Fisher–Tropsh synthesis technology evolution

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Abstract. The article considers the development stages of technologies for producing hydrocarbons based on syngas. XTL technology is based on the Fischer–Tropsch process. Carbon-containing substances in any aggregate state can be used as a raw material of XTL technology, which will affect the chemistry and process parameters. Currently, interest in these technologies has increased in connection with the advent of scientific and technological innovations. The latest generation of XTL technology has already entered the industrial production phase. The article presents the results of a comparative analysis of XTL technology of different generations, the main indicators of which were the state of raw materials, the type of reactor devices, the chemical composition of the catalytic systems and the resulting product. The advantages of the technology proposed by INFRA Technology Company involving an innovative reactor design for a high-performance multifunctional catalyst, are shown. At the same time, the necessity of combining gas and liquid flows in an innovative microchannel reactor, increasing the conversion of synthesis gas, as well as the high cost of the fourth-generation XTL technology are urgent problems that need to be addressed at the current stage of the evolution of Fischer–Tropsch processes.

1. Introduction
Fischer–Tropsch process technology (XTL) has been used to synthesize fuels and synthetic oil for nearly a century. At the stage of modern development, much attention is focused on this synthesis and the search for new developments to improve the process continues. According to recent literature, there are four generations of Fischer-Tropsch synthesis technologies, each of which has characteristic features.

2. Comparative analysis of Fischer–Tropsch synthesis technology of different generations
In 1919, German scientists Franz Fischer and Hans Tropsch discovered that from synthesis gas (a mixture of CO and H2) obtained during the processing of carbon-containing raw materials, it is possible to synthesize liquid synthetic hydrocarbons, which is usually termed synthetic oil. The main idea of this process was to obtain a liquid from a gas.

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\begin{align*}
\text{Co} & \quad \text{Fe} \\
n\text{CO} + (2n+1)\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \\
2n\text{CO} + (n+1)\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{CO}_2
\end{align*}
\]

In the years 1920–1930 the era of coal gave way to the oil age. The production of cheap oil began, rail and shipping routes for its delivery developed resulting in rapid transition from one fuel to another.
And the opportunity to make liquid fuel out of the aging coal, which Germany was rich in, was seen as a chance for the coal industry.

The Second World War led to the appearance of the first generation of the Fischer–Tropsch synthesis due to the emergence of German ersatz fuel. The equipment for the synthesis plant, with annual productivity of about 50 thousand tons, was exported from Germany in the post-war period and found its application in Novocherkassk since 1954. Coal was used as the raw material for the plant, and the plant’s products included not only gasoline and diesel fuel, but also other products: special reagents, solvents, soap, etc. The process took place in a tubular reactor with a stationary catalyst bed, which was a German deposited cobalt-thorium (Co-Th) catalyst [1]. But the Fischer–Tropsch process proved to be inappropriate, since the cost of producing fuel from synthetic oil exceeded that of extracted oil. The installation worked until 1992 and was stopped for economic reasons, although in a modernized form [2].

The second generation was booming in South Africa. Almost forgotten German technology got a chance to continue its further development in connection with the imposition of sanctions in South Africa, the absence of its own oil fields and the presence of impressive coal reserves. The country rebuilt industry, creating, in particular, the production of synthetic oil from coal in order to live solely on its own resources. The catalyst was refined, the process became more efficient and environmentally friendly. The synthesis is carried out at 2–2.5 MPa and 340 °C in a reactor in a layer of suspended powdery iron catalyst, with a total capacity of 180 thousand tons/year. This technology made it possible to obtain a spectrum of hydrocarbons of the gasoline fraction, olefins (mainly C2–C4) and oxygen-containing compounds, etc. [3].

The impetus for the development and implementation of the third generation of technology was the oil crisis in the early 1970s. Then the states of the Middle East sharply limited access of the USA and Europe to hydrocarbon reserves. Well-known companies BP and Shell have begun active development of synthetic oil production technology. But the crisis was over, oil has fallen in price again, and industrial production of synthetic oil was never launched. They did not abandon the created technology, and Shell in 1993 in Bintulu (Malaysia) built a plant that included 4 Fischer–Tropsch multi-tube reactors with a capacity of 125 thousand tons/year each. Each reactor contains about 10,000 tubes. The synthesis is carried out in a three-phase reactor with a suspended layer of cobalt catalysts. The process was given the name “Synthesis of Middle Distillates” [4, 5]. This synthesis was distinguished by products of mainly long-chain hydrocarbons – waxes, requiring the presence of additional plants and equipment at the plant for their processing. A truly large, with a capacity of over 1.5 million tons/year, the third-generation Oryx plant reached its operational capacity in 2009 in Qatar using Sasol technology. At the end of 2011, Shell completed the construction of the largest in the history of the Pearl plant for the production of synthetic fuel with a capacity of 6 million tons/year [6].

The prospect of a wider introduction of GTL technology (“gas to liquid”) led to the improvement of all technological stages of the process, affected the direct production of synthetic oil and conditioned an increase in the productive forces of this process. Performance is one of the key parameters of the Fischer–Tropsch synthesis, because it determines the economic benefits of all stages, the result of which is the necessary synthetic fuel. In modern installations, the Fischer–Tropsch catalyst, which has high performance and selectivity, allows you to change the economic performance of XTL technology in a positive direction, as well as reduce the dimensions of the reactor, which has a height of 30 m and a diameter of 8 m.

The fourth generation of Fischer–Tropsch synthesis technology, which is tested in pilot plants, seeks to reduce to zero the disadvantages of the third. Scientists who are developing, resort to high-performance structured catalysts [7] or microchannel reactors with intensified heat transfer [8], but there are other proposals of varying degrees of sophistication.

The main changes introduced into the Fischer–Tropsch synthesis stage entail significant changes in other stages and in general energy-technological solutions. Despite the differences in the technological methods used by different developers, the fourth-generation XTL is characterized by common features:

- a multiple increase in the productivity of catalysts in an industrial environment;
the possibility of compact modular placement of installations;
radical simplification of the technological scheme by obtaining a single product directly in the Fischer–Tropsch reactor.
At present, the technologies of the new generation are going through the transition stage: experiments should begin to be implemented on an industrial scale. The developers of the fourth generation of XTL technology see as their goal the creation of a perspective that can open new industrial horizons through simplicity, compactness and a significant reduction in economic performance.

3. Conclusions
A comparative analysis of XTL technology of different generations is given in Table 1 [3, 9].

| Generation of XTL Technology | Raw Material | Reactor Type | Catalyst | Prevailing Product |
|------------------------------|--------------|--------------|----------|--------------------|
| I (1930–1950)               | coal         | with a stationary catalyst bed | Co-Th (Co-Zr) | gasoline+diesel fuel+olefins |
| II (1950–1980)              | coal         | fluidized bed catalyst | Fe       | gasoline + olefins + oxygenates |
| III (1980–1990)             | syngas       | with a suspended catalyst bed | Co       | diesel fuel + naphtha + LNG + oxygenates |
| IV (2000–2019)              | HC→syngas    | microchannel | Co/zeolite | single product (light fractions <3600 °C) |

Unlike previous generations, the advantages of the fourth generation representative–INFRA technology–lie not only in obtaining a single product directly in the reactor, high productivity and selectivity of the catalytic system, but also in the intensification of heat transfer and environmental friendliness of the process [9].

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