HYDROGEN PRODUCTION VIA METHANE STEAM REFORMING. PLASMA REACTORS vs. CHEMICAL REACTORS

Jean Marie Cormier\textsuperscript{1}, \textit{Iulian Rusu}\textsuperscript{2} and Nicolae Apostolesc\textsuperscript{2}

\textsuperscript{1} GREMI, Universit\textsuperscript{e} d’Orl\textsuperscript{\textae}s, 14 rue d’Issoudun, BP 6744-45067, Orl\textsuperscript{\textae}s Cedex 2, France
\textsuperscript{2} Technical University "Gh. Asachi", Faculty of Industrial Chemistry, Bd. D. Mangeron 71, Iasi 6600, Romania

Abstract

Almost 20\% of the world production of hydrogen is obtained by steam reforming (SR) of methane in different kinds of reactors. SR is a mature technology, but there is fertile ground and room for technological improvement. The classic steam reformers with their enhanced variants are taken into account on one hand, and on the other hand special interest is paid to the plasmatrons and gliding arc reformers. The comparative analysis is made in terms of advantages and disadvantages coming from the exploitation parameters, methane conversion, selectivity, energy efficiency and investment costs.

1. INTRODUCTION

Hydrogen is an important feedstock for the synthesis of NH\textsubscript{3}, CH\textsubscript{3}OH, HCl, etc., and on the other hand, it should become the ultimate nonpolluting fuel. About 50\% of all hydrogen is produced from natural gas by several methods: (a) thermal cracking (TC), (b) partial oxidation with oxygen (PO), (c) steam reforming (SR), (d) steam reforming with oxygen (SRO), (e) steam reforming with CO\textsubscript{2} (SRCD), (f) CO\textsubscript{2} reforming (CDR) and (g) CO\textsubscript{2} reforming with oxygen (CDRO) but most of it (40\%) is obtained by SR [1]. Each process can be performed using catalysts by means of various reactor models. The aim of the present paper is to make a comparative analysis of the chemical reactors and of the plasma reactors used for SR.

2. Reactions

The main reactions (1, 2) of the process are strongly endothermic, so the forward reaction is favoured by high temperatures (>800°C in most of SR units) and low pressures, but many customers of modern H\textsubscript{2} plants require the H\textsubscript{2} product at more than 20 atm, therefore the operating pressure is about 20-30 atm [2],

\begin{equation}
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2, \quad \Delta H_{298} = 206 \text{ kJ} \tag{1}
\end{equation}

\begin{equation}
\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2, \quad \Delta H_{298} = 164.9 \text{ kJ} \tag{2}
\end{equation}

These reactions are completed by secondary reactions of the methane with carbon dioxide, which are also endothermic:

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\[ \text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2, \quad \Delta H_{298} = 260.2 \text{ kJ} \quad (3) \\
\text{CH}_4 + 2\text{CO}_2 \rightleftharpoons 3\text{CO} + \text{H}_2 + \text{H}_2\text{O}, \quad \Delta H_{298} = 295 \text{ kJ} \quad (4) \\
\text{CH}_4 + 3\text{CO}_2 \rightleftharpoons 4\text{CO} + 2\text{H}_2, \quad \Delta H_{298} = 329.2 \text{ kJ} \quad (5) \\
\] The water-gas shift reaction (6) is moderately exothermic:

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad \Delta H_{298} = -41 \text{ kJ} \quad (6) \]

Other reactions that are less favourable to the hydrogen production lead to the carbon formation.

Addition of excess steam \((\text{H}_2\text{O}/\text{CH}_4 = 2.5-3)\) shifts the reaction away from carbon formation.

3. Chemical reactors

3.1. Classic SR

The reactor is in fact a furnace box structure resembling a large rectangular or cylindrical barn that contains the tubes with catalyst. The usual catalyst is a Ni catalyst supported on a refractory material containing a variety of promoters. The additives are potassium and/or calcium alkali ions, which mainly serve to suppress excessive carbon deposition on the catalyst [3]. Large multiple burners are mounted along the inside walls of the firebox unit (Alcorn, Foster Wheeler, Selas, Haldor Topsoe) [4]. The key challenge in SMR is the heat transfer. About 50% of the combustion heat is used for the reaction and a great deal of effort is spent to recover the waste heat by preheating feeds and steam generation [2].

