

RESEARCH, DESIGN, CALCULATIONS, AND OPERATING EXPERIENCE

CHEMICAL EQUIPMENT

COMPACT ENERGY-SAVING HYDROGEN PLANT

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The wide use of hydrogen in the chemical and petrochemical industries, petroleum refining, metallurgy, and other industrial sectors is making it necessary to further improve the process by which it is produced.

The most widely used and least costly method of producing hydrogen involves the steam catalytic conversion of a hydrocarbon raw material, subsequent conversion of carbon monoxide, and separation of the hydrogen by the method of short-cycle adsorption (SCA).

The main problems to be solved in improving existing hydrogen plants and developing new such plants are:

- cutting energy consumption;
- reducing capital costs;
- decreasing harmful emissions.

The production of hydrogen by the conversion of hydrocarbons includes several stages: removal of sulfur, steam catalytic conversion of hydrocarbons, steam catalytic conversion of carbon monoxide, and SCA. Catalytic processes are traditionally carried out in units in which the reaction medium is moved axially or radially through a packed bed.

Units in which the medium moves axially through the bed of catalyst are distinguished by the simplicity of their design, but limited cross-sectional area of the vessel (which is related to manufacturing and transportation constraints and the fact that the catalytic processes take place at high pressures) means that the reaction medium moves through the bed at high linear velocities [1–3]. This in turn limits the productivity of the unit and leads to nonuniform distribution of the flow of the medium in the bed and an increase in the bed's hydraulic resistance. Such units are thus usually operated with a catalyst having large granules and, hence, a small specific surface area.

A temperature regime that is close to optimum for conducting catalytic processes in axial-flow units is created either by heating or cooling the medium ahead of the bed of catalyst [1, 2] or by heating or cooling the reaction zone through tubular heat-exchange surfaces located in or around the bed [1, 2, 4]. The shortcomings of these methods of supplying or removing heat are the nonuniformity (stepped character) of the temperature distribution in the direction of flow of the medium and (when heat is removed) dilution of the reaction gas by fresh gas ahead of the next layers of catalyst. In addition, installing heat exchangers inside catalytic units (outside the catalyst bed) to provide intermediate cooling (heating) of the reaction medium complicates the design, increases hydraulic resistance, and reduces the reaction volume of the unit.

Units in which the medium moves radially through the bed of catalyst have a low hydraulic resistance, which allows the use of a fine-grained catalyst [1, 2, 5, 6]. However, the linear velocity of the medium in the radial direction changes from a maximum value (near the axis of the unit) to a minimum (toward its periphery), which leads to nonuniform distribution of the flow of the medium over the packed bed and lowers the volume utilization factor of the catalyst.

The requisite temperature regime in such units is achieved by the same methods as in axial-flow units [1, 2, 6]. The installation of tubular heat-exchange elements in a radial bed of catalyst [7–9] creates nonuniform heat exchange because the flows of the reaction medium and the heat-transfer agent cross one another.

Thus, it is important to use a fine-grained catalyst in order to ensure low hydraulic resistance and uniform flow of the medium over the catalyst bed. It is also important to optimize the temperature regime for the catalytic operation so as to ensure that the necessary quantity of heat is supplied to the reaction zone or removed from that zone.

Tube-and-shell-type heat exchangers or plate-type heat exchangers are the heat exchangers most commonly used for heat-transfer processes.

The tube-and-shell heat exchangers which have traditionally been used – including exchangers with floating heads and U-shaped tubes – are cumbersome, contain a large amount of metal, have a substantial hydraulic resistance, and offer limited possibilities for use at high temperatures and pressures [10].

Plate heat exchangers made of fixed soldered and welded structures are compact and have a high heat-transfer coefficient and a low metal content. However, they also have a high hydraulic resistance and offer limited possibilities for operation at high temperatures and pressures [11]. For example, for soldered heat exchangers, the maximum working temperature is normally no greater than 225°C and the working pressure is 3 MPa. The corresponding figures for welded heat exchangers are 350°C and 4 MPa.

