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Manufacture of hydrogen

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Abstract

The demand for hydrogen is ever growing, with major applications in refinery use and as component in synthesis gas for manufacture of methanol, ammonia and GTL products. Fuel cell applications represent an emerging market, and a hydrogen economy with a hydrogen fuelled automotive sector could result in a large demand for hydrogen. Recent developments in hydrogen manufacture by steam reforming focusing on energy efficiency and steam reformer development are presented together with challenges for the future integration with fuel cell applications and issues surrounding CO_2 sequestration.

Keywords: Hydrogen; Steam reforming; Efficiency; Hydrogen economy; CO_2 sequestration

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1. Introduction

Hydrogen is an important reactant and an energy carrier that can be manufactured from a range of energy sources such as fossil fuels, biofuels and by renewable sources and nuclear energy via electricity. Hydrogen can also readily be produced from synthesised hydrogen carriers such as methanol, ammonia and synfuels.

The most economical route is production of hydrogen from hydrocarbon feedstock by steam reforming, which covers a wide capacity range [1]. Refinery usage of hydrogen is one of the major contributors to new hydrogen plants at large capacities, which is driven by regulations requiring evermore stringent desulphurization and fewer aromatics in fuels. Typical capacities range from 10,000 to 100,000 Nm^3/h or larger. Hydrogen is also produced in large quantities in mixtures with nitrogen or carbon oxides for manufacture of ammonia or methanol and in GTL processes. Hydrogen production for fuel cell applications is an emerging market. Typical capacities are from 5 to 1000 Nm^3/h. Especially, a hydrogen economy with a hydrogen fuelled automotive sector could result in a large demand for new hydrogen production capacity.

This paper summarises the recent developments in hydrogen manufacture by steam reforming, focusing on improved energy efficiency, reduced steam reformer size and cost and presenting some of the challenges for the future integration with fuel cells applications.

2. Energy efficiency

As energy prices increased, the operating cost becomes an increasing part of the total hydrogen production cost. In today's hydrogen plants, the operating cost (hydrocarbon cost − steam credit) amounts to about 2/3 of the hydrogen production cost (∼€4 per GJ natural gas price), and it is therefore important to have a very energy efficient process. In recent years, the hydrogen process has been improved significantly. It is important to understand the thermodynamic limit for energy efficiency that one is up against.

The principal reactions for converting hydrocarbons into hydrogen are:

$$CH_4 + H_2O \rightarrow CO + 3H_2 (-\Delta H^{\circ}_{298} = -206\,\mathrm{kJ/mol}) \qquad (1)$$

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$$CO + H_2O \rightarrow CO_2 + H_2(-\Delta H^{\circ}_{298} = 41\,\mathrm{kJ/mol}) \qquad (2)$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m+2n}{2}\right)H_2 \qquad (3)$$

Consider an ideal process in which a stoichiometric mixture of CH_4 and H_2O is converted completely to H_2 and CO_2 by reactions (1) and (2), and the heat of reaction is supplied by combustion of CH_4. For this ideal process, it is possible to determine the theoretical CH_4 (LHV) energy required to produce hydrogen. The theoretical efficiency of the hydrogen production from methane by steam reforming is 2.59 Gcal/1000 Nm^3 H_2 when starting from water vapour, and 2.81 Gcal/1000 Nm^3 H_2 when starting from liquid water as the real process.

Hydrogen plants designed with old technology utilises reforming temperatures well below 900 °C and high steam to carbon ratios (above 2.5). These plants are characterised by poor energy efficiency, as significant amounts of process steam has to be condensed by large air coolers and water coolers. Also investment costs are high, as large volumetric process flows have to be handled.

Modern hydrogen plants utilise the new developments in steam reforming and shift technology, allowing hydrogen plants to be designed with reforming temperatures above 900 °C and steam to carbon ratios below 2.5 even below 2.0. These conditions are easily handled by the side-fired reformer and using a medium temperature shift catalyst. For many years, CO and oxo-gas plants have been operated with side-fired steam reformers having outlet temperatures of about 950 °C, and many hydrogen plants have operated with reformer outlet temperatures of about 920 °C. The reasons for using these Advanced steam reforming [2] conditions are improved energy efficiency and reduced hydrogen production cost.

Advanced steam reforming conditions (high reforming temperature combined with low steam to carbon ratio) have made it possible to operate hydrogen plants with an energy efficiency of less than 3 Gcal/1000 Nm^3 H_2, allowing for export steam credit (feed + fuel amounts to ~3.5 Gcal/1000 Nm^3 H_2), which is only 6% more than the theoretically possible 2.81 Gcal/1000 Nm^3 H_2. The only losses are heat losses from the equipment and heat losses with the flue gas. This is illustrated by a typical pinch diagram below (see Fig. 1).

Radiant steam reformers utilise about 50–60% of the fired heat for the steam reforming reaction, the rest of the energy is used for process heating and steam production, making these plants steam exporting.

