HYDROGEN PRODUCTION FROM SIMPLE COMPOUNDS VIA PLASMA REACTORS

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HYDROGEN PRODUCTION FROM SIMPLE COMPOUNDS VIA PLASMA REACTORS

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Abstract

Hydrogen is an important feedstock for the synthesis of NH₃, CH₃OH, HCl, etc., and on the other hand, it should become the ultimate non-polluting fuel. The article presents a comparative analyse between different hydrogen production methods by means of plasma reactors. The case study includes the methane reforming with its variants and the decomposition of water and hydrogen sulphide. Special interest is paid to the plasmatrons and to the gliding arc reactors.

1. Introduction

Taking into account the large increases in natural gas proven worldwide, the production of hydrogen starting from this source has also received more attention. About 50% of all hydrogen is produced from natural gas by several methods as: thermal cracking (TC), partial oxidation with oxygen (PO), steam reforming (SR), steam reforming with oxygen (SRO), CO₂ reforming (CDR) and CO₂ reforming with oxygen (CDRO) [1].

Large quantities of hydrogen sulphide are commonly present in industrial gases and in non-condensable gases from natural gas production and geothermal energy exploitation. A typical mixture of acid gases in natural exploitation consists of 80% CO₂ and 20% H₂S. In such a case one can obtain hydrogen and sulphur by a controlled reaction of the mixture [2].

There are different water splitting techniques that lead to hydrogen, such as: electrolysis, thermochemical water splitting and solar energy water splitting. From these techniques only the electrolysis is in industrial use due to the low overall efficiency (20-35%). Suib and co-workers have performed an interesting study regarding the hydrogen production from water by means of plasma reactor [3].

The aim of the present paper is to make an analysis in terms of advantages and disadvantages coming from the exploitation parameters, conversions, selectivity, energy efficiency and investment costs. Some thermodynamic aspects of the analysed reactions are also taken into account.

2. Plasma treatment of CH₄

TC is a highly endothermic reaction, the major hydrocarbon product being the acetylene. In order to overcome the energetic limitation, plasma reactors have been employed in several
contexts in the last 15 years [4-6]. Large pilot Huls plasma systems have been built (50-500 kW) and optimised for acetylene production. By operating at high gas temperatures more than 60% hydrogen was obtained in the reformate gas mixture [7]. According to the thermochemically nonequilibrium models for microwave reactors, the acetylene is rapidly produced very near the reactor inlet and transported to the discharge region where its concentration remains practically constant [8]. The experiments performed by Plotczyk and co-workers, at the Nitrogen Plant Tarnow, into a plasma installation with an arc power of 50-100 kW indicated a energetic cost of 181 to 208 MJ/kg H₂ [6].

A more recent technology (CB & H Process), with large plasma devices, has been developed by the Norwegian company Kværner Oil & Gas to produce hydrogen and carbon black [9]. In a reactor, a plasma torch supplies the necessary energy for pyrolysis. The plasma gas is hydrogen that is recirculated from the process. A heat exchange system conducts the heat-transfer from the products to the feedstock and plasma gas, which are preheated to set values. Excess heat is used to produce steam for external use. The conversion of methane is almost 100%. The investment cost rises up to 1471 USD/Nm³, h⁻¹. The specific electricity consumption is of 44 MJ/kg H₂. For an input cost of 0.03 USD/Nm³ of methane and of 150 USD/tonne of carbon black (that directly influences the price of hydrogen) a hydrogen cost of 0.07 USD/Nm³ has been estimated.

There are several studies presenting calculations on methane pyrolysis [10, 11]. In France, Fulcheri and Schwob have estimated an energetic cost of 40-77 MJ/kg H₂. In this case an investment of 440 USD/kW of electric power and prices of 0.15 USD/Nm³ CH₄ and 0.0441 USD/kWh lead to a final cost of the hydrogen of 0.05 USD/Nm³.

Laboratory tests performed by means of thermal plasmas requested a large range of energy inputs (110-250 MJ/kg H₂) depending on author [12, 13]. The literature presents some attempts of using catalysts on corona discharge [1] and microwave plasmas [14]. In the first case the use of catalyst increased the methane conversion from 12 to 38% and the selectivity for hydrogen production from 29 to 76.2%. In the second study methane conversions as high as 52% have been found.

Czernichowski and co-workers performed the methane pyrolysis in non-equilibrium plasma of a gliding arc discharge [15]. Up to 34% of the natural gas was converted mostly to hydrogen and acetylene. The minimum achieved energy cost was of 40 MJ/kg H₂.

PO consists of the reaction of an almost stoichiometric CH₄+O₂ gas mixture, leading to hydrogen and carbon monoxide as major products. The actual reaction process is exothermic and more complicated. The disadvantage of PO is the need of oxygen as a feed component.