Converted hydrocarbon gas is usually obtained by the steam catalytic conversion of a hydrocarbon raw material in tubular furnaces or shaft reactors on a nickel catalyst [1, 12].

Heat for the endothermic reaction is supplied in one of two ways: heat enters through the wall of the reaction tubes from flue gases formed either by the combustion of a fuel in the inter-tube space of the furnace or by the combustion of part of the hydrocarbon raw material above the catalyst. In the latter case, oxygen or air is fed into the reactor for the combustion process.

After the radiant zone of the furnace, the heat of the flue gases and the heat of the converted gas are used to preheat the process flows (natural gas, air) and produce steam. The heat-exchange process occurs through the built-in heat-exchange surfaces in the convective zone of the furnace and in individual heat exchangers that have been installed in the unit [1, 12, 13].

In order to make use of the low-potential heat and reduce the load on the tubular furnace, it has been proposed that pre-reforming be carried out ahead of the furnace [12, 14]. In pre-reforming, the conversion process takes place under adiabatic conditions. One of the advantages of pre-reforming in the steam catalytic conversion of oil or gas containing homologues of methane is the reduction of heavy hydrocarbons to methane.

To make the process more cost-effective by making greater use of the heat supplied for the endothermic reaction, researchers developed and implemented schemes in which the conversion process is carried out in two stages: in a tubular reactor, and in a shaft reactor. The conversion process in the tubular reactor takes place by making use of the heat of the gas after the shaft reactor [12, 15].

Another way of making the process more cost-effective is to perform the conversion with separation of the steam-gas mixture into two parallel flows: the first flow is sent to a tubular reactor heated by flue gases through the wall of the reaction tubes, while the second flow is sent to a tubular heat-exchange reactor heated by the converted gas after the tubular reactor [12, 16, 17].

There is also a unit designed for the steam conversion of natural gas in which pairs of coaxial tubes form annular spaces filled with a catalyst [18]. These spaces and the internal cavities of the reaction tubes are connected with gas intake and outlet pipes. The heat needed to conduct the conversion process is supplied through the walls of the annular spaces. The walls are washed by flue gases and the reaction gases.

Tubular furnaces and reactors used for the steam catalytic conversion of hydrocarbons are usually cumbersome, heavy, and costly structures that occupy large areas. For example, a tubular furnace (a reactor in which natural gas undergoes steam catalytic conversion) with an ammonia production capacity of 450,000 tons/yr has dimensions of 25 × 38 × 20 m and weighs more than 2100 tons. The cost of such a furnace is about 20 million U.S. dollars.

The conversion process is often carried out at high pressures (1–4 MPa) and high temperatures (800–900°C). In connection with this, the reaction tubes and the other elements of the furnace are made of expensive heat-resistant nickel alloys. To ensure that the hydraulic resistance of the packed bed is low, a catalyst with 10–20-mm granules of complex shape [19–21] is used in existing reactors. It should be mentioned that the tubular furnaces continually release into the atmosphere waste gases which contain such harmful components as NO_x, CO, and SO₂.

The steam conversion of carbon monoxide is usually done in adiabatic reactors in which the medium flows axially or radially through an iron-chromium catalyst [1]. The heat of the conversion reaction is also used to produce steam and preheat the process flows in individual heat exchangers. Hydrogen is separated from the converted hydrogen-bearing gas by the SCA method, which makes it possible to obtain highly pure hydrogen. The injected gases left after SCA are used as fuel for the reactor in the steam conversion of hydrocarbons.