The different conceptions for these reactors are regarding: the geometry of the furnace, the arrangement of the tubes, the supports for the tubes, the burner type, the connections between tubes and the energy recovery. The main characteristics of such a reactor are: 25-30 m height and 500-600 tubes divided in 2-4 modules (for a production of 265 tones of \(\text{H}_2/day\)). The reaction tubes of 10-12 m long, 12.5 cm inner diameter and the wall thickness of 0.8-2 cm are made of high Ni alloy (20-25%). There are several constructive variants of the tubes, the difference concerning mainly the shape of the support grid for the catalyst. Depending on the shape of the furnace the tubes may be arranged on ranges, in angle, radial or concentric. The used supports for the tubes must to be conceived in order to face a dilatation of about 20 cm at the working temperature.

There are different types of burners as a function of fuel’s nature. When the methane is used as fuel the burner a 1.2 m long flame at a consumption of 150 m\(^3\)/h, the burning gases are circulating in the same direction with the reaction mass from the tubes (Humphreys Glasgow, I.C.I., Kellog, Power Gas).

The \(\text{CH}_4\) conversion at the exit is typically 90-92% and the mixture composition approaches that predicted by thermodynamic equilibrium for a ratio \(\text{H}_2\text{O}/\text{CH}_4 = 3\) [5]. By assessing total energy input and output, the thermal efficiency of SR varies from 81% to 90% depending on author [2, 4, 6].

Obviously, there are some shortcomings of the classic chemical SR: such large reactors clearly imply large investments and exploitation costs [5]; there are limitations on rapid response; the catalyst is very sensitive to poisons; the extreme operating conditions limits the lifetime of reactor tubes; poorly prepared catalyst can lead to migration of the alkali from the catalyst producing downstream corrosion of the steel within the plant.

Changes in the plant layout could in the challenge of finding alternative uses for the reaction heat. Another improving direction for the SR is represented by the in situ separation of the products. Such hybrid configurations may substantially improve reactant conversion or product selectivity and establish a more favourable reaction equilibrium. This means that the reaction could be carried out at much lower temperature, with less demand on heat supply and with the potential of cheaper construction materials [7]. For gas-phase catalytic reactions, the
separation can be based on adsorption, selective permeation through membrane, or through simultaneous reaction of the targeted molecule (e.g. the reaction inhibitor) with a chemical receptor [8].

3.2. Enhancement of SR by adsorption

Older SR operations used a solvent system (e.g. monoethanolamine) to reduce the CO₂ levels from the exiting process gas from 22% to about 0.01% [2]. Han and Harrison studied hydrogen production by SR using CaO as CO₂ acceptor in a tubular reactor [9]. They have reported CO conversions to CO₂ that exceed the thermodynamic equilibrium conversion under specified operating conditions. Russian researchers showed a significant enhancement of methane conversion to hydrogen in a fluidised bed reactor containing Ni-based catalyst balls and a specially treated for of dolomite as adsorbent [10]. Hutton and co-workers have used a hydrotalcite-based CO₂ adsorbent and a commercial Ni-based catalyst achieving a CH₄ conversion to H₂ of 82% and a content >95% vol. H₂ at 450°C and 480 kPa [11]. With a conventional reactor this could be achieved at 650°C. However, this method will necessitate a periodic regeneration of the adsorbent that encumbers other specific costs (heating, new materials, etc.).

3.3. Catalytic membrane reactors

There are two types of catalytic membrane reactors [12]:

- A microporous membrane layer, the catalyst being contained within the wall of the membrane or is deposited on the outer surface of the membrane;
- A permeate-selective membrane, which can be the catalyst, and allows only one component to pass through.

The reactor is formed from two concentric tubes: an outer tube made of stainless steel that is heated and the inner tube (the membrane). The reactants circulate between the tubes, with the hydrogen getting out by the inner tube.

