HIGH EFFECTIVE SYNTHESIS GAS PRODUCTION BY STEAM HYDROCARBON CONVERSION

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ABSTRACT

Synthesis gas production by steam hydrocarbon conversion underlies of the series processes as hydrogen, methanol, dimethyl ether, ammonia, petrol, etc.

It is known that the stage of synthesis gas production takes 70% of capital and operation costs of total final product production. Synthesis gas production is complicated, expansive and power-consuming process.

Traditionally the process of steam hydrocarbon conversion is carried out in the tubular reformers and shift reactors over a nickel catalyst. The heat supply required for endothermic reaction is carried out by fuel gases through the walls of the reaction tubes at the expense of fuel gas burned in the intertubular space or at the expense of a part of the hydrocarbons to be burned inside the reactor above the catalyst bed combined with oxygen or air.

The using «FAST ENGINEERING» ® design of catalytic reactors, heat exchanger and mass-transfer apparatuses for synthesis gas production enables to decrease too much capital investment, energy consumption as well as to solve environment problems.

«FAST ENGINEERING» ® catalytic reactor design is compact, provides optimal temperature conditions for carry out catalytic process, effective heat supply (remove) to (from) the reaction zone, an opportunity of using the most active fine-grained catalyst keeping low pressure drop in the granular bed and wide range of loads, pressures and temperatures for a catalytic process.

Compact «FAST ENGINEERING» ® heat exchanger design provides low pressure drop, an opportunity to carry out the heat exchanging process in wide range of temperatures (from minus 269 till 1100°C), pressures and loads of heat exchange mediums, has maximum specific surface for heat exchanging in volume unit of cylindrical apparatus. They could be used as air-cooled apparatus, evaporator, condenser, etc.

The using «FAST ENGINEERING» ® catalytic reactors and heat exchanger apparatuses for synthesis gas production by steam or steam and carbon-dioxide natural gas conversion enables exclude oxygen and basically compressor equipment using. Synthesis gas production and following final product synthesis are carried out under common pressure, so could be used well or gas pipeline pressure.

Synthesis gas produced by new process is 2 times cheaper in comparison with ones manufactured by traditional process. Cost price reduces at the expense of considerable decreasing of capital investment (about 2-5 times depends of the unit capacity), energy consumption (about 30-40%) as well as excluding of oxygen use in the process of steam natural gas conversion.

Hydrogen cost price produced from synthesis gas manufactured with new process using is less about 30-50%.

New process of synthesis gas manufactured by natural gas conversion and further its treatment to fuel provides competitive ability this fuel in comparison with traditionally manufactured from oil ones in price and quality.

The process diagram, material balance and basic characteristics of 25 m³/hr synthesis gas production unit with using of catalytic reactor, heat exchanger and mass-transfer apparatuses of «FAST ENGINEERING» ® design are presented.
1. INTRODUCTION

Synthesis gas production by steam natural gas conversion is underlined of the series processes as hydrogen, methanol, dimethyl ether, ammonia, petrol, etc. (Fig.1).

![Diagram of the follow synthesis gas treatment.](image)

It is known that the stage of synthesis gas production takes 70% of capital and operation costs of total costs of final product production. Synthesis gas production is complicated, expansive and power-consuming process. [1].

Compressors, natural gas and synthesis gas compression as well as oxygen manufacture take the main part of the capital investments and operating costs of synthesis gas production.

The main commercial methods of synthesis gas production are catalytic steam, steam and oxygen, steam and carbon dioxide natural gas conversion. Natural gas conversion is carried out on the follow reactions [1]:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3\text{H}_2 - 206,41 \text{ kJ/mole} \quad (1) \\
\text{CH}_4 + \text{CO}_2 & = 2\text{CO} + 2\text{H}_2 - 248,28 \text{ kJ/mole} \quad (2) \\
\text{CH}_4 + 0.5\text{O}_2 & = \text{CO} + 2\text{H}_2 + 35,6 \text{ kJ/mole} \quad (3) \\
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 + 41,03 \text{ kJ/mole} \quad (4)
\end{align*}
\]

Reaction of methane homologues oxidation comes similarly:

\[
\text{C}_n\text{H}_m + \text{H}_2\text{O} = n\text{CO} + 0.5(2n + m)\text{H}_2 - Q \quad (5)
\]

Depends on required synthesis gas composition for its follow treatment is used:

- Steam conversion reactions (1,4)
- Steam and carbon dioxide conversion reactions (1,2,4)
- Steam and oxygen conversion reactions (1,3,4)
- Steam and air conversion reactions (1,3,4)

Equilibrium composition of synthesis gas depends on the base mixture composition as well as temperature and pressure of the conversion process. It is possible to receive synthesis gas of the required composition for the follow synthesis by changing of oxidant relation \( \text{H}_2\text{O}, \text{CO}_2 \) and \( \text{O}_2 \) to \( \text{CH}_4 \).
Traditionally used equipment for commercial units do not enable to create a compact synthesis gas production unit of a small capacity as well as for hydrogen production for motor vehicles fuel cells using.