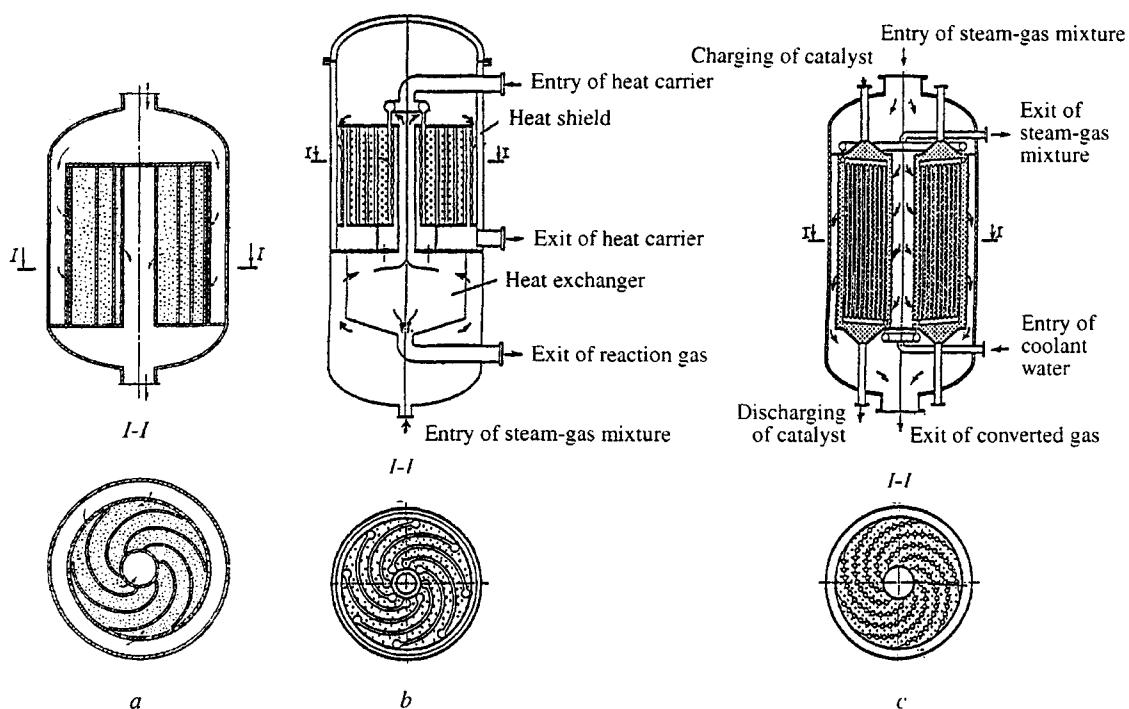


Fig. 1. Reactors designed by FAST ENGINEERING for conducting catalytic processes: *a*) under adiabatic conditions; *b*, *c*) steam conversion of natural gas and CO, respectively.

The company FAST ENGINEERING has come up with several new designs.

The scheme proposed above for making hydrogen involves the operations of sulfur removal, steam catalytic conversion of natural gas, steam catalytic conversion of CO, and separation of hydrogen for SCA with the use of catalytic reactors and adsorbers designed by FAST ENGINEERING. One feature of the construction of these units is the installation of hollow spiral walls in the annular space of the radial reactors, between the perforated internal and external shells. The spiral walls form spiral channels, which are filled with a granular material (a catalyst or an adsorbent). The channels all have the same cross section in the direction perpendicular to direction of flow of the medium. The spiral walls can be made solid (Fig. 1*a*) in order to conduct the process under adiabatic conditions, or they can be made hollow (Fig. 1, *b* and *c*) if it is necessary to supply or extract heat for the process to take place. In the latter case, the internal cavity of the walls is connected by pipes that deliver and discharge the heat carrier.

Main advantages of the new design of catalytic reactor:

- the possibility of using the most active fine-grained catalyst (adsorbent) while keeping the hydraulic resistance of the bed low;
- efficient delivery (extraction) of heat to (from) the reaction zone;
- uniform distribution of the medium over the packed bed;
- a significant reduction in the metal content and size of the reactor;
- the possibility of transporting the reactor in assembled form, i.e., the elimination of pre-assembly operations at the installation site;
- the possibility of conducting the process in the isothermal regime;
- the possibility of using the reactor within a broad range of productivities, pressures, and temperatures;
- a decrease in unit capital expenditures.

