



Methane and Methanol Steam Reforming in a Membrane Reactor for Efficient Hydrogen Production and Continuous Fuel Cell Operation

Savvas Vasileiadis¹, Zoe Ziaka^{2,1}, Magda Dova¹

¹Hellenic Open University, Patras, Greece, 26335

²International Hellenic University, Themi-Thessaloniki, Greece, 57001

ABSTRACT

Our goal in this paper is the description and analysis of new findings and results on membrane reactors and catalytic reactors/heterogeneous processors for the steam reforming reactions of methane, natural gas, and methanol for use in power generation systems and fuel cells.

The current communication continues this research by giving emphasis in the so-called “Improved Reaction” and “Reforming-Fuel Cell” systems.

We examine the use of methane/methanol based gases (hydrogen generating feedstocks) as sources for Power/Electricity generation via Fuel Cell Technology (i.e., SOFCs). The work focuses on the analysis of methane steam reforming data from two types of reactors. The membrane based reformer and the conventional catalytic plug flow reformer. It was found that the membrane reformer offers higher yields of hydrogen than the plug flow reformer. The same is true for the methane conversions and the CO₂ yields. It is expected that the integration of the membrane reformer into the fuel cell network will offer an improved design for this process operation.

Keywords: methane steam reforming, methanol steam reforming, catalytic reactor, SOFC, membrane reactor model, hydrogen production, environmental processes

1. INTRODUCTION

There is a recent emphasis on the development and commercialization of such methane/methanol based systems for hydrogen/fuel cell generation applications. Such installations can be applied both in stationary and transportation fuel cell power applications [15,19,20]. New models of both systems are under development and operation with variable kW size. Methane can come from a variety of sources with primary use this of the natural gas coming from the municipal gas network. The same is true for methanol, having also the option of using methanol coming from various renewable biomass sources. Related computational modeling of such multifunctional microreactors and membrane systems for the aforementioned applications is under way to describe their function, operational conversion range, yield and capacity. The models used, simulate relevant acquired data and predict conditions for best membrane reactor and process operation by variation of key intrinsic parameters. The models utilize also kinetic data of the reactions involved as these were reported earlier. The proposed efficient membrane reactor configurations and their

specific fuel cell-power generation applications seek to perform multiple unit operations within a single or integrated module which makes them advanced in comparison with up to now proposed and utilized conventional type of reactors. They project a promising advancing technology for primary and secondary hydrocarbon to hydrogen upgrading membrane-reactors for use in continuous (inline) fuel cell and power cycle processes. The described positive technical aspects/effects are fortified in view of the environmental and economic benefits that these processes possess especially in connection with directly powering fuel cell stacks. There is still a need to improve the characteristics of such reforming processes because of their large magnitude of operations.

Shen and Song have studied the methanol conversion under different catalysts [22, 23]. Conversions up to 100% can be achieved for specific catalytic conditions, as shown at the figure 1a.

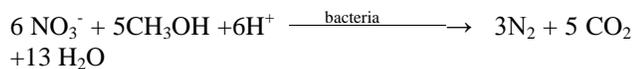
Better understanding of the methane and methanol importance can be analyzed based on the table and analysis below [22].

Table 1: Physicochemical Properties of Methanol

Dipole moment	1.69 D
Melting point	-97 °C
Boiling point	64.7 °C
Density	791.8 kg/m ³
Viscosity 20 °C)	0.59 mPa (at
Phase	Colorless liquid
pKa	-15.5
Octane number	96
Least flash point	12 °C

The Importance of Methanol Use

Consumption of methanol worldwide was around 42 millions of tons. Based on economical estimations its yearly consumption is going to be increased about 13% by 2014 and 4.1% by 2019. The 30% of the produced methanol is used for the production of formaldehyde and for this plenty of chemical compounds such as polymeric materials, dyes, explosive materials, textiles, resins, anti-freezing liquids for automobiles e.t.c. It is a very common solvent for lab use and extremely useful for HPLC and UV/VIS spectroscopy. It can consider as a very good fuel. Methanol is converted into fuel (benzene) according to a process developed by Mobil in 1970. One of the current uses of huge quantities of methanol is in the area of biodiesel. One more interesting application of methanol is the direct methanol fuel cells, DMFC. Moreover, methanol is an ideal source of carbon during the treatment of liquid chemical wastes containing large amounts of NH₃. It can accelerate the reaction rate in presence of bacteria according to the following reaction.