The researchers from Haldor Topsoe have operated at a lab scale using a commercial Ni catalyst contained within a 100μm Pd/Ag tubular alloy membrane. At 6 atm and 500°C, they obtained a CH₄ conversion of 51% corresponding to an equilibrium temperature of 639°C, and at the same temperature and 10 atm the conversion was of 61% corresponding to an equilibrium temperature of 707°C [13]. Members of the same group carried out a process economic analysis of an SR reactor assuming ideal conditions with a Pd alloy coated ceramic tube [14]. In their model, they incorporated the tubular membranes directly into a traditional SR catalyst bed. The membrane assisted SR was only attractive if the cost of electricity was very low and the membranes were 100% selective to hydrogen. The conclusion, based on current information at the time, was that a membrane-integrated process is currently not competitive with traditional SR.

In 1991 Kikuki and co-workers showed that SR can be enhanced using Ni catalyst contained within an 20μm palladium membrane reactor, at 500°C and 10 atm, with a H₂O/CH₄ ratio of 3 [15], claiming a methane conversion of 80%. Later, in order to reduce the thickness of Pd membrane without reducing permeability and mechanical strength, he have proposed a composite membrane consisting of thin Pd later deposited on the outer surface of asymmetric porous ceramics by an electroless-plating technique [16]. This membrane was applied by Tokyo Gas and Mitsubishi Heavy Industries to a membrane reformer on a larger scale to develop a practical apparatus. The reactor operated in the temperature range of 500-600°C and in the pressure range of 2.67-6 atm. The gas conversion was of about 60% while the permeated gas was only hydrogen (~50 Nm³/h).
The weak point of the membrane reactors is the mass transfer, limited if one does not have a membrane with sufficient flux to satisfy the productivity of the catalyst. Other practical issues, such as membrane pore blockage, thermal and mechanical stability, and the dilution caused by the need of sweep (i.e. permeate purge) gases, have limited the usefulness of these systems.

3.4. Solid oxide fuel cells reformers (SOFCR)

Variants of the membrane reactors are the solid oxide fuel cells and in the last decade an increased interest has appeared regarding the use of SOFC to produce H\textsubscript{2} [17, 18]. The membrane is in this case also an electrode (the anode), made of porous carbon plates laced with a catalyst. The hydrogen combines with HO\textsuperscript{-} ions to produce water vapours and electric current. Therefore, the chemical energy is converted directly in electricity. On the anode side, natural gas is first ejected into a reforming chamber where it draws waste thermal-energy from the stack and is converted into H\textsubscript{2} and CO. It then flows into the anode manifold where most of the H\textsubscript{2} and CO is oxidised. This gas stream is then partly recycled to the reforming chamber where the resulted water is used a reagent. On the cathode side, air is first blown into a heat exchanger where it reaches nearly operating temperature. The air is brought up to the operating temperature by combustion of the remaining H\textsubscript{2} and CO from the anode. The oxygen in the cathode manifold is converted into oxygen ion that travels back to the anode. For hydrogen users, the CO can be converted in the established fashion into CO\textsubscript{2} and H\textsubscript{2} using a shift reactor followed by CO\textsubscript{2} separation.

For a cell voltage ranging between 0.5 and 0.8 V, the thermodynamic calculations show an efficiency of electricity and hydrogen generation of about 80%. The system is simple, efficient, tolerant to impurities and uses cheap catalysts. Due to the high operating temperatures air compression is not required. Another advantage is that both hydrogen and CO are used in the cell. While in other cases the CO is a poison, in SOFC is a fuel.

The SOFC is running at temperatures of 800 to 1000°C and therefore, a few minutes fuel burning is required to reach operating temperature. This delay time is considered a disadvantage for automotive applications. On the other hand, most of the cells generate H\textsubscript{2} at 1 atm or less [3]. For bulk production this will then require higher compression to apply the chemical technology.

3.5. Photochemical reactors

Only few studies have been reported about the solar SR of methane [19]. Tamura and co-workers have investigated the solar steam reforming of methane on Ni catalyst, for a molar ratio H\textsubscript{2}O/CH\textsubscript{4} = 1/1, at 650°C using quartz reactor and a Xe lamp with a beam intensity of 900W as light source (solar simulator). The thermodynamic calculations and the analysis of outlet products indicate that the reaction of this study attained equilibrium. However, these are only laboratory approaches, much more work having to be put in order to achieve consistent results.