The literature presents a limited amount of information concerning the methane PO by means of plasma reactors. The plasmatron experiments performed at Michigan Institute of Technology (MIT) revealed that for energy inputs less than 25 MJ/kg CH₄, hydrogen output reaches 38% of equilibrium levels and CO output is 65% of equilibrium [16]. In these conditions the resulted energy cost was as high as 267 MJ/kg H₂ because most of the hydrogen turns into water. Czernichowski and co-workers used their installation for the PO process with a similar energy cost [2, 17, 18].

The main reactions of the SR process are strongly endothermic, so forward reaction is favoured by high temperatures (>800°C in most of chemical SR units) and low pressures [19]. These reactions are completed by secondary reactions, which are also endothermic. Among these, only the water-gas shift reaction is moderately exothermic. Addition of excess steam (H₂O/CH₄ = 2.5-3) prevents the carbon formation.

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 CH₄ conversion was of 44%, with an output energy efficiency of 33% at an energy cost of about 97 MJ/kg H₂ [20]. Cormier and his team have used a reactor with an inner conic shape electrode and an external metallic tube as a second electrode [21]. This plasma reactor generates gliding turning 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 H₂ and to 125 kJ/mol of converted methane, when a H₂O/CH₄ = 4.5 was used through. The electric power ranged between 0.1 and 0.3 kW with an output energy efficiency of 40%.

SRO is a combination of non-catalytic partial oxidation and steam reforming developed by Haldor Topsøe in the late 1950s in order to perform reforming in a single reactor [22]. The partial oxidation is an exothermic process, while the steam reforming is an endothermic one. The thermal energy generated by the former can be adjusted by its molar air/methane ratio so that the overall auto thermal process can be carried out without an extra external heat source for the SR process.

Taking into account the use of plasma reactors, Bromberg and co-workers [23] have simulated the homogeneous SRO process (CH₄ + 0.5O₂ + 1.88N₂ + H₂O) by means of non-equilibrium thermodynamics [24]. The method has been used to determine the reaction trajectory in an adiabatic reactor. The calculations indicate that the reaction is characterised by two distinct stages. During the first stage, complete combustion of part of methane occurs, producing mainly CO₂ and water, increasing the temperature of the system. In the second stage, the remaining methane reacts with CO₂ and H₂O producing syngas and decreasing the system's temperature. The as calculated methane conversion ranged between 97.5 and 100%, leading to a final hydrogen mole fraction of about 35% and of 8-16% for the CO.

The SRO reaction performed at MIT by means of a plasmatron, without catalyst, resulted in a hydrogen yield of 40% (defined as the ratio of hydrogen released to hydrogen content in methane) for an input power of 3.5 kW [13]. At low values of input power, the homogeneous plasma process resulted in low methane conversions (about 40%). The device's productivity was of about 4000 m³/h H₂ per m³ of reactor. The minimum power consumption without heat recovery was about 100 MJ/kg H₂. Furthermore, in order to decrease this specific power consumption a nickel-based catalyst on alumina support was used through. The hydrogen yield increased up to 80%, for an input power of 2.7 kW and methane conversion of 70%. The required specific energy was reduced to less than 17 MJ/kg H₂. The productivity also increased to about 10 000 m³/h H₂ per m³ of reactor.

Scientists from Kurchatov Institute of Moscow have studied experimentally the SRO using only 5% oxygen for a ratio H₂O/CH₄<1 [25]. The reaction was performed using continuous microwave discharge. The discharge power was up to 200 kW, the frequency was 915 MHz, the gas-flow rate up to 200 m³/h, and the gas pressure in the reaction zone varied in the range of 0.1-1 atm. In this case the energy consumption was of 42-47 MJ/kg H₂ for a methane conversion higher than 90%.

Here are some preliminary results concerning the costs of syngas production by means of plasma reformers [26]. There are three major costs in the manufacturing of hydrogen-rich gas: the natural gas cost, the electricity cost and the capital cost of the reactor system. For both the plasmatron and the turning gliding arc reactor it is estimated a capital cost of about 60 USD per Nm³ h⁻¹ of hydrogen. This includes the cost of power supply and the reactor. However, larger systems will produce hydrogen at lower costs. The methane cost is assumed to be 0.11 USD/m³, while the electricity cost is considered to be 0.05 USD/kWh. For a specific energy consumption of 16 MJ/kg H₂ the cost of the produced hydrogen is about 0.23 USD/m³.
CDR is currently of great interest both for transformation of natural gas and for environmental control. Chapelle has performed the reaction on both transferred arc and gliding arc reactor [20]. In the first case the hydrogen concentration in the exit gases decreased from 48 to 22% for a CO₂/CH₄ ratio increasing from 0.5 to 2. Proposing a set of possible reactions, he also has found a good agreement between the experiment and the thermodynamic equilibrium data (T = 2000K). The necessary energy for production of one kilo of hydrogen was of 234 MJ, corresponding to an energy efficiency of about 27%. In the second case the energy cost decreased to 226 MJ/kg H₂, with an energy efficiency of about 31%.

