FISCHER-TROPSHA GAS PROCESSING

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ANNOTATION

Non-oxidative pyrolysis of solid organic raw materials produces syngas, which can be used directly as fuel without being converted by the Fischer-Tropsch process.

Keywords. synthesis gas, carbon monoxide mixture, synthetic hydrocarbons, hydrogen

INTRODUCTION

The first stage of the Fischer-Tropsch process consisted in the production of synthesis gas from solid hydrocarbons (usually coal):

For this purpose, superheated water vapor was blown through a layer of hot coal. The product was the so-called water gas - a mixture of carbon monoxide (carbon monoxide) and hydrogen. Further, the Fischer-Tropsch process is described by the following chemical equation:

A mixture of carbon monoxide and hydrogen is called synthesis gas, or syngas, and the term water gas is also used.

The mixture of the resulting hydrocarbons is purified to obtain the target product - synthetic gasoline. Obtaining heavier fuels by the Fischer-Tropsch method is economically unprofitable due to the rapid poisoning of the catalyst.

Carbon dioxide and carbon monoxide are formed by the partial oxidation of coal and wood fuels. The benefits of this process are predominantly in its role in the production of liquid hydrocarbons or hydrogen from solid feedstocks such as coal or various types of solid carbonaceous waste.

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If a liquid substance similar to fuel oil, lubricating oils or paraffin wax is required, the Fischer-Tropsch process can be used. If it is required to increase the yield of hydrogen, then water vapor is taken in excess, which shifts the equilibrium of the reaction, as a result of which only carbon dioxide and hydrogen are formed.

Thus, liquid fuel is obtained from a mixture of gases.

After the invention of the process by German researchers Franz Fischer and Hans Tropsch, who worked at the Kaiser Wilhelm Institute in the 1920s, many improvements and corrections were made, and the name "Fischer-Tropsch" is now applied to a large number of similar processes (Fischer-Tropsch synthesis or chemistry Fischer-Tropsch).

The Fischer-Tropsch synthesis can be considered as reductive oligomerization of carbon monoxide:

Both reactions are exothermic with a significant thermal effect of ~ 165 kJ / mol with respect to carbon monoxide (CO).

The catalysts are Group VIII transition metals: ruthenium (Ru) is the most active, then cobalt (Co), iron (Fe), nickel (Ni). To increase the reaction catalytic surface, they are often applied on porous inert supports, such as, for example, silica gel and alumina. Only Fe and Co. have found

application in the industry. [2] Ruthenium is too expensive, in addition, its reserves on Earth are too small for use as a catalyst in large-tonnage processes. On nickel catalysts at atmospheric pressure, mainly methane (n = 1) is formed, while increasing the pressure in the reactor, volatile nickel carbonyl is formed, which is carried away from the reactor with the reaction products.
Side reactions of the synthesis of hydrocarbons from CO and H_2 are:
• hydrogenation of carbon monoxide to methane: + 214 кДж/моль
• Bell-Boudoir reaction (CO disproportionation):
• chemical equilibrium in water gas:
The latter reaction is of particular importance for iron-based catalysts; it hardly proceeds on a cobalt catalyst. In addition, oxygen-containing organic compounds - alcohols and carboxylic acids - are formed on iron catalysts.
Typical process conditions are: pressure from 1 atm (for Co catalysts) to 30 atm, temperature 190 – 240 ° C (low-temperature version of the synthesis, for Co and Fe catalysts) or 320 – 350 ° C (high-temperature version, for Fe).
The mechanism of the reaction, despite decades of studying it, is still unclear in detail. However, this poor knowledge of reactions is typical of heterogeneous catalysis.
The thermodynamic laws for the products of the Fischer-Tropsch synthesis are as follows.
1. Formation of hydrocarbons of any molecular weight, type and structure from CO and H2 is possible, except for acetylene, the formation of which is energetically unfavorable.
2. The probability of formation of hydrocarbons decreases in the order: methane> other alkanes> alkenes. The probability of formation of normal alkanes decreases, and of normal alkenes - increases with increasing chain length.
3. An increase in the total pressure in the system promotes the formation of heavier products, and an increase in the partial pressure of hydrogen in the synthesis gas favors the formation of alkanes.
The ASF distribution imposes limits on the maximum selectivity for any hydrocarbon or narrow cut. This is the second problem after the problem of removing the heat of reaction in the Fischer-Tropsch synthesis.
Syntheses based on carbon monoxide and hydrogen [3]