Advantages and Disadvantages of Methanol

Methanol is an attractive fuel and producer of hydrogen. It has a high ratio of H/C (4:1) equal of that of methane. It is liquid in atmospheric pressure in contrast with methane and LPG.

It has also low boiling point as it shown in table above. From environmental view point, methanol is transferred easily through the organisms in the nature because it is dissolved well with the water in contrast with the benzene and gas oil.

Its flash point is 12 while benzene is -43 °C that makes methanol better mixture with air. EPA has estimated that the replacement of benzene by methanol will reduce the fires of fuels by 90%.

It can also be converted to hydrogen in much lower temperatures (150-350 °C) than the other fuels (>500 °C). This fact leads to lower levels of CO.

It does not contain sulfur, so it does not need desulfurization units and the corresponding catalysts use. However, it is a toxic chemical for this reason its use, transportation, storage and distribution have to be done with precaution.

Besides, it contains less energy per volume (15.6 MJ/L) in comparison with benzene (32.4 MJ/L).

2. PROCESS DESIGN AND OPERATION

The designed reformer under consideration can be a fixed bed catalysis-reactor operating under plug flow conditions or a membrane based reactor. Its outlet gas stream can be used directly as feed in the accompanied fuel cell system (SOFC) for direct electricity or power generation. The outlet streams are rich in hydrogen, carbon monoxide, and carbon dioxide, and consist the proper mixture for SOFC operation. It is moreover beneficial, to operate the reformer/ membrane reformer at a lower temperature regime for increasing the reactor and catalyst life times and for reducing the endothermic heating load (Btu/hr) of the endothermic reformer/membrane reformer.

Such methane/methanol based power systems require the development, use and commercialization of an effective catalytic reformer (or membrane reformer) utilizing active catalysis metals such as Ni, Rh, Ru, and Cr, also Zn, Cu, Pd, or bimetallic combinations of those [3-11]. Enrichment of the catalyst with earth metals, such as Ca, Mg, and K promotes the catalyst stability on stream and minimizes the deactivation from carbon deposition, especially at the reactor inlet.

The following possible reactions may take place in the reformer, by adding steam as the oxidant in the methane/methanol feedstock, as shown below:

- $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$ ($\Delta H_{298}^{\circ} = +206.1$ kJ/mol) (1)
(methane - steam reforming reaction)
- $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ($\Delta H_{298}^{\circ} = -41.15$ kJ/mol) (2)
(possibly a parallel water gas shift reaction)
- $\text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2$ ($\Delta H_{298}^{\circ} = +49.50$ kJ/mol) (3)
(methanol - steam reforming reaction)

Mathematical modeling for a steady-state membrane methane-steam reformer under plug-flow conditions includes the following equations:

$$dX_A/dz = (\pi d_{T2} / 4n_{A0}) r_B R_A - (2\pi/n_{TA0}) P_{A,e} [(p_{FA} - p_{PA}) / \ln (r_1/r_2)] \quad (4)$$

Species A can be any of the reactants and products of the reactions (1) and (2) above.

- With: $R_{CH_4} = -R_1$
- $R_{CO_2} = R_2$, $R_{CO} = R_1 - R_2$,
- $R_{H_2} = 3R_1 + R_2$, $R_{H_2O} = -R_1 - R_2$,

Where R_1 and R_2 are the descriptive heterogeneous reaction rates of the reactions (1) and (2) given above.

The thermal balance in a non-isothermal membrane reformer for the reactions (1) and (2) is given as follows:

$$dT_T/dz = (\pi d_{T2} / 4) (1/m'c_p) \{ \rho_B [(-\Delta H_{r1}) R_1 + (-\Delta H_{r2}) R_2] - 4(U/d_T)(T_T - T_s) \} \quad (5)$$

The reformer pressure balance along the fixed bed of catalyst particles is given as follows:

$$-dP_T/dz = (2 f \rho_g u_{s2} / g_c d_p) \quad (6)$$

The initial conditions are also shown below:

at $z=0$ (reactor inlet), $X_A=0$, $T_T=T_0$, $P_T = P_{T_0}$

For the methanol reforming reaction (3), similar equations are also valid, with the reaction term to be as follows:

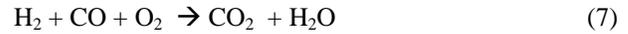
With: $R_{CH_3OH} = -R_3$,

$R_{CO_2} = R_3$, $R_{H_2} = 3R_3$, $R_{H_2O} = -R_3$,

Where R_3 is the descriptive heterogeneous reaction rate of the reaction (3) given above.