The main requirements for creation of a small capacity synthesis gas production unit are compactness, efficiency, easy to start up and shut-down, an opportunity to operate in a wide range of capacity and minimum off gases to environment.

Synthesis gas production is the main part of the price of final product. So the main task of increasing the efficiency of the final product production is advancing the synthesis gas production.

2. EXISTING DIAGRAMS AND EQUIPMENT OF SYNTHESIS GAS PRODUCTION

Desulphurization, catalytic conversion of natural gas and steam generation are the main stages of synthesis gas production [1].

The process of natural gas purification form sulfur compounds is successfully solved in commercial units. In this process effective catalysts of hydrogenation of organic sulfur compounds and adsorbents of hydrogen sulphide are widely used.

For synthesis gas generation is used catalytic natural gas conversion in the tubular reformers or shift reactors over a nickel catalyst.

The heat supply required for endothermic reaction is carried out by fuel gases through the walls of the reaction tubes at the expense of fuel gas burned in the intertubular space in the tubular reformers or at the expense of a part of the natural gas to be burned inside the reactor above the catalyst bed combined with oxygen in the shift reactors.

The heat of flue gases and converted gas are used for heating streams of process gas and steam production.

In order to increase efficiency of the process a number of diagrams were realized where the process of conversion in the tubular reactor is carried out at the expense of heat of the reaction gas after shift reactor [2].

The disadvantages of traditional methods of catalytic natural gas conversion are the follows:

• Limitation of heat supply to the reaction zone for carrying out process of conversion
• Limitation of output (particularly minimal)
• High pressure drop of the catalyst bed
• Bulky design
• Considerable losses of heat with off gases to environment

As a rule, in catalytic reactors for catalytic natural gas conversion the catalyst with big sizes and complicated geometrical shapes are used in order to provide its low pressure drop of the catalyst bed and increasing specific geometrical surface of the grains (Fig.2) [3].

The creation of synthesis gas production for a small capacity with using of traditionally applied equipment for carrying out catalytic natural gas conversion is problematically.

Tubular and plate heat exchangers are commonly used for carrying out heat exchange processes in synthesis gas production units.

Traditionally used shell-and-tube heat exchangers including with floating heads and U-form tubes are bulky, metal consuming and have considerable pressure drop for heat exchanger mediums [1].

Plate heat exchangers in comparison with shell-and-tube ones are compact, have higher heat transfer coefficient, less metal consumption, but they also have considerable pressure drop and limited opportunities for applying under increased temperatures, pressures and consumptions [4].
3. NEW FAST ENGINEERING® SYNTHESIS GAS PROCESS

High efficiency process of synthesis gas production by steam natural gas conversion with using catalytic reactors and heat exchanger apparatuses of FAST ENGINEERING® design was designed and realized by FAST ENGINEERING LTD. firm. This process enable too much reduce capital investment and operation costs.

Along with natural gas as a raw material could be used any hydrocarbons as oil gases, oil-well gas, oil, etc.

Compact small capacity synthesis gas production by, for example, steam catalytic natural gas conversion has the main stages as existing processes: desulphurization, steam catalytic conversion of natural gas and steam generation. Process improvement is at the expense of using high effective fine-grained catalysts in catalytic reactors of FAST ENGINEERING® design, effective heat supply to the reaction zone as well as no oxygen using. [5-10].

FAST ENGINEERING® process diagram of synthesis gas production unit is presented in Fig.3.

Fig.3. The process diagram of the small capacity synthesis gas production unit.
NG – Natural Gas, SG – Synthesis Gas.
A new catalytic reactor design features, so that in annular space of a radial reactor, filled with the granular material (catalyst or adsorbent), the walls were placed in the form of a planar Archimedean spiral (in a plane drawn perpendicularly with respect to the longitudinal axis of the reactor), forming spiral-shaped passages, which have the same sections to the direction of fluid flow. The spiral-shaped walls are made of solid metal for adiabatic processes (Fig.4) and with hollows if heat supply or removal from the catalyst bed (Fig.5). Inner spaces of hollows of spiral shaped walls are connected with pipes of inlet and outlet of the heat carrier.