Steam export is not always desirable. So, it is a challenge to design a reformer and an energy efficient process, which does not export steam. The convective reformer, HTCR, developed by Topsoe, utilises about 80% of the fired heat for the steam reforming process, and the product gas is at a reduced temperature due to a bayonet design of the reformer tube. With the convective steam reformer, it is possible to reach energy efficiencies of about 3.15–3.25 Gcal/1000 Nm^3 H_2 without steam export [3]. This is significantly less than the ~3.5 Gcal/1000 Nm^3 H_2 obtained with a radiant steam reformer when steam credit is not taken into account. The lower overall natural gas consumption obtained with the convective reformer results in hydrogen production with significantly reduced CO_2 emissions.

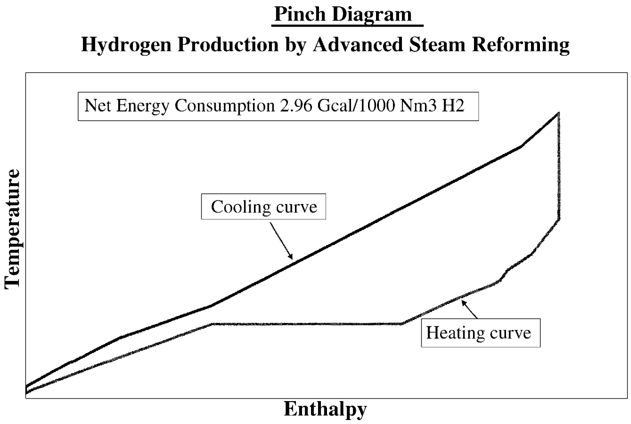

Fig. 1. Pinch diagram for a hydrogen plant using Advanced steam reforming conditions. The heating and cooling curves are ideally matched meaning that all heat contained in cooled process steams is used to heat other process steams and no air or water cooling is necessary.

3. Steam reformer development

Significant progress has been made in improving the tubular reformer, reducing the size and cost while at the same time, allowing Advanced steam reforming conditions. New improved tube materials allow reformers to be designed for tube wall temperatures up to 1050 °C, which is a known practice in ethylene crackers. Better understanding of the influence of temperature levels and temperature gradients on the tube life has indicated that the most critical parameter is the temperature difference over the tube wall. It has been shown [4] that the number of tubes in a reformer is independent of the tube diameter. However, as it is possible to place tubes of a smaller diameter close together, the size of the steam reformer is reduced by decreasing the tube diameter. In addition the weight of the tubes is significantly reduced. By taking advantage of these improvements, Topsoe has introduced the high flux reformer (HFR), which offers a 15% cost reduction as compared to the side-fired steam reformer of 7–10 years ago.

When using the HFR, the flux has been increased such that today's reformers operate with an average flux exceeding 100,000 kcal/(h m^2), which is about twice the flux of 20 years ago, thus significantly reducing the number of tubes. When at the same time, applying smaller diameter tubes, the size and cost of the reformer is significantly reduced. Such reformers are today built for capacities up to about 300,000 Nm^3/h H_2, when using the better control of the tube wall temperature achieved with the side-fired furnace. The above trend in steam reformer development is shown in Fig. 2 [4].

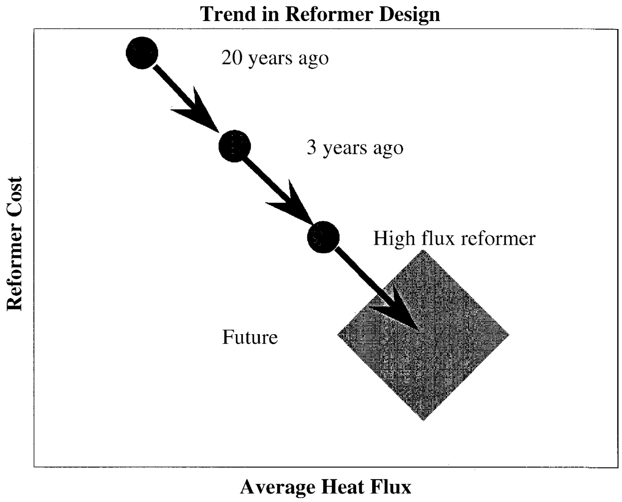

Fig. 2. The trend in steam reformer development has been towards higher average heat flux and smaller tube diameters leading to reduced reformer cost [4].

Even with the reduced catalyst volume of modern reformers (e.g. HFR), there is a plenty of catalyst activity available in the tube [5]. However, a high local activity allows the same flux to be transferred at a lower gas temperature, thus lowering the tube wall temperature and prolonging the life of the catalyst tube. Also, the advances in understanding the carbon formation has assisted the design of reforming and pre-reforming catalysts, which allows better performance of plants operating on heavy hydrocarbons.

