Review of Yield Intensification on Steam Methane Reforming through Micro Reactor and Rare Earth Catalyst

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Abstract – *This paper reviews the potential of process intensification of steam methane reforming yield using micro reactor and rare earth catalyst. The world's energy sources are facing critical deficient as the world energy consumption increases rapidly. A few alternative sources have been discovered to minimize the energy depletion rate. It is widely accepted that hydrogen is the cleanest, most efficient and abundant energy sources in the future. Production of hydrogen through catalytic steam methane reforming (SMR) is an important yet challenging process which involves intensifying the methane conversion and hydrogen yields. A performing catalyst will favour the thermodynamic equilibrium while ensuring good hydrogen selectivity. Review of the synthesis micro reactor and rare earth catalyst has the potential to create an interesting relation towards SMR intensification process. The expected outcome of this review is to establish the groundwork for optimizing kinetic rate reaction; enhancing the methane conversion and hydrogen yield at product stream and preparation of basic kinetic model for production's scale up towards making it a good candidate for industrial applications.* **Copyright © 2015 Penerbit Akademia Baru - All rights reserved.**

Keywords: Steam methane reforming, micro reactor, catalyst, process intensification.
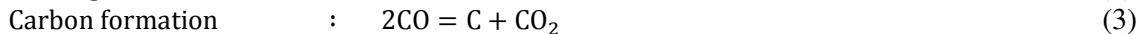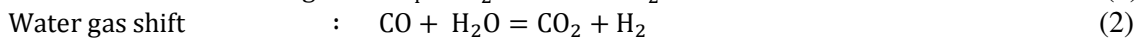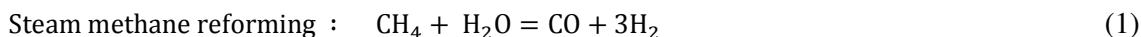
1.0 INTRODUCTION

The world's energy sources are facing critical challenge to meet the ever increasing demand of energy consumption. A few alternative energy sources have been discovered to address such needs. It is widely accepted that hydrogen is among the cleanest, efficient and pollution free energy source in the future. Moreover, lots of attention has been paid to hydrogen production technology in order to obtain a stable source of hydrogen. Currently, almost 96% of the world's hydrogen demand is supplied by traditional fossil fuels, and about half of it comes from natural gas, which the main composition is methane. The production of hydrogen from various hydrocarbons especially methane mainly comes from the chemical reaction process of catalytic reforming technologies which consist such as steam reforming, partial oxidation, and auto thermal reforming. Among these, catalytic methane steam reforming has the advantage of relatively low reaction temperature and high hydrogen content in the reforming products, and it is currently regarded as the most cost effective and highly

developed type of reforming for hydrogen production. Whereby, since the early 1950s, a considerable effort has been put into the investigations of methane steam reforming and its kinetics [1-8].

The steam reforming of natural gas, composed mostly of methane also known as Steam Methane Reforming (SMR), is commonly produced in tubular reactors packed with Nickel (Ni) based catalysts. The product of SMR is a synthetic gas, which is the mixture of hydrogen and carbon monoxide that become important feedstock to the chemical industry with large scale production. This SMR is a strongly endothermic reaction requiring the external heating of the reactor tubes which is carried out either by direct firing (as in radiant reformers) or by heat exchange with a hot stream (as in convective reformers) [3-7].

1.1 Catalytic steam methane reforming

The catalytic steam reforming of methane basically is described as the endothermic reaction of methane with steam over a catalyst at elevated temperatures (400–900 $^{\circ}$C) and pressures (1–30 bar). The main reactions that take place during the catalytic steam reforming of methane are as below [4-9].

Steam methane reforming	:	$CH_4 + H_2O = CO + 3H_2$	(1)
Water gas shift	:	$CO + H_2O = CO_2 + H_2$	(2)
Carbon formation	:	$2CO = C + CO_2$	(3)

1.2 Catalyst based

The current production of hydrogen through SMR, the Nickel (Ni) catalysts based is most widely used due to its less expensive cost, well establishes and accepted technology at industries. However, in comparison with the noble metal rare earth based catalysts (such as rhodium, palladium, platinum and ruthenium), the supported nickel catalysts are less active and usually more prone to be deactivated by carbon formation or oxidation. The main problem that occurs is the formation of coke by the decomposition of methane at higher temperatures and straight decreases the catalyst activity leading to drop in the conversion of methane and hydrogen yield [1-10].

Recent works reported that the noble metal rare earth catalyst based is highly active, mechanical stable and less prone to coke, and also allow operation at lower steam to the methane ratios, which enhance process intensification methane conversion and increased the hydrogen yield. The researcher reported that rare earth was able to achieve complete conversion over a certain inlet reactant flow rate at temperatures below the materials stability limit. Unlike the Ni-based, the methane conversion is only around 60% at the materials stability limit. This is due to the catalyst mechanical stability which is an important issue. Furthermore, Ni is too slow to cope with the rate of heat release and leads the temperatures in the reactor to increase. This is because the intrinsic SMR chemistry on Ni is rate limiting. Therefore a fast reforming catalyst is needed, and the rare earths fulfil this requirement [3-11].

