 mm and 5 mm given the thermo-physical properties of aluminum oxide. The experimental test was done for 1, 3, and 5 mm of granules. Fig. 10 provides the temperature variations in the reactor outlet with aluminum oxide granules at different diameters in a reactor with a diameter of 30 mm, a length of 30 cm and equivalence ratio of 1.5 and 2. In Fig. 11 also displays the changes in the mole percentage of hydrogen along with changes in granule diameter. As can be observed, the lower granule diameter leads to greater mole percentage of hydrogen. This is because of the surface area of porous structure affecting the fuel conversion in the partial oxidation process. Lower diameters of aluminum oxide granules create larger surface area and a more tortuous paths for the gas flow inside the porous matrix and intensifying the prorogation. This in turn leads to greater heat transfer between the gas and solid porous matrix, which can subsequently achieve greater fuel conversion. Fig. 12 displays the mole percentage distribution of CO mole fraction produced in the reactor.

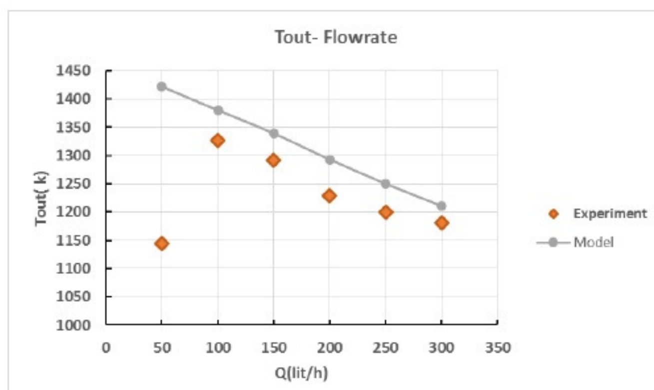

Fig. 10. Temperature variation with diameter of granule, D=30mm & L= 30cm

7. CONCLUSION

Partial oxidation of methane for hydrogen production in an inert porous media is studied numerically and experimentally. A tabular pack bed rector considered and methane–oxygen mixtures is used for feeding in the reactor. Al2O3 as inert porous

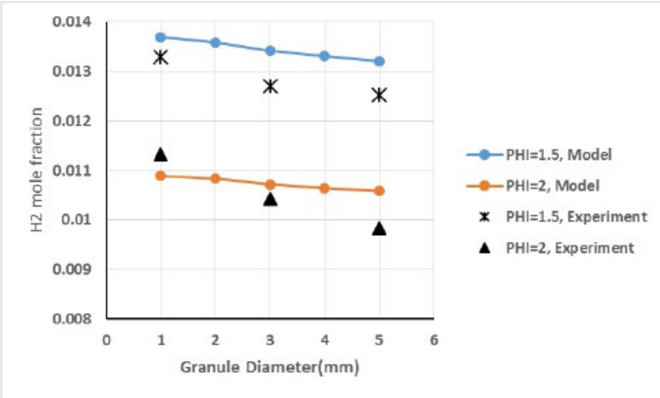

Fig. 11. Hydrogen mole fraction variation with diameter of granule, D=30mm & L= 30cm

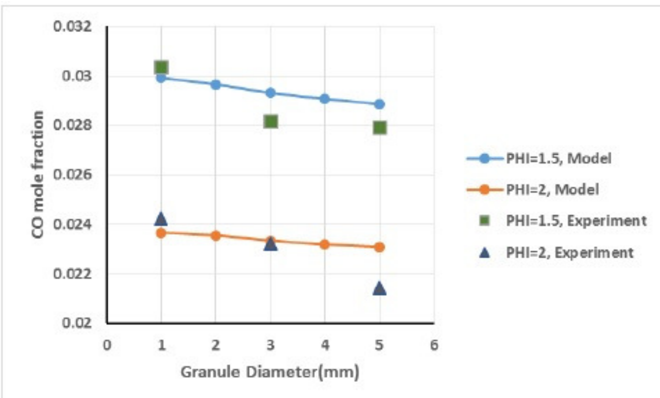

Fig. 12. CO mole fraction variation with diameter of granule, D=30mm & L= 30cm

media is applied in this study. The various parameters that may effect on the performance of the rector for hydrogen production were investigated. Regarding to the different concept of running the test set, the maximum difference between the models and experimental results are about 10% that shows a good match between the model and experimental tests.

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