4. Plasma reactors

Generally, the plasma used for chemical applications is desired to provide high operating power together with high selectivity of the energy input while simultaneously maintaining non-equilibrium conditions [20]. Thermal plasma reactors (plasmatrons) have different constructive variants (induction, DC and microwave plasmatrons) [21, 22]. Basically, the plasmatron comprises two water-cooled metallic tubular electrodes. A spark occurs in the gap.
between electrodes, and the incoming feedstock gas blows the arc into the arc chamber. The working gas can be injected directly or tangentially into the gap between electrodes. The reactants can be mixed prior to the entrance in the plasmatron or the steam can be injected below the arc and the methane beyond the arc in order to minimize the formation of carbon deposits on electrodes. Applying an external magnetic field can enhance the gas rotation. The electrodes are usually made on copper but it is possible to use some new improved alloys, such as beryllium bronze and tungsten-copper-nickel. The main drawback of using thermal plasmas is the overheating of the reaction media, when the reagents into all degrees of freedom uniformly consume energy. Because of this the energy efficiency and selectivity of such systems are rather small.

An alternative approach for plasma SR is the cold plasma (silent, glow, corona, short pulse, microwave or radio frequency). Here, the ionization processes induced by the electric field dominate the thermal ones and give relatively high-energy electrons as well as excited ions, atoms or molecules that promote efficiently selective chemical transitions. In the last decade, a simple technique offering similar advantages has been proposed—the gliding arc. Such a gliding arc occurs when the plasma is generated between two or more diverging electrodes placed in a fast gas flow. The average residence time of the reagents in the reaction zone is about $10^3$ s. This fact allows very high specific throughputs in the reaction zone, which generally exceeds four orders of magnitude other chemical methods, including electrochemical and thermal ones.

The experiments for generation of syngas by SR in gliding arc reactors were performed just in laboratory. Chapelle and co-workers have used a classic gliding arc reactor, with an electric power of 1.4 kW and steam to methane ratios of 2:4. The maximum CH$_4$ conversion was of 44%, with an output energy efficiency of 33% at an energy cost of about 97 MJ/kg H$_2$ [22].

The researchers from GREMI, Université d'Orléans, have used a reactor with an inner conic shape electrode and an external metallic tube as a second electrode [23]. This plasma reactor generates gliding traveling discharges, produced by the radial injection of the gas mixture. Approximately 40% of methane are submitted to chemical transformation at a conversion cost of about 89 MJ/kg H$_2$ and to 125 kJ per mole of converted methane, when a H$_2$O/CH$_4$ = 4.5 was used through. The electric power ranged between 0.1 and 0.3 kW with an output energy efficiency of 40%.

5. Conclusion

Therefore, despite the fact that the SR by chemical reactors is a mature technology that will continue to be used for the next decade (see Table 1), different authors admit that a 25% capital cost reduction in the current technology would have a major impact on overall SCL economics [24-26]. From this point of view the plasma reactors represent an incisive approach by their simplicity, compactness and low price. For small scale units providing hydrogen for fuel cells, not only for automotive applications, the choice of technology may be dictated by parameters as simplicity and quick response to transients. Much more work has to
be put on the use of catalysts, on the reactor design (including heat recovery) and on coupling of plasma reactors with the SOFCs.

<table>
<thead>
<tr>
<th></th>
<th>CH₄ conversion</th>
<th>H₂ content</th>
<th>Power cons. (MJ/kg H₂)</th>
<th>Energy efficiency</th>
<th>Investment cost (USD/Nm³ h⁻¹ H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical reactors</td>
<td>60-92 %</td>
<td>60-100 %</td>
<td>40-45</td>
<td>80-90 %</td>
<td>900-1000</td>
</tr>
<tr>
<td>Plasma reactors</td>
<td>40-44 %</td>
<td>25-75 %</td>
<td>90-100</td>
<td>30-40%</td>
<td>60-70</td>
</tr>
</tbody>
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Table 1. Comparative data for the SR reactors

**6 - REFERENCES**
