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Report Abstract

Hydrogen Production in Refineries
PERP06/07S1

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For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.chemsystems.com.

INTRODUCTION

This ChemSystems report provides an assessment of hydrogen production in refineries, including:

- A profile of conventional hydrogen production and purification/recovery technologies.
- An overview of new technologies under development, including patents.
- Economic analyses of representative technologies in use today, including cost of production and sensitivity analyses.
- A review of commercial hydrogen production capacity from global and regional standpoints, showing current and planned hydrogen capacity.

CONVENTIONAL TECHNOLOGY

On-Purpose Hydrogen Production

Continuous catalytic steam reforming forms the backbone of worldwide on-purpose production of hydrogen in refineries. The reforming technique is applicable to natural gas, refinery off-gas and light liquid hydrocarbons, up to naphtha. While such raw materials can also be converted by partial oxidation, continuous steam reforming is usually the more economical route. The most common feedstock by far is natural gas.

In plants now being designed, the synthesis gas produced in the reforming process is typically converted into high purity hydrogen via one or more shift converters and the use of pressure swing adsorption (PSA) or membrane technology to remove CO_2 and residual CO. A representative flow diagram for the process is presented in and described in this section of the report.

In addition to methane, natural gas may also contain higher hydrocarbons, nitrogen, carbon dioxide, and/or helium. None of these additional components needs to be removed, provided that the process parameters and reforming catalysts have been selected to suit the raw material. However, the reforming catalysts are very sensitive to sulfur compounds, halogens, and heavy metal poisons and these must be removed, if present.

Steam reforming catalysts were originally developed for converting methane into synthesis gas. They consist mainly of nickel, with various activators, deposited on a porous alumina support. The essential reaction is the endothermic methane-steam reaction, converting methane to carbon monoxide and hydrogen:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H = +206 \text{ kJ/mol @ } 25^{o}C$$

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This reaction is equilibrium-limited, with maximum conversion increasing with increasing temperature and with increasing steam/methane ratio in the feed, but decreasing with increasing pressure.

From a technical point of view, steam reforming of naphtha to make synthesis gas and, thus hydrogen, is similar to reforming natural gas, and only marginally more complicated. The reaction of the heavy naphtha components is analogous to that of methane described above and is represented in the equation shown below.

$$C_nH_m + nH_2O \longrightarrow nCO + (n+m/2)H_2$$

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An additional process step is Adiabatic pre-reforming which refers to the steam reforming of feed hydrocarbons. This process is also discussed in this section of the report.

The HyTex™ process developed by Texaco Development Corporation (TDC) involves the partial oxidation of natural gas with pure oxygen. It consists of three commercially proven processing steps:

- Texaco gasification process
- Carbon monoxide shift
- Pressure swing adsorption

This process is also detailed in the report.

The section is completed with a discussion about heat exchange reforming - the use of hot syngas product to heat the process gas for use in processes to produce hydrogen (and methanol and ammonia).

Hydrogen Recovery and Purification

The modern refinery is an integrated complex of hydrogen producing and hydrogen consuming processes. As the number of hydrogen consuming processes within a refinery increases, there is more likely to be a need and an opportunity to recover hydrogen from fuel gas streams. Several areas where hydrogen recovery and purification are often employed are:

- Recovery of hydrogen from purge streams of catalytic hydrotreaters and hydrocrackers
- Hydrogen recovery from refinery fuel gas streams
- Upgrading refinery hydrogen stream purity

Catalytic hydrotreaters and hydrocrackers require that a purge be taken off the recycle stream to meet and maintain hydrogen partial pressure requirements. These streams can be processed for hydrogen recovery, with the recovered hydrogen being recycled to the loop or used as a high purity hydrogen stream for other hydroprocessor operations.

Hydrogen partial pressure requirements for hydroprocessing operations often favor the use of relatively pure hydrogen to keep system operating pressures at an economical level. In these instances the hydrogen available from a catalytic reformer is not pure enough and must be upgraded. This can be done by passing it through a hydrogen recovery process.

This section goes on to discuss the Pressure Swing Adsorption (PSA) and Membrane Separation processes.