A fine-grained catalyst of type GIAP-18, with 3–5-mm granules [21], is used in the reactor for the steam catalytic conversion of natural gas. The use of a highly active fine-grained catalyst makes it possible to decrease the volume of catalyst that is used and reduce the size of the reactor while maintaining low hydraulic resistance in the packed bed.

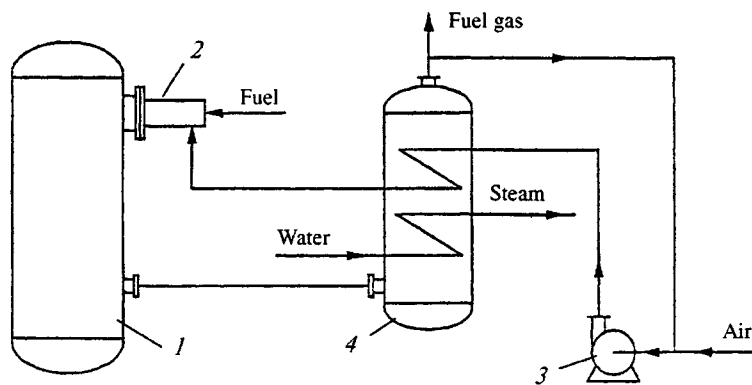


Fig. 2. Diagram of the flows in the steam catalytic conversion of natural gas: 1) FAST ENGINEERING reactor; 2) catalytic burner; 3) blower; 4) waste-heat boiler.

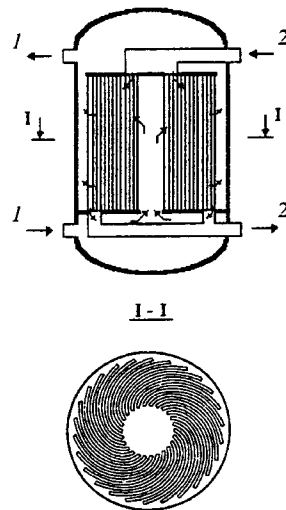


Fig. 3. Heat exchanger designed by FAST ENGINEERING: 1, 2) heat-exchanging media.

The developed heat-exchange surface which exists inside the catalyst bed in the new reactor ensures the necessary supply of heat to conduct the process. Flue gas is used as the heat carrier in the cavity of the spiral walls. The area occupied by the reactor is 10–15 times smaller than the area occupied by a tubular furnace of similar capacity.

Energy consumption is decreased significantly due to a reduction in the hydraulic resistance of the reactor by a factor of 5–6, efficient heat transfer, and the use of high-potential heat inside the reactor.

The load-bearing shell of the reactor is made of standard boiler plate. A protective heat shield is used as the lining, i.e., the new design does not use traditional heat-insulating materials.

In any case, the cost of the new reactor will be 3–8 times lower than the cost of the reactors presently in use. The exact difference in cost will depend on the capacity of the reactor.

A catalytic burner designed by FAST ENGINEERING is used to obtain flue gas as the heat carrier. The burner is similar in design to catalytic reactors that operate under adiabatic conditions. Tests of the burners and the corresponding catalysts demonstrated their efficiency. Figure 2 presents a diagram showing how the catalytic burner is connected to the reactor.