In summary, the existing steam reforming technology for hydrogen production has been improved significantly. The cost of hydrogen production has been reduced by lowering operating cost through more energy efficient process design, and lowering investment by reducing the size and cost of the tubular reformer. When considering steam export, the energy consumption has been reduced as far as practically possible by applying Advanced steam reforming conditions (high steam reforming temperature and close to stoichiometric steam to carbon ratio) possible with the side-fired tubular reformer. The convective reformer, HTCR, allows a process concept with no steam export at only slightly higher energy consumption, and is therefore an attractive option at capacities of up to ~25,000 Nm^3/h, where the technology is available.

Hydrogen production by steam reforming appears to be well optimised, but as the following sections will show, the special requirements of the new hydrogen economy will result in many new challenges to the design of steam reformers and the hydrogen production process.

4. New challenges

The emerging hydrogen economy wrestles with a number of issues [6]. Should the hydrogen production be centralised or localised? Will one have to consider CO_2 sequestration? What are the best energy carriers from which to produce hydrogen? And so forth. However, it is evident that hydrogen production by steam reforming of hydrocarbons will play an important role for many years to come, in a transition to renewable energy sources. But the steam reforming process will be faced with many new challenges depending on the chosen distribution scheme, which one does not know today. As an example, one can mention the effort supported by the US DOE to develop on-board fuel processing base on steam reforming for automotive applications. The purpose was to bridge the gap between existing cars and fuel cell cars with on-board hydrogen storage. DOE stopped the programme in the summer of 2004. The announced reason being that technical targets were not met, competing hybrid technology has bridged the gap, and diminishing interest from automakers in the technology [7].

5. Centralised production—large capacity

Hydrogen can be produced in large centralised plants, using today's technology as described above, at a reasonable cost. However, there is a high cost associated with the distribution of hydrogen, e.g. to fuelling stations increasing the cost of hydrogen about three times, whereas gasoline cost only is increased to about 1.4 times production cost [8]. This is especially true during the early stages of introduction of a hydrogen economy, where hydrogen consumption is low and dispersed. Also, there are many issues concerning the safety of a hydrogen distribution system. Therefore, it is reasonable to assume that in the early stages of a transition to a hydrogen economy, hydrogen would be produced locally at the fuelling station using the natural gas distribution system that exist in many places.

6. Localised production – small capacity

Decentralised hydrogen production for localised power production and hydrogen fuelling stations require small scale plants with many new requirements to size, by-products, start-up time, production cost, etc. In areas where natural gas is not available, hydrogen could be produced from hydrogen carriers, such as methanol, via electricity (e.g. from renewable energy such as wind or solar), from biofuels, etc.

The requirements present a challenge and necessitate the development of new types of steam reformers. There are many options, ranging from designs inspired by conventional reformers to designs based on plate heat exchanges, utilising catalysed surfaces, etc. Many groups are working on the development of different designs of small-scale steam reformers [9].

An alternative to steam reforming at smaller capacities is catalytic partial oxidation (CPO). However, for production of pure hydrogen, CPO is less efficient and more costly than steam reforming.

7. CO_2 sequestration

The global environmental debate may lead to a requirement of hydrogen produced from fossil fuels will have to include CO_2 sequestration.

A group of oil companies have created a Joint Industry CO_2 Capture Project (CCP) with the air of developing technology to produce hydrogen fuel and capture the CO_2 for storage in geologic formations. A study was carried out by Topsoe for CCP [10], analysing the application of natural gas fed membrane steam reformer and coal gasifer syngas fed membrane shift reactor as cost effective means of producing hydrogen with CO_2 sequestration. These membrane reactors have a potential for meeting the requirements. However, further development of membrane technology would be required, lowering cost. With this type of technology, even coal could be used to generate hydrogen with CO_2 sequestration.

Topsoe conducted a study with Norsk Hydro ASA, determining the state-of-the-art technology for production of 1200 MW power from natural gas with CO_2 sequestration [11]. The study focused on three options: pre-combustion decarbonisation, combustion with pure oxygen and post-combustion decarbonisation. The study found that the most realistic scheme was pre-combustion decarbonisation. Here, a hydrogen/nitrogen fuel mix is produced by autothermal reforming followed by CO_2 removal, which is inspired by Topsoe ammonia plant front end. Norsk Hydro ASA concluded that the technology was feasible without extensive further development.

Finding a solution for delivering hydrogen economically in a hydrogen economy is challenging especially if one has to consider CO_2 sequestration. It is a dilemma between centralised and decentralised hydrogen production. Centralised large-scale hydrogen production fits into a hydrogen economy in combination with a hydrogen distribution system. The centralised production offers reasonable options for CO_2 sequestration, e.g. by membrane reforming. However, it suffers from high distribution costs. The alternative is localised hydrogen production, which fits better with fuel distribution systems, but CO_2 sequestration is difficult.

8. Conclusion

Significant progress has been made in medium to large-scale hydrogen production, both in energy efficiency and investment. A new emerging hydrogen economy, and especially a hydrogen fuelled automotive sector, presents a new set of challenges to reformer design, catalysts and process layout. Issues such as centralised versus decentralised production and whether CO_2 sequestration catches on, will have a major impact on the direction of the development. These decisions will likely be driven politically through legislation.

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