Suib and a Japanese team performed the same reaction by glow discharge and by micro-arc plasmas [27]. The reaction was carried out into an Y-type reactor, both reactants being excited at an average voltage of 1.91 kV. The average current was of 17.4 mA. Contrary to Chapelle’s work, as the CO₂/CH₄ ratio increased from 1/9 to 9/1, the hydrogen selectivity increased from 47.9 to 66% for the glow discharge plasma and from 28.6 to 74.5% for the micro-arc plasma. However, the energy efficiency was quite low, the maximum reached about 16% at CO₂/CH₄ = 1, with the presence of micro-arcs.

The advantage of oxygen addition in the CDRO process is the supply of additional energy for the methane conversion, due to a parallel reaction of methane oxidation. The laboratory scale experiments gave 100% conversion but at very high energy expenditure (190-270 MJ/kg H₂, the energetic efficiency ranging between 23 and 42% [18].

Fridman’s team has used a pulsed corona discharge reactor with preheating of inlet gases (at about 900°C) to promote an efficient reforming process [28]. They succeeded to lower the plasma energetic cost to 34 MJ/kg H₂. However, the energy spent for preheating the mixture was about 340 MJ/kg H₂.

3. Plasma treatment of H₂S and H₂O

The economic and environmental advantages of hydrogen and sulphur recovery from H₂S were recognised in the 1970s [2]. The lowest theoretical limit for the molecule's dissociation by a thermal process is of 10.08 MJ/kg H₂.

Plasma chemical dissociation of H₂S was studied in microwave plasmatrons by Russian researchers [29, 30]. The experiments were performed 0.02 to 0.10 atm and they claimed a minimum energy requirement of 34 MJ/kg H₂. Based on the low energy cost, a big pilot installation (power up to 1 MW and productivity up to 1000 m³/h) has been built at Orenburg (Russia) [31]. The installation treats a H₂S/CO₂ gas mixture, the results confirming the energy cost up to a pressure of 0.8 atm. Encouraged by the claimed energy requirements, Canadian researchers performed similar experiments but with different results (81-202 MJ/kg H₂) [32].

Studies carried out by means of gliding arc reactors showed a lower limit of 161 MJ/kg H₂ for the hydrogen sulphide dissociation and of 443 MJ/kg H₂ for the H₂S/CO₂ reaction [2].

The hydrogen production from water started to be studied quite recently by means of atmospheric dielectric discharges in a tubular reactor with metal coated inner electrodes (Ni, Pd, Rh, Au) and outer electrodes made of aluminium foil [3]. Feed compositions were 2.3 mol% water with balance of argon. The use of excitation temperature as a diagnostic parameter suggested that metal/argon interaction may play an important role in the reaction mechanism. The actual conversion was of about 14% at an energetic cost of about 97 MJ/kg H₂.
4. Conclusions

In Table 1 are summarised the best results reported on the hydrogen production via plasma reactors. As can be observed the laboratory experiments gave better results than larger installations. Among these, the catalysed SRO by means of plasmatrons seems to be the most interesting process to develop.

At industrial scale, the TC of methane process, developed by Kvaerner Oil & Gas has no concurrent at the moment, the price of the obtained hydrogen being similar with that produced by the classic chemical processes.

The use of hydrogen sulphide for hydrogen production is a very inciting direction as far as it is economically competitive and also environmentally protective. Unfortunately, some of the best results reported on this field are contested by other authors [32].

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Process</th>
<th>Reactor</th>
<th>Energetic cost (MJ/kg H₂)</th>
<th>Conversion (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>TC</td>
<td>Plasma torch (CB&amp;H Process)</td>
<td>44</td>
<td>100</td>
<td>Industrial</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gliding arc</td>
<td>40</td>
<td>34</td>
<td>Laboratory</td>
</tr>
<tr>
<td>SRO</td>
<td></td>
<td>Plasmatron</td>
<td>17</td>
<td>70</td>
<td>Laboratory catalysed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Microwave discharge</td>
<td>42-47</td>
<td>90</td>
<td>Pilot</td>
</tr>
<tr>
<td>CDRO</td>
<td>Corona discharge</td>
<td>34</td>
<td>100</td>
<td>Laboratory preheating at 900°C</td>
<td></td>
</tr>
<tr>
<td>H₂S +CO₂</td>
<td>Microwave discharge</td>
<td>34</td>
<td>45</td>
<td>Pilot contested results</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The best results reported in the last decade regarding the hydrogen production by means of plasma reactors.

References