Process	Catalyst	Catalyst carrier	Temperature, ° C	Pressure MPa	Product
Methane synthesis	Ni	ThO_2 MgO	250–500	0,1	Methan
Synthesis of higher hydrocarbons	Co, Ni	ThO_2, MgO, ZrO_2	150–200	0,1–1	A mixture of paraffins and olefins with a carbon chain length C1–C100
Synthesis of higher hydrocarbons and oxygen-containing compounds	Fe	Cu, NaOH (KOH), Al_2O_3, SiO_2	200–230	0,1–3	Mainly paraffins and olefins mixed with oxygen-containing compounds
Synthesis of paraffins	Co	TiO_2, ZrO_2, ThO_2, MgO	190–200	1	Predominantly hard paraffins with a melting point 70–98°C
	Ru	MgO	180–200	10–100	High molecular weight paraffins
Synthesis of higher alcohols	Fe, Fe-Cr, Zn-Cr	Al_2O_3, NaOH	180–220, 380–490	1–3, 15–25	Methanol and higher alcohols

During the Third Reich, a number of enterprises for the production of energy resources from coal were built in Germany, the deposits of which are located in large quantities on the territory of the country. Basically, production was based on the Bergius-Pir process developed in 1913, less significant capacities were allocated for the Fischer-Tropsch process. Until the end of World War II, a total production capacity was realized up to 4.275 million tons per year using the first process and up to 1.55 million tons per year using the latter process. Both industries turned out to be uncompetitive compared to oil production and were stopped at the end of the war. Research resumed during the oil crisis in the 70s. XX century An enterprise arose in the city of Bottrop, but in the late 80s. the price of oil dropped to $ 20 per barrel, and due to unprofitability, the development had to be interrupted again [4].

Currently, two companies are using their Fischer-Tropsch technology commercially. Shell in Bintulu uses natural gas as a feedstock and produces predominantly low-sulfur diesel fuel. In 1955, in Sasolburg (South Africa), Sasol put into operation the first plant for the production of liquid fuel from coal using the Fischer-Tropsch method. Coal is supplied directly from coal mines via a conveyor to produce synthesis gas. Then the Sasol-2 and Sasol-3 plants were built. The process was used to meet energy needs during isolation under the apartheid regime. Attention to this process has renewed in the search for ways to obtain low-sulfur diesel fuels to reduce the environmental damage caused by diesel engines. Currently, South Africa produces 5 – 6 million tons of hydrocarbons per year by this method. However, the process is unprofitable and is subsidized by the state as a national treasure [5]. Production in South Africa is focused not so much on the production of motor fuel, but on the production of certain more valuable fractions, for example, lower olefins.

There are large reserves of hard coal that can be used as a fuel source as oil depletes. Since coal is abundant in the world, this technology can be temporarily used if conventional oil becomes more expensive. The combination of biomass gasification and Fischer-Tropsch synthesis is a promising way to produce renewable or green vehicle fuels. Synthetic fuels made from coal are competitive when oil prices are above $ 40. per barrel Capital investments that must be made in this case are from 7 to 9 billion dollars. for 80 thousand barrels. facilities for the production of synthetic fuels from coal. For comparison, similar oil refining capacities cost about $ 2 billion. [6]

In 2015, the INFRA Group, which developed and patented a new generation of technology for the production of liquid synthetic fuels based on the Fischer-Tropsch synthesis process from natural or associated gas (GTL), biomass and coal (XTL), put into operation a catalyst plant. The production facility with a capacity of 15 tons per year produces a patented catalyst for the Fischer-Tropsch synthesis reaction, developed by the company's specialists. The task of the factory is the production of catalysts for the GTL INFRA plants, as well as the development of processes for the production of new modifications of the catalyst on an industrial scale. In 2016, INFRA designed and built a modular GTL (gas-to-liquid) transportable plant for processing natural and associated gas into synthetic oil M100 in Wharton (Texas, USA). The company's plans include the commercial operation of the refinery and the sale of synthetic oil. By order of the oil and gas company, INFRA Group began designing the GTL plant, which is planned to be located in the Nenets Autonomous Okrug. The plant with a capacity of 20 thousand oil products per year will produce winter diesel fuel and high-octane gasoline from natural gas from the

Vasilkovskoye gas condensate field. The implementation of the plan for the construction of a gas processing plant using the advanced GTL technology of INFRA will provide the market of the Nenets Autonomous Okrug with high-quality commercial fuel - diesel and gasoline - and significantly reduce the cost of purchasing an expensive northern delivery. The development of a feasibility study for the construction was carried out in 2017, the design will be completed in 2019. [7]

Technologies for converting coal into liquid fuels raise many questions from environmentalists. The most serious problem is carbon dioxide emissions. Recent work by the US National Renewable Energy Laboratory has shown that full cycle greenhouse gas emissions for coal-fired synthetic fuels are roughly double their gasoline-based equivalent. Emissions of other pollutants have also increased strongly, yet many of them can be collected during production. Dumping carbon has been proposed as a way to reduce carbon monoxide emissions. Injection into oil reservoirs will increase oil production and increase the service life of fields by 20 – 25 years, however, this technology can be used only if oil prices are stable above 50 – 55 USD. per barrel.

An important problem in the production of synthetic fuels is the high water consumption, which ranges from 5 to 7 gallons for each gallon of fuel produced.

LITERATURE

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