Applied Energy 232 (2018) 79–88

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Methanol partial oxidation accompanied by heat recirculation in a Swiss-roll reactor

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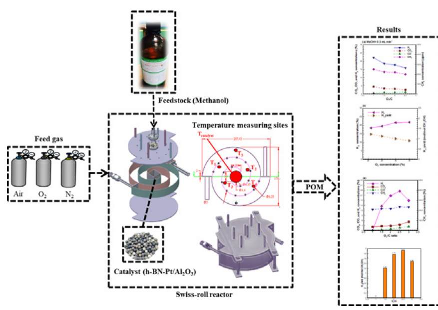
HIGHLIGHTS

- Methanol partial oxidation and heat recirculation in a Swiss-roll reactor are investigated.
- Excess enthalpy in the product gas is recovered by the feed gas in the reactor.
- Sufficient oxygen supply is essential in accomplishing H_2 production in the reactor.
- The optimal O_2/C ratio at GHSV = 10,000 h^{-1} is 2.5 with the maximum H_2 yield of 1.93 mol (mol methanol)$^{-1}$.
- Heat recirculation in the Swiss-roll reactor can efficiently produce H_2.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Methanol partial oxidation
Swiss-roll reactor
Heat recirculation
Excess enthalpy recovery
H_2 yield
Water gas shift reaction

ABSTRACT

Hydrogen production with high efficiency is a crucial issue for prospective hydrogen economy and carbon emission reduction. Methanol partial oxidation triggered over an h-BN-Pt/Al_2O_3 catalyst from a cold start in a Swiss-roll reactor with heat recirculation are investigated experimentally. The effects of methanol flow rate (0.5 and 0.6 mL min^{-1}), O_2 concentration (21–35 vol%), and O_2-to-methanol (O_2/M) molar ratio (1.0–3.0) on the performance of methanol partial oxidation are examined. Heat exchange by transferring the excess enthalpy in the product gas to the feed gas is achieved in the reactor where the temperature of the feed gas before entering the catalyst bed can be promoted to around 100 °C. The experimental results indicate that a methanol flow rate of 0.5 mL min^{-1} leads to more H_2 production compared to those obtained with a flow rate of 0.6 mL min^{-1}. In the conducted Swiss-roll reactor, oxygen supply plays an important role in accomplishing the partial oxidation, and the O_2/M ratio should be controlled beyond 1.0. By increasing the O_2 concentration, the H_2 concentration at O_2/M = 1.5 increases from 18.5 to 21.8%. However, the H_2 yield decreases, resulting from progressively dominant combustion mechanism. At a fixed gas hourly space velocity of 10,000 h^{-1}, the optimal O_2/M ratio for H_2 production is 2.5, for which the H_2 concentration and H_2 yield are 23.5% and 1.93 mol (mol methanol)$^{-1}$, respectively. The highest H_2 yield is close to the theoretical result. Overall, methanol partial oxidation along with heat recirculation in the Swiss-roll reactor can efficiently produce H_2, and the excess enthalpy recovery in the reactor can improve energy utilization.

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https://doi.org/10.1016/j.apenergy.2018.09.208
Received 21 June 2018; Received in revised form 24 September 2018; Accepted 25 September 2018
0306-2619/

Nomenclature

CPOM	catalytic partial oxidation
GHSV	gas hourly space velocity (h^{-1})
$\dot{n}$	molar flow rate (mol min^{-1})
O_2/M	oxygen-to-methanol molar ratio
POX	partial oxidation
SR	steam reforming

Subscripts

H_2	hydrogen
O_2	oxygen

1. Introduction

Hydrogen has recently become a promising fuel [1]. For example, a solar-powered hydrogen fueling station has been developed for cities [2]. The production, storage, and refueling systems of hydrogen have been demonstrated in safety conditions. Sakr et al. [3] found that when a polymeric membrane was employed between electrodes, the efficiency of hydrogen production became higher than that obtained with an acrylic separator. Hydrogen has also been applied in transportation. In Norway, hydrogen produced from municipal solid waste is used by local vehicles and ferries. In addition, local SO_2 and CO_2 emissions can be reduced via appropriate product gas treatment and carbon capture [4]. Using "power to gas (PtG)" technology [5], hydrogen can be generated from surplus or intermittent electricity and then used as an energy carrier for conversion back to electricity when needed via fuel cells [6].

Methanol partial oxidation is a method that can quickly produce hydrogen [7]. It is an exothermic reaction, and thus no additional heating equipment is needed. Methanol has a high H/C ratio and no C-C bonds; it is easy to be transported and thus regarded as a suitable hydrogen carrier [8]. The methanol partial oxidation reaction can be expressed as:

$$CH_3OH + 0.5O_2 \rightleftharpoons 2H_2 + CO_2, \quad \Delta H^0_{298} = -192.3 \text{ kJ mol}^{-1} \tag{1}$$

In past studies, noble and non-noble metal catalysts have been employed to trigger methanol partial oxidation. Rednyk et al. [9] prepared three different catalysts of PtO_x/a-C/Si, Pt/Si, and PtO_x/Si for methanol partial oxidation. Their results indicated that the PtO_x/a-C/Si catalyst had higher activity for methanol partial oxidation than the other two catalysts, and was thus considered as a potential catalyst for the reaction. Chang et al. [10] utilized Au-Ru-Fe_2O_3 at various calcination temperatures for methanol partial oxidation to determine the optimal conditions. For non-noble metal catalysts, Chen et al. [11] found that copper catalysts supported on rice husk ash (Cu/RHA) had better thermal stability and selectivity for methanol partial oxidation to produce H_2 compared to those of Cu/SiO_2.