The burner is installed directly on the reactor. Some of the flue gas is mixed with air between the waste-heat boiler and the blower and is sent to the burner along with fuel gas. The fuel used in the hydrogen production process can be injected gas

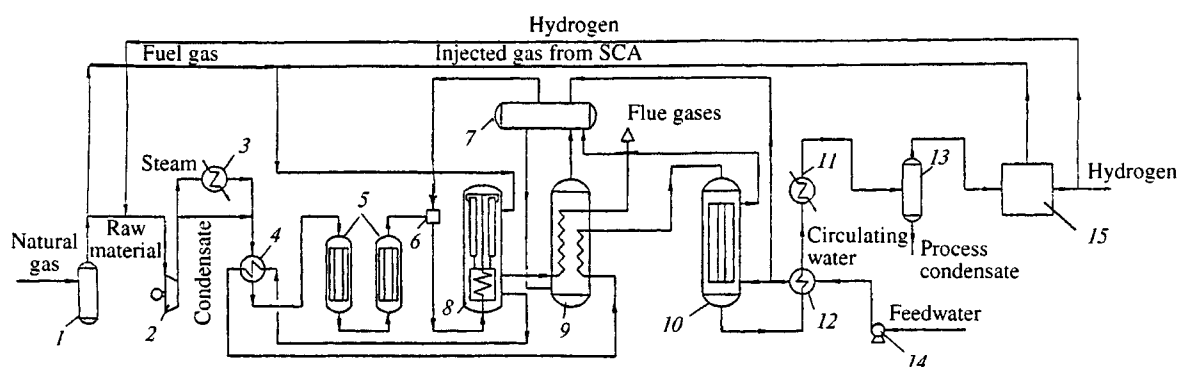


Fig. 4. Diagram of the production of hydrogen with the use of FAST ENGINEERING catalytic and heat-exchange equipment: 1) natural-gas separator; 2) natural-gas compressor; 3) superheater for crude gas; 4) preheater for crude gas; 5) reactors for removing sulfur; 6) mixer to mix the raw material and steam; 7) steam separator; 8) steam-conversion reactor; 9) waste-heat boiler; 10) CO converter; 11) cooler; 12) feedwater preheater; 13) separator; 14) feedwater pump; 15) SCA unit.

from SCA, natural gas, or a mixture of these gases. The temperature of the flue gas after the burner is regulated by changing the proportions of flue gas, air, and fuel gas at the burner inlet.

The flue gas, having a temperature of 950–980°C after the burner, enters the reactor and is uniformly distributed in the cavities of the spiral walls. In the process, the gas returns heat to the reaction zone. The gas then leaves the cavities of the walls, enters a collecting main, and is exhausted from the unit.

The use of a catalytic burner for the new reactor solves pollution problems, ensuring the emission of flue gases that are free of harmful components.

The process of the steam conversion of CO is carried out in an isothermal reactor designed by FAST ENGINEERING (Fig. 1c). The process is conducted in a single stage on a fine-grained Cu–Al–Zn catalyst of the selective type [22, 23, 25–27]. The granules of the catalyst are 3–5 mm in size and are close to spherical in form. The catalyst has a high activity, high thermal conductivity, and good mechanical strength.

Use of the new reactor allows the conversion process to be carried out under optimum temperature conditions, with a low hydraulic resistance in the packed bed and a low content of CO in the converted gas at the outlet of the reactor.

Heat-exchange processes in the improved hydrogen plant are conducted in heat-exchange equipment designed by FAST ENGINEERING (the heat exchanger of the reactor in which hydrocarbons are converted, a waste-heat boiler, and heat exchangers for the gas and liquid flows) [25–27]. Figure 3 presents a diagram of one of the heat exchangers.

Heat exchangers of the new design provide for the following:

- the possibility of conducting the heat-exchange process at high temperatures (up to 1000°C) with large pressure and temperature gradients in the heat-exchanging media;
- low hydraulic resistance;
- maximum specific heat-transfer surface per unit volume of the cylindrical heat exchanger;
- a reduction in metal content;
- the possibility of efficient operation of the heat exchangers as units for cooling air.

Installing spiral walls in the bed of adsorbent in radial adsorbers makes it possible to use a fine-grained adsorbent, keep hydraulic resistance low, allow for the delivery or removal of heat, and uniformly distribute the flow of the medium through the adsorbent.