If the water gas shift reaction participates as well with the methanol steam reforming then the reaction rates are modified accordingly.

- The interconnected solid oxide fuel cell (SOFC) produces electricity by the following dual electrochemical reaction:
- In the SOFC anode:
- $H_2 + O^{2-} \rightarrow H_2O + 2e^-$
- $CO + O^{2-} \rightarrow CO_2 + 2e^-$
- In the SOFC cathode:
- $O_2 + 4e^- \rightarrow 2O^{2-}$
- With the overall reaction to be:



Computational modeling of the described reformers in this paper was also performed which shows performance measures (methane-reactant conversion, products yield, H_2 rich gas composition) versus the variation of intrinsic model parameters (reactor space time, reaction temperature and pressure, feed composition, space velocity), [18,19].

The models also analyze and show performance measures under new operating conditions which are of interest to new methane/methanol-fuel cell process and project applications [18,19].

The interconnected or integrated fuel cell is fed directly by the fuel-gas/(syn-gas) generated by the described reformers/membrane reformers.

The focus of our studies includes solutions in a number of problems associated with the installation, operation, efficiency, and mass, energy conservation of the entire reformer-SOFC unit.

The solutions focus into the operative improvement of the combined reformer-fuel cell unit and include catalysts and reformer internal and wall materials optimization, and feedstock specifications.

Catalysis studies focus to install improved catalysts with minimal deactivation on stream for continuous reliable reactor and fuel cell operation on a long term basis.

Materials studies focus to improve on the life and constant activity of materials including catalysts, electrodes, and internal components of the reformer and fuel cell systems. Design and process studies focus on system integration, efficient operation, increased power output (kW/m^3), and adaptability to different methane/methanol-based feedstocks.

3. RESULTS AND DISCUSSION

The apparatus used in the experiments consists of mass flow controllers, a bubbler to generate steam for the reaction, the reactor housing wherein the plug flow reactor or the membrane reactor was placed. The reactor is equipped with thermocouples to read the temperature and with pressure transducers to read the pressure. At the exit of the reactor the apparatus consists of steam traps and a gas chromatograph to analyze the exit stream. The gas chromatograph operates in the TCD mode and is equipped with a porapack Q column for the gas analysis. We show below experimental results on the methane conversion capacity of an experimental plug flow

reactor/reformer and the use of the above model to simulate the experimental points/results. The plot, Fig.1, has been generated with experiments that have occurred at different space times and reaction temperatures. The feed composition is $\text{CH}_4:\text{H}_2\text{O}:\text{H}_2=1:4:0.20$. Hydrogen was added in the reactor to prevent the catalyst deactivation, especially at the reactor inlet. The catalyst used in the reformer was a 15% NiO catalyst on calcium aluminate and magnesium aluminate supports. 8.02g of this catalyst was loaded in the reformers in the form of particles with 0.92mm average diameter. The pressure in the reactor was maintained at about 10psig. The experimental points are simulated well by the reactor model (dashed line) which was described above [11,18].

In the next plot, Fig.2, one can see the yield to carbon dioxide that comes from the reforming reaction and the water gas shift reaction. The variation in yield is again due to the variation of space time and the reaction temperature. There are also the model results which simulate the experimental data. The modeling lines show a good agreement with the experimental results.