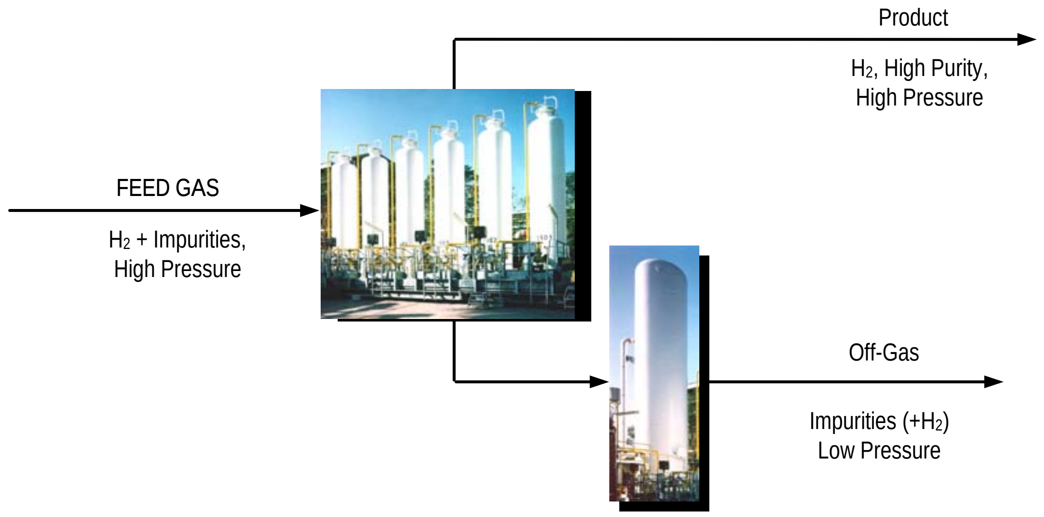
Hydrogen Producers

An extensive discussion of the production processes in use at plants of & licensed by the major hydrogen producers listed below is given:

- Foster Wheeler
- Haldor Topsoe
- Air Products PRISM Membrane
- UOP
- Technip

An example of one of the processes discussed is the UOP PSA system. UOP PSA Systems can be tailored to produce various high purity hydrogen product to meet specific end-user processing objectives. Pressure Swing Adsorption works on the principle that the adsorbents attract and retain impurities at a high pressure and release them at a low pressure; thus the expression "Pressure Swing Adsorption". A simplified UOP PSA process flow diagram is shown below.

UOP PSA Process Flow Diagram



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RECENT DEVELOPMENTS

On-going research has sprouted some new advances in reforming and purification technologies. While thermal and environmental efficiency are motives for reforming improvements, the emerging purification methods are driven by savings in capital cost and production efficiency.

New Reformer Developments

Dry reforming (or CO_2 reforming) refers to the production of syngas from methane and carbon dioxide:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

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Like steam reforming, the reaction is endothermic and therefore more favorable at higher temperatures. Since four gas molecules are produced from two reactant molecules, lower pressures are also more favorable.

Developments to improve the design of Foster Wheeler's TERRACE WALL™ Reformer have been made and are discussed in the report.

Haldor Topsoe (HT) second generation heat exchange Convective Reformer (HTCR) and third generation heat exchange reforming, known as the Exchange Reformer (HTER) are discussed.

New Purification Technologies

The following new developments are discussed:

- Recovery of hydrogen to be used for hydrodesulfurization of middle distillates at Shell's Gothenburg refinery.
- Argonne's development of a ceramic hydrogen membrane made of dense conductive materials that only allow electrons and hydrogen ions to pass through.
- QuestAir's Rapid-Cycle PSA technology capable of boosting cycle speeds by two orders of magnitude relative to conventional PSA.

ECONOMIC ANALYSIS

The economic evaluation of hydrogen production processes presented in this section utilizes Nexant's Cost of Production (COP) methodology.

Economic analysis for the following processes have been carried out:

- Steam reforming of methane to hydrogen.
- Purification of hydrogen using Pressure Swing Adsorption technology.
- Purification of hydrogen using a membrane process.

The hydrogen production capacity was varied by 50 percent higher and lower, relative to the actual capacity, to determine the sensitivity of the production cost to changes in plant capacity. Sensitivity to changes in capital cost & feedstock prices were also carried out.

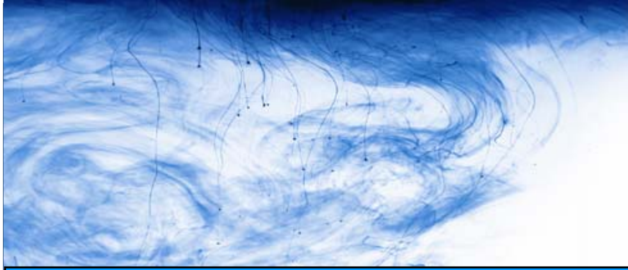
COMMERCIAL ANALYSIS

The petroleum refining industry is by far the largest producer as well as consumer of hydrogen. Therefore, this section profiles the current situation and outlook for the global refining industry.

Regional differences in processing capabilities of the global refinery industry are quite pronounced, reflecting different product mix requirements and available crude oil qualities. Refineries in the USA, Japan, Canada and the Middle East have above average levels of hydrogen plant capacity relative to crude oil capacity.

This section includes **an extensive listing of existing and new hydrogen plant capacity throughout the world**. Details of **company, plant site, hydrogen capacity at the specified plant, and the country where the plant is located** are given in tables compiled according to region as indicated below:

- U.S.
- Canada
- Western Europe
- Australasia
- Eastern Europe/CIS
- Middle East
- Africa
- Latin America
- Asia
- Japan.



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