Figure 4 presents a basic diagram of the hydrogen plant. The main processes: compression of natural gas; removal of sulfur compounds from natural gas; steam catalytic conversion of natural gas; steam catalytic conversion of CO; use of the heat of the gas flows to create steam; cooling and separation of the hydrogen-bearing gas; SCA.

The natural gas (NG), with an addition of 7% hydrogen, is precompressed by a compressor to the necessary pressure, heated in a preheater to 350–380°C, and sent to a component where sulfur is removed by hydration of the organic sulfur com-

TABLE 1

| Component of the gas | NG, % | Process hydrogen for hydrogenation, % | Gas before sulfur removal, % | SGM for NG conversion, % | Converted gas, * % |
|--------------------------------|-------|---------------------------------------|------------------------------|--------------------------|-----------------------|
| H ₂ | – | 99.9 | 9.09 | 9.09 | <u>73.99</u> 76.65 |
| CH ₄ | 97.54 | – | 88.67 | 88.67 | <u>4.98</u> 4.48 |
| C ₃ H ₈ | 0.4 | – | 0.37 | 0.37 | |
| C ₄ H ₁₀ | 0.2 | – | 0.18 | 0.18 | |
| C ₅ H ₁₂ | 0.01 | – | 0.01 | 0.01 | |
| N ₂ | 0.94 | 0.1 | 0.86 | 0.86 | <u>0.23</u> 0.19 |
| CO ₂ | 0.03 | – | 0.03 | 0.03 | <u>9.17</u> 18.44 |
| CO | – | – | – | – | <u>11.63</u> 0.24 |
| Steam/gas | – | – | – | 3.2 | <u>0.61</u> 0.45 |

* The numerator and denominator show data for after NG conversion and after CO conversion, respectively.

pounds on an Al–Co–Mo catalyst and the absorption of H₂S on ZnO. After sulfur removal, the gas flow is sent to a mixer for mixing with steam in a steam/gas ratio equal to 3.2. The mixture is sent to the reactor in which natural gas is converted. The steam-gas mixture (SGM) enters the reactor through an inlet pipe, is heated in a heat exchanger, passes through a cylindrical internal cavity and a perforated external shell, and enters spiral channels filled with a catalyst. The reaction in which natural gas is converted takes place in the catalyst. The converted gas leaves the catalytic bed through a perforated internal shell and travels through the annular space between this shell and the shell that forms the cylindrical internal cavity. The gas is then directed to a heat exchanger, where it is cooled, and it leaves the reactor through an outlet pipe. After the heat of the converted gas has been used, the gas is sent to the component where CO is converted. The flue gas is released into the atmosphere at a temperature of 140°C after its heat has also been used. The CO conversion process is carried out in an isothermal reactor at 200–220°C. After conversion of the CO, the hydrogen-bearing gas is cooled and sent off for SCA. After SCA, the hydrogen is sent to the customer, while the injected gases (used as a fuel) are sent to the burner of the reactor in which natural gas undergoes steam conversion. Table 1 presents an example of the material balance.

Advantages of using equipment of the new design in hydrogen production:

- a decrease in capital expenditures by a factor of roughly 2–3;
- a reduction in operating costs (mainly due to energy conservation) by roughly 20%;
- elimination of harmful emissions into the environment.

The use of a catalytic burner in which the temperature of the heat carrier can be closely regulated creates the optimum temperature conditions for conducting the process. Thus, it is possible to change the load on the reactor from zero to the maximum value without overheating the walls.

The new catalytic reactor will make it possible to design hydrogen plants of any desired capacity for operation within a broad range of pressures.

The proposed design may find wide application both in the reconstruction of existing plants and in the construction of new plants. Positive results obtained from use of the new reactor in the synthesis of ammonia demonstrate its workability.

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