The next figure, Fig.3 shows the permeability data from the membrane reactor for the various gases. The permeability of the membrane is plotted as a function of the average transmembrane pressure (KPa). The membrane tube was kept at 35°C constant temperature. Hydrogen has the highest permeability through the membrane tube followed by the other four gases. In our membrane reaction studies we utilized mesoporous aluminum oxide membrane tubes having a thin permselective layer (3-5 μm thickness, 50% porosity) with 40-50Å pore diameter [8,12,13,18,19]. The alumina based membrane tube length is $L=25.4\text{cm}$, with an ID of 0.7 cm, and an OD of 1.0 cm. The next to the top inner layer with a pore size of about 200 nm and a thickness of 15-30 μm , is partly contributing to the total permselective ability (permeance) of the membrane tube including the higher selectivity for hydrogen. There are two more successive layers that act as supports to the previous top layers and do not contribute in the selective permeance of the membrane tube. Overall, the gas permeation effect results in the higher separation of hydrogen via the membrane as seen in the Fig.3.

The next plot, Fig.4, shows the methane conversions in a number of systems. The methane conversion in the tubular membrane reactor is shown as a function of the reaction temperature. The membrane reformer methane conversions exceed the equilibrium conversions calculated at the tubewise reactions conditions. The plug flow reformer conversions are very close to the equilibrium calculated conversions. Moreover, the membrane reactor conversions are simulated well by their respective modeling line. The models use data from both reformers and from the reaction conditions which occur

within the catalyst. The kinetic data and the permeation/permeability data used within the models were obtained from separate/independent experiments which took place earlier [11,18,19]. The membrane reformer conversions are higher because of the equilibrium shift of reaction (1) due to the effect of the membrane in the reformer. The membrane assists in the continuous hydrogen permeation and separation which leads into the above beneficial increases of the methane conversion and the CO_2 yield as also shown in the next figure (Fig.5).

It is characteristic that the methane conversion reaches 75% at the 600 °C especially for the membrane reformer case.

The beneficial increase in CO_2 yield with the use of the membrane reformer is shown in Fig.5 below, together with the other data. The CO_2 yield is indicative of the extent of the water gas shift reaction (reaction (2)). The CO_2 yield also corresponds to the CO conversion according to reaction (2). Moreover, there is a good fit by the modeling results (simulation lines) to the experimental membrane reactor CO_2 yield data. The plug flow reformer data is very close to the equilibrium calculated CO_2 yields. The reaction conditions are the same with those described above. The above plots (Figs. 1, 2, 3, 4, 5) are shown the type of syngas (in terms of composition) which is entering into the SOFC system for electricity generation according to reactions (1) and (2), [12-14,18-20].

The next figure, Fig.6 is indicative of the hydrogen yield by the various reaction systems. The membrane reformer offers higher hydrogen yields than the conventional plug flow reformer and the equilibrium calculated yields. The yields of the plug flow reformer are close to the calculated equilibrium yields. Such type of membrane reformer can be integrated well with an accompanied SOFC system for electricity and heat generation.

In the case of methanol steam reforming (reaction 3) similar experiments will take place to examine the effects of varying the reaction temperature and the space time of this reaction system. This reaction is also endothermic and similar results are expected as with the methane steam reforming case [16,19]. A methanol steam reforming reactor can be integrated well with an SOFC system for hydrogen and fuel gas provision. The whole system can provide efficiently electricity and heat.

4. CONCLUSIONS

Fuel cells (i.e., SOFCs) can be coupled effectively with reforming operations of methane based gases coming from various types of resources. The specific electricity and heat generation systems can operate in series or

integrated with a catalytic reformer/membrane reformer which converts methane feedstocks at various operating conditions into hydrogen rich fuel gas.

These feedstocks are rich in CH₄ and are converted into a H₂, CO rich mixture suitable for the continuous operation of the fuel cell (SOFC) unit. Our reformers have been also simulated by computational models which account for the reactions taking place within the membrane/reformers. Several flexible operating conditions in the reformers have been tested via these models and results have been derived. The membrane reformer results at higher overall methane conversions, CO₂ yields, and hydrogen yields than the conventional plug flow reformer.

Useful distributed power generation within a wider power grid can be accomplished with this operation, which can cover the local needs of municipal, suburban and remote areas rich in methane and methanol sources.

Final power output relates to the reformer conversion and the efficient utilization of the syngas by the SOFC system. The waste heat from the conversion of syngas to electricity can be possibly reduced through the SOFC operation and higher overall efficiencies can be achieved. Fuel cell operation from methane and methanol, in a continuous operation mode offer as well pollution reduction (specifically NO_x, CO, HCs reduction), higher power density and increased efficiency (reduced waste heat) in comparison with conventional power systems. Work in this area is continuing.