The main advantages of a new catalytic reactor design in comparison with conventional one are as follows:

- An opportunity of using the most active fine-grained catalyst or adsorbent keeping low pressure drop in the granular bed
- An opportunity of effective heat supply or removal from or to the reaction zone and carry out the catalytic process in optimum temperature conditions, including isothermic conditions
- Uniform spread of a fluid flow through a granular bed
- Considerable reducing of reactor dimensions and metal consumption
- An opportunity to use a wide range of loads, pressures and temperatures for a catalytic process

Figure 4 shows a sketch of apparatus for carry out processes of desulphurization in adiabatic conditions [5-7,9].

Such design with solid spiral-shaped walls installed into the granular bed provides uniform spread of fluid flow through a granular bed, low pressure drop and high degree of granular material using.

Figure 6 shows the version of process diagram of steam catalytic natural gas conversion. The version of the sketch of reactor for carrying out process of steam catalytic natural gas conversion is presented in Fig.5 [5-7,9,10]. Reactor is filled with CFE-10 (Catalyst of FAST ENGINEERING) catalyst with a 1.5-3 mm particle size (Fig.7). Using most active fine-grained catalyst allows reducing catalyst value and value of the reactor and keeping low pressure drop of the catalyst bed.

The developed heat exchanger surface inside the catalyst bed of the reactor of a new design provides heat supply required for carrying out the process. The fuel gas as heat-carrier is supplied to the hollows of spiral-shaped walls.
Fig. 5. A sketch of reactor for carrying out steam natural gas conversion.

Fig. 6. The process diagram of steam catalytic natural gas conversion.
Heat exchangers of FAST ENGINEERING® design are used for carrying out heat exchange processes in compact hydrogen production unit [6-10]. Figure 8 shows a sketch of the new heat exchanger design.

The advantages for using of a new heat exchanger design in comparison with conventional ones are as follows:

- An opportunity to carry out the heat exchanging process under the temperatures from minus 269 to 1100°C
- An opportunity to carry out the heat exchanging process in high temperature drop and pressure difference of heat exchange mediums
- Low pressure drop
- Maximum specific surface for heat exchanging in volume unit of cylindrical apparatus
- An opportunity to carry out heat exchanger processes of unlimited quantity of heat exchanger mediums in a one apparatus
- Space-saving design

New heat exchanger design in comparison with plate-type ones are compact and has weight less by around 2 times, and in comparison with tubular-type ones less by around 7-10 times.

Figure 9 shows micro heat exchanger (steam boiler after steam natural gas conversion) of FAST ENGINEERING® design with capacity 720 W and working pressure 10 bar.
In a new synthesis gas production unit a few functional apparatuses are placed in a one casing in order to create compact unit, use heat efficiently and reduce pressure losses of process flows. Figure 10 shows the sketch of the pilot synthesis gas production unit.

Figure 11 shows pilot synthesis gas production for manufacture of 30 m³/hr hydrogen.

Fig.10. A sketch of the pilot synthesis gas production unit.


Fig.11. Pilot synthesis gas production for 30 m³/hr hydrogen production unit.

Figure 12 shows pilot synthesis gas production under the pressure 6.4 MPa.

Fig.12. Pilot synthesis gas production unit under the pressure 6.4 MPa.
It is important for synthesis gas manufacture under the pressure of the follow synthesis of the final product and use pressure of oil well or gas pipeline. So compressors of natural gas and synthesis gas are excluded from the process diagram. It gives considerable reducing of capital investment and operation costs.

4. CONCLUSIONS

Carried R and D works confirm efficiency compact synthesis gas production units on the basis of using catalytic reactors and heat exchangers of FAST ENGINEERING® design. New process synthesis gas production could be designed for any required capacity.

FAST ENGINEERING® process of synthesis gas production enables to exclude oxygen and basically compressor equipment using. Synthesis gas production and following final product synthesis are carried out under common pressure, so could be used well or gas pipeline pressure.

Synthesis gas produced by new process is 2-5 times (depends of the unit capacity) cheaper in comparison with ones manufactured by traditional process. Cost price reduces at the expense of considerable decreasing of capital investment (about 2-5 times depends of the unit capacity), energy consumption as well as excluding of oxygen use in the process of natural gas conversion.

Such synthesis gas production units could use both natural gas and liquid hydrocarbons as kerosene, naphtha, etc.

REFERENCES