1.3 Micro reactor

The strong endothermic nature of SMR and the different heat supply methods for this reaction shows a very different performance for hydrogen production in traditional fixed bed

and micro scale reactors. The usage of tubular packed bed reactor had shown a few constraints such as of heat transfer coefficient, high steam to methane ratio flow rate and unstable kinetic rate of reaction, and for example, a cold spot always exists at the entrance region of a fixed bed reactor. Literature reported that in order to avoid the drawbacks of conventional fixed bed reactor, researcher had switched to pay attention at micro scale reactors. This is due to its applicability of process intensification on basic transport phenomena, which leads to the improvement of SMR performance in terms of kinetic data acquisition, energy efficiency and process size reduction [4-13].

However, the SMR process through the micro reactor in literature is limited. This is due to the performance of the reactor which depends on the catalyst microstructure. Furthermore, in micro reactors, it is quite difficult to load conventional catalyst particles due to the structured catalyst supports such as foams and monoliths used for gas phase reactions that are generally ceramic based. However, a few studies managed to prove that wall coated micro channel geometry led to higher methane conversions and hydrogen production rates as well as lower hydrogen to carbon monoxide ratios in the output stream [5-17].

1.4   Evaluation of methane conversion

Recent work by researcher showed via extensive proof-of-concept simulations that steam reforming on rare earth at micro scale (sub-millimeter characteristic length scale) and millisecond contact times is feasible and thus, methane conversion can be intensified by hundred to thousand times [10-18].

The steam methane reforming process depends on micro reactor geometry configuration, thermal and flow parameters. Besides that, its intensification also depends on catalyst characteristics, and reactant contact time. The technique of steam methane reforming on micro reactor and rare earth catalyst based is still new, therefore, the catalyst characteristics, methane conversion rate, and intensification of this technique need to be measured and evaluated fundamentally, especially when unique catalyst characteristics are being tested. Therefore this basic equation is used as the fundamental guide [14-24].

$$\text{Conversion of methane (\%)} = \frac{F_{CH4,in} - F_{CH4,out}}{F_{CH4,in}} \times 100 \qquad (4)$$

$$\text{Hydrogen yield (\%)} = \frac{F_{H2,out}}{F_{CH_4,in} - F_{CH_4,out}} \times 100 \qquad (5)$$

$$\text{CO selectivity (\%)} = \frac{F_{CO_{out}}}{F_{CH_4,in} - F_{CH_4,out}} \times 100 \qquad (6)$$

$$\text{CO}_2 \text{ selectivity (\%)} = \frac{F_{CO_2,out}}{F_{CH_4,in} - F_{CH_4,out}} \times 100 \qquad (7)$$

$$-r_{CH4} = \frac{dX_{CH4}}{d(W/F_{CH4,in})} = C_1 + 2C_2 \left(W/F_{CH4,in}\right) + 3C_3 \left(W/F_{CH4,in}\right)^2 \qquad (8)$$

Where:

$$
\begin{array}{ll}
-r_{CH4} & = \text{kinetic rate of reaction methane} \\
F_{CH4,in} & = \text{molar flowrate methane in} \\
F_{CH4,out} & = \text{molar flowrate methane out} \\
F_{H2,out} & = \text{molar flowrate hydrogen out} \\
F_{CO,out} & = \text{molar flowrate carbon monoxide out} \\
F_{CO2,out} & = \text{molar flowrate carbon dioxide out}
\end{array}
$$

W   = weight % catalyst

$C_{1,2,3}$ = obtained at different reaction temperature and

$$\text{reactant flowrate} \left(\frac{\text{kmol}}{\text{kg. cat. h}} \right)$$

The basic evaluation of methane conversion can be simply presented as in Figure 1. There are two main streams consist of steam, methane and hydrogen. Whereby steam and methane are the main reactant and hydrogen gas functionally act as catalyst activation agent. Both reactants will undergo preheating stage before entering reformer, then proceed to the quenching and lastly collected gas will be analysed. The optimum temperature and pressure inside the reformer will influence the final stream output of methane conversion and hydrogen yields [19-24].
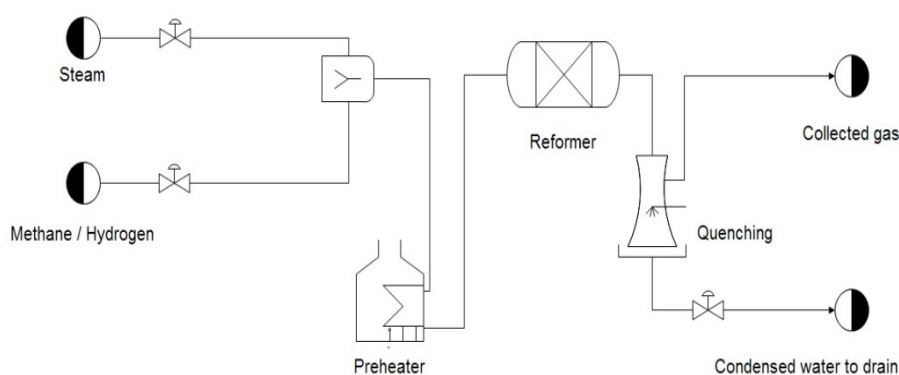

Figure 1: Basic process flow diagram for the process intensification on steam methane reforming through micro reactor and rare earth catalyst based

2.0 CONCLUSION

The findings of the review are summarized as follows:

i.   The enhancement of the hydrogen yield at product stream via steam methane reforming on rare earth catalyst based in micro reactor can be achieved.
ii.   The fundamental kinetic model for the production scale up through the validation of relationship among catalyst and reactants characteristics needs to be established.
iii.   The establishment of the micro reactor geometry configuration for the intensification methane conversion rate towards making it good candidate for industrial applications.

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