

Processes for Obtaining Syngas and Hydrogen

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The growing demand for high-quality chemical products has already stimulated an increased interest in the conversion of hydrocarbon gases (natural gas, methane, biogas) into motor fuels and high value-added chemical products, as well as into hydrogen, which is increasingly in demand on the market. The conversion of natural gas into hydrogen and syngas is still the most complex and costly stage of modern gas chemical processes, the low efficiency of which hinders the development of modern gas chemistry.

Keywords: non-catalytic partial oxidation ; natural gas ; methane ; conversion ; hydrogen ; synthesis gas ; modeling ; reactor

1. Introduction

Due to the lack of economically justified methods for the direct selective conversion of methane into heavier hydrocarbons, this process is implemented by preliminary oxidative conversion of natural gas or other hydrocarbon gases into syngas (a mixture of CO and H₂ with a different ratio of these gases, depending on the method of its production). The resulting syngas is a raw material for the production of various chemical products, in particular liquid fuels based on the Fischer–Tropsch synthesis (gas-to-liquid technology, GTL). Therefore, the conversion (reforming) of natural gas into syngas and hydrogen is the basis of almost all modern large-tonnage natural gas processing technologies.

The global syngas market was valued at USD 43.6 billion in 2019. According to the forecasts of the analytical company Research and Markets, in the period 2022–2028, the syngas market will develop at a high rate, at the level of 6.6% per year, and will increase from USD 50.1 billion to USD 73.4 billion ^[1]. The chemical segment is expected to account for the largest share of syngas consumption in the global market, which will exceed USD 39 billion by 2027, up from USD 25.6 billion in 2019. This is due to the growing demand for environmentally friendly raw materials for the production of many chemical products. Syngas with various H₂/CO ratios is used to produce various petrochemicals, fertilizers, oxygenates and other high value-added products. Syngas also plays a key role in the synthesis of ammonia, the most common petrochemical product on the market, with over 100 years of technology behind it ^[2].

Syngas is not only a semi-product of the synthesis of more complex organic compounds, but also the main source of hydrogen production. In 2021, the world production of hydrogen amounted to ~90 million tons ^[3], and world demand for it reached 94 million tons, which is equivalent to approximately 2.5% of world energy consumption ^[4].

2. The Main Processes for Obtaining Syngas and Hydrogen

Currently, there are several main processes for the conversion of natural gas/methane to syngas:

- steam methane reforming (SMR);
- autothermal reforming (ATR);
- partial oxidation (POX);
- catalytic partial oxidation (CPOX);
- dry methane reforming (DMR);
- combined methane reforming (CMR);
- tri-reforming of methane (TRM);

- reforming using membrane reactors.

Each of these processes has certain advantages and disadvantages. While SMR, ATR, POX and CMR are used on an industrial scale (SMR is by far the leader), the rest of the processes remain under development and are the subject of research into the prospects for their application to reduce greenhouse gas emissions, minimize energy consumption and increase reforming productivity. CPOX, due to its relative simplicity and compactness, is often used in pilot and small-scale installations.

Brief information about the three most common processes for producing syngas and hydrogen is given in **Table 1**.

Table 1. Comparative characteristics of the three most common methods for producing syngas and hydrogen [5].

Production Method	Temperature (°C)	Pressure (atm)	Molar Ratio H ₂ /CO
SMR	750–900	15–40	3–5
ATR	850–1000	20–40	1.6–2.65
POX	1200–1500	20–150	1.6–1.8

SMR has been widely introduced on an industrial scale since the 1960s, when natural gas was used instead of coal as a feedstock for producing syngas.



This process is also the most popular and cheapest way to produce hydrogen, as compared to the electrolysis of water per unit of energy expended, it allows the acquisition of 5–6 times more H₂ [6].

Usually, the SMR process is carried out on nickel catalysts at temperatures of 750–900 °C, pressures above 1.5 MPa and a high (to reduce catalyst coking) ratio of H₂O/CH₄ of 2.5–3.0 and higher. When implementing industrial steam reforming processes, the most serious problems are associated with hydrogen sulfide poisoning of catalysts, coke formation and significant sizes of apparatuses. Steam reforming natural gas reformers typically use externally heated reaction tubes containing a relatively inexpensive nickel catalyst. The two most important parameters of the SMR process are the H₂O/C ratio and the reaction temperature. Low values of these parameters are preferred to increase energy efficiency, however, this increases the risk of carbon deposits on the catalyst and its poisoning [5].

The ATR autothermal reformer was developed by Haldor Topsoe (the ATR process is currently marketed under the name Autothermal Reformer Process TOPSOE™'s SynCOR™ [7]). ATR is a combination of partial oxidation and steam reforming processes, which allows reducing the total enthalpy of the process to almost zero [8][9]. A consequence of this is that the H₂/CO ratio obtained in the ATR process is intermediate between the values obtained in SMR and POX (**Table 1**). It takes place in two zones: a partial oxidation zone, which generates the heat required for the subsequent endothermic steam reforming stage, and a catalytic steam reforming zone, in which the final composition of the syngas is reached. Operating temperatures of the process range from 850–1500 °C with a sharp increase in temperature in the oxidation zone and a uniform decrease in the zone of endothermic catalytic transformations, and the operating pressure of the process is more than 2 MPa.

An industrial process for the oxidative conversion of methane to syngas was developed in the early 1950s [10]. As a rule, the process is carried out at a pressure of 30–100 atm using oxygen, which is supplied in a slight excess compared to the reaction stoichiometry. This makes it possible to reach the temperature required for process stability and high methane conversion. However, this leads to the formation of a certain amount of deep oxidation products (CO₂ and H₂O). In addition to methane, raw materials such as oil residues, biogas, etc. can be used to produce syngas by partial oxidation.