As far as a Swiss-roll reactor is concerned, its main feature is the spiral structure in the reactor [12]. Chemical exothermic reactions normally occur at the center of the reactor, and the heat released from the flue gas is recovered by the influent in the counter-current pattern, enabling heat exchange. The Swiss-roll reactor has been utilized to enhance thermal efficiency, stabilize combustion, and facilitate chemical reactions. Chen et al. [13] simulated the catalytic partial oxidation of methane (CPOM) in a Swiss-roll reactor, and showed that over two-thirds of useful work contained in the product gas could be recovered to preheat the reactants in the reactor, thereby enhancing the performance of CPOM. Shih et al. [14] designed and analyzed the model of a Swiss-roll recuperator for a micro gas turbine. Their results showed that the effectiveness of the recuperator increased with the number of turns, but the optimal conditions between the effectiveness and the pressure loss should be considered. Kim et al. [15] investigated three kinds of Swiss-roll combustor and found that flame could be stabilized for a wide range of equivalence ratios. In addition, CO emissions increased with decreasing combustion chamber size and could be eliminated by adding a catalytic reactor. Zhong et al. [16] tested methane/air mixtures at various equivalence ratios in Swiss-roll combustors, and found that the combustors greatly enhanced combustion stability in their central regions.

The Swiss-roll reactor can also be applied for hydrogen production. Chen et al. [17] simulated CPOM and a two-stage water gas shift reaction (WGSR) in a Swiss-roll reactor. The operation at gas hourly space velocity (GHSV) of 10,000 h^{-1}, O/C = 1.2, and S/C = 4–6 was suggested as the optimal conditions for hydrogen production. Chen et al. [18] added CO_2 into methane as the feed gas for CPOM and found that heat recirculation in the Swiss-roll reactor increased syngas formation by up to 45%. Chein et al. [19] investigated steam reforming in methanol with a Swiss-roll reactor for hydrogen production, and showed that the reactor produced H_2 with the thermal efficiency ranging from 13 to 35%. Tsai et al. [20] designed a Swiss-roll recuperator and investigated it through simulations and experiments. Their results showed that an engine with a recuperator used at least 1.5 times less fuel than did an engine without a recuperator. Aziznia et al. [21] combined a Swiss-roll reactor design with a fuel cell and obtained superficial peak power densities of up to 1000 W m^2. After improvements and optimization, durability was improved. The reviewed literature is summarized in Table 1.

According to the literature review, Swiss-roll reactors have been used in heat recovery [22], heat recirculation for enhancing chemical reactions [18], gas turbine [14], fuel combustion [16], and reducing air pollution [23]. Though the Swiss-roll reactor has been applied in CPOM by simulation [24], the literature review suggests that the experimental study of methanol partial oxidation in a Swiss-roll reactor for hydrogen production is still absent. For this reason, the present study is intended to explore hydrogen production characteristics from methanol partial oxidation in a Swiss-roll reactor, while an h-BN-Pt/Al_2O_3 catalyst is used to trigger the partial oxidation from a cold start. To figure out the influences of operating conditions upon the methanol partial oxidation, a number of parameters such as methanol flow rate, oxygen-to-methanol molar ratio, and gas hourly space velocity are taken into account. Meanwhile, the oxy-fuel combustion has been widely studied for improving combustion efficiency and CO_2 capture. For instance, Han et al. [25] indicated that the enhancement in oxy-fuel combustion efficiency was approximately 50% compared to air-fuel combustion. Inspired from this technology, the impact of the oxygen concentration in the feed gas upon methanol partial oxidation performance is also evaluated in this study. The temperature distributions in the Swiss-roll reactor are measured to demonstrate the heat recirculation behavior. The obtained results are conducive to fulfilling hydrogen production from methanol partial oxidation with high efficiency.

2. Experiments

2.1. Experimental setup

The experimental system for methanol partial oxidation and adopted apparatus are shown in Fig. 1. The components in the system could be categorized into feeding unit, Swiss-roll reactor, temperature measurement unit, gas treatment unit, and gas analysis unit. In the feeding unit, the volumetric flow rate of fuel (methanol) was controlled by a syringe pump. The flow rate of the feed gas, namely, air or the gas mixture of oxygen (oxidant) and nitrogen (balance gas), were supplied from cylinders that were individually controlled by electric flow rate controllers. When the gas mixture was employed, prior to entering the reactor a gas mixer was used to mix oxygen and nitrogen where their flow rates were displayed on a readout. For the Swiss-roll reactor, its internal structure was spiral, and the number of turns of the inflow and