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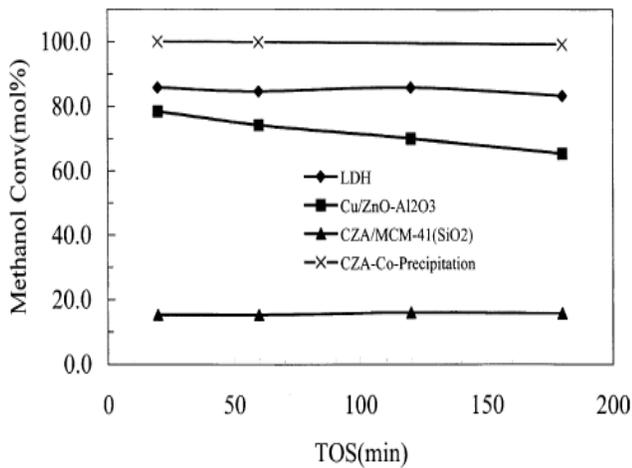


Fig.1a: Methanol conversion under different catalysts, at 230 °C [22, 23], by kind permission of Elsevier

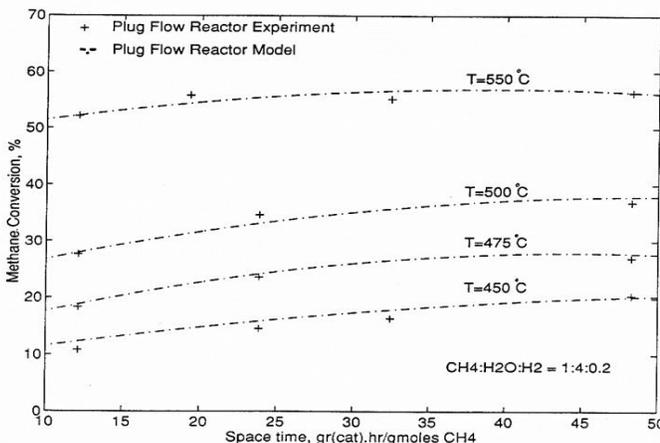


Fig.1: Effect of space time and temperature on the methane conversion capacity of the plug flow reformer

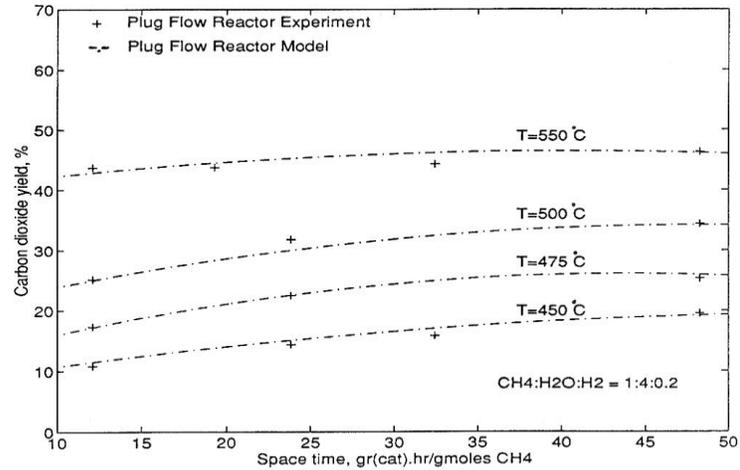


Fig.2: Effect of space time and temperature on the CO₂ yield of the plug flow reformer

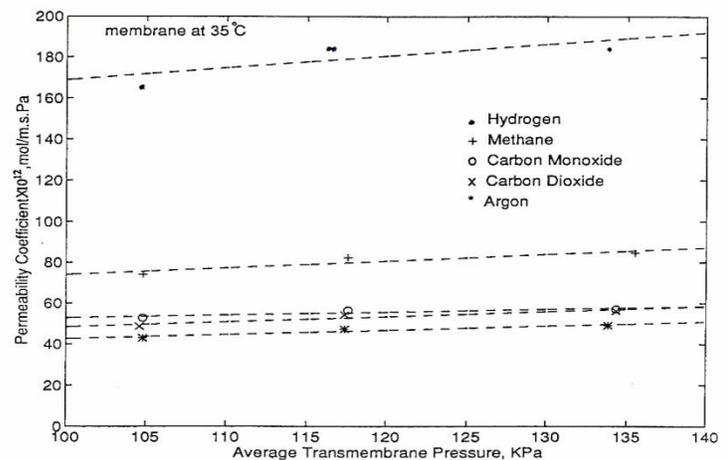


Fig.3: Permeability data via the membrane reactor tube, for the gases participating in the reaction scheme