Nickel or rhodium catalysts are usually used to carry out catalytic partial oxidation, most often on ZSM-5 zeolites. At the same time, the process proceeds under relatively mild conditions (800–900 °C, 2.5–3.5 MPa), which makes it possible to implement it on a small scale. The process can proceed according to two mechanisms: (a) a sequential mechanism (through deep oxidation of some of the methane to CO₂ and H₂O and subsequent steam and carbon dioxide conversion of the remaining methane), which is promoted by high temperatures, short contact times and catalysts reduced to a metallic state; (b) a direct mechanism (through the complete dissociation of CH₄ → C_{ads} + 4H_{ads} and O₂ → 2O_{ads} on the catalyst surface with subsequent formation of final products C_{ads} + O_{ads} → CO and 2H_{ads} → H₂), which is observed at low temperatures and long contact times on oxidized catalyst surfaces.

The industrial implementation of catalytic partial oxidation is associated with great technical difficulties. These include a high probability of self-ignition of the reaction mixture before contact with the catalyst, a sharp temperature profile and a high probability of the formation of hot spots in the catalyst, which contribute to its sintering, deactivation and metal carryover. This negatively affects the stability and safety of the CPOX process, making it unlikely to be used for large-scale production.

The largest developers and licensors of non-catalytic processes for the partial oxidation of various types of hydrocarbon feedstock into syngas are Shell, Texaco and Lurgi. ^[11] Of the commercialized POX technologies, Shell's Shell Gasification Process (SGP) technology, implemented at the plant in Bintulu (Malaysia) and the world's largest natural gas conversion plant Pearl GTL in Qatar ^[12]; Texaco Syngas Generation Process (TSGP) technology ^[13]; the High Pressure POX (HP POX) process by Lurgi in Freiberg (Germany) ^[14]; and the Gas POX process by Air Liquide Engineering & Construction ^[15] are the most well-known. It is worth noting that Shell SGP's POX gasification process is a flexible process for producing syngas for the production of high-pressure high-purity H₂, methanol, ammonia, fuel gas, domestic gas or reducing gas ^[16].

Numerous reviews, including ^{[17][18][19][20]}, are devoted to the analysis of industrial methods for producing hydrogen. The most common of them is carried out in three steps: (a) preliminary conversion of natural gas into syngas, which is implemented in one of three ways: steam, carbon dioxide and oxidative conversion; (b) steam reforming of formed CO (water–gas shift reaction, WGSR); (c) CO₂ removal.

From the point of view of greenhouse gas emissions during its production, the resulting hydrogen is usually divided into the following categories: (a) “gray” hydrogen, obtained from coal, oil and gas, (b) “blue”, obtained at combined cycle power plants using the technology of capturing and storing carbon dioxide capture and storage (CCS) or, at nuclear power plants, (c) “green” hydrogen obtained from renewable energy sources (solar, wind, etc.) and water electrolysis. Unlike well-established SMR hydrogen production processes, carbon dioxide capture and storage technologies are still far from full-scale commercialization. Companies are using CCS technology to extract CO₂ from industrial emissions and then pump the CO₂ underground. In 2022, 61 new CCS projects were announced, bringing the total number of commercial plants under development to 196, of which 30 are currently in operation, 11 are under construction and the remainder are under development ^[21]. After the completion of the implementation of all the above projects, a total of 244 million tons of carbon dioxide per year will be captured in the world. However, according to the feasibility study given in ^[22], in the case of introducing CCS into the technological scheme of the hydrogen production process using steam reforming technology, capital costs (CAPEX) increase by 87%, and operating costs (OPEX) by 33%. Therefore, the present value of the produced hydrogen in this case increases one and a half times (up to 1.8 euros per kg), and the price of carbon dioxide utilization is EUR 70 per ton of CO₂.

Currently, more and more energy companies are declaring their intention to take an active part in the transition to carbon-neutral energy. Shell has developed a new highly efficient process for producing “blue” hydrogen without a carbon footprint—Shell Blue Hydrogen Process (SBHP). SBHP combines two of the company's successful technologies—SGP gas partial oxidation technology to convert steam cracking residues into syngas and ADIP ULTRA absorption technology to capture CO₂ from high-pressure POX processes ^[23].

For separation of pure hydrogen from the products of the oxidative conversion of hydrocarbon gases, one of three methods is usually used: membrane separation, pressure swing adsorption and cryogenic separation ^[24]. Membrane systems can separate hydrogen from impurities, but are not able to provide high purity of the resulting hydrogen. Pressure swing adsorption systems can produce ultra-high-purity hydrogen (up to 99.999%). They operate at elevated pressures, require complex control systems and high capital and operating costs. Cryogenic separation is a much more capital- and energy-intensive and complex process compared to the two above, so it is used only for very large-scale hydrogen production or very high purity requirements.

Comparative data on the efficiency of H₂ production in processes of various degrees of commercial readiness are presented in **Table 2**.

Table 2. Comparative data on the efficiency of hydrogen production methods ^[17].

Process	Feedstock	Thermal Efficiency
Steam reforming	Hydrocarbons	70–85%
Partial oxidation	Hydrocarbons	60–75%

Process	Feedstock	Thermal Efficiency
Autothermal reforming	Hydrocarbons	60–75%
Plasma reforming	Hydrocarbons	9–85%
Electrolysis	H ₂ O + electricity	50–70%

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