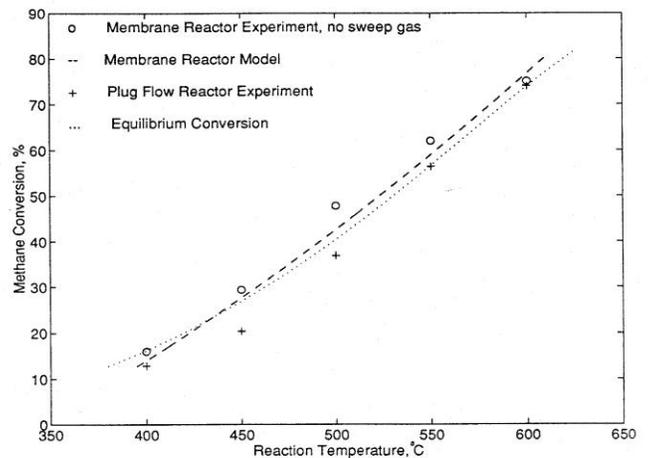


Fig.4: Effect of reaction temperature on the methane conversion capacity of the membrane reactor/reformer and the conventional reformer

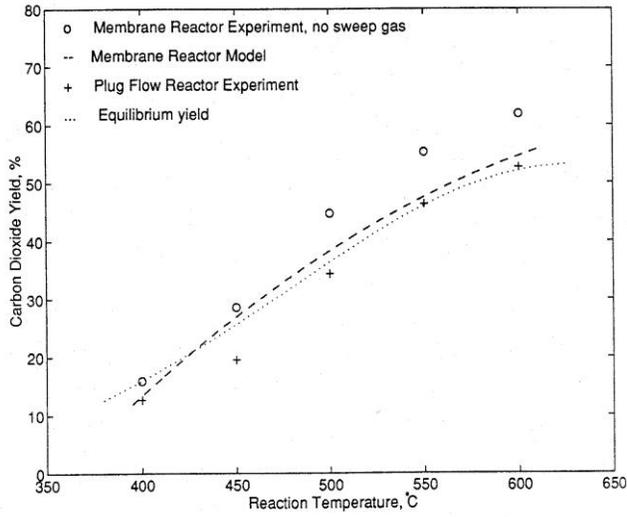


Fig.5: Effect of reaction temperature on CO₂ yield/CO conversion of the membrane reactor/reformer and the conventional reformer

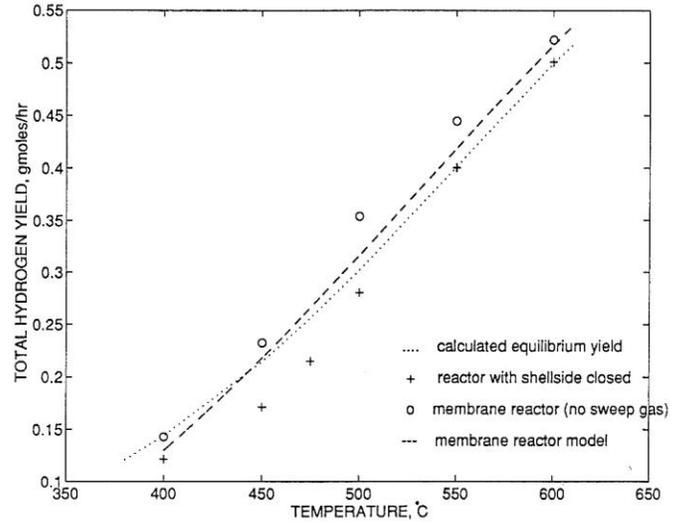


Fig.6: Effect of reaction temperature on total hydrogen yield of the membrane reactor/reformer and the conventional reformer