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## GTL AS A MODERN PROCESS FOR OBTAINING HIGH QUALITY OILS

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*In this article theoretical and practical aspects of the GTL technology were overviewed. Proofs that motor oils obtained by GTL are the best on the market were provided and prospects for the development of this technology in the near future were exposed.*

### Introduction

Gas to liquid (GTL) – is a process of converting natural gas or other gaseous hydrocarbons into long chain hydrocarbons such as gasoline and diesel fuel.

In 1902, The French chemist Paul Sabatier with Jean Baptiste obtained methane from a mixture of carbon monoxide and hydrogen in the presence of powdered nickel. A few years later the Russian chemist Egor Orlov obtained from the same mixture in the presence of nickel and palladium - ethylene, thereby showing the possibility of the synthesis of higher hydrocarbons. But the first who used this technology in a commercial way were Franz Fischer and Hans Tropsch. The process described was called Fischer-Tropsch process.

Main natural gas reserves are concentrated in the Asian part of Russia and the Middle East, and the main consumers are in the US and Europe. It is necessary to transport gas over thousands of kilometers, which represents a technical challenge. For European customers shipping is mostly realized through pipelines. Asian region uses LNG tankers transporting refrigerated liquefied gas [1]. Both options are very expensive. There is a third way - the construction of GTL plant. Subsequent transport and storage of liquid natural gas conversion products can use infrastructure (tankers, oil storage) that is much cheaper.

In recent years, all over the world research aimed at the use of natural gas for the production of motor fuel, design and construction of a number of objects have been intensively developing. From an environmental point of view, natural gas has great potential not only as an energy source, but also as a raw material for the chemical and petrochemical industries: obtained motor fuels meet current and future standards of the industrialized countries in their content of olefins, benzene and other aromatic hydrocarbons, and sulfur impurities. [2]

Nowadays there are two existing plants for processing natural gas into synthetic liquid fuel Sasol companies in Mossel Bay (South Africa) with a capacity of 1.15 million t/year, and Shell in Bintulu (Malaysia) with a capacity of 625 thousand t/year.

### The synthesis of liquid hydrocarbons from natural gas

Shell is the leading company - licensee synthesis of hydrocarbons from natural gas.

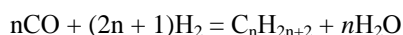
At the first stage from a mixture of natural gas and oxygen at a temperature of about 1500 °C syngas is produced - a mixture of carbon monoxide and hydrogen. In the process of manufacturing a synthesis gas emits a lot of heat and produces a lot of steam, which is used to rotate the turbine generators and produce electricity.

At the second stage the syn-gas is fed to the synthesis reactor, where the molecules are combined into a long chain hydrocarbon with a catalyst. The main product is long saturates - paraffins.

At the third stage paraffins are subjected to hydrocracking, during which the long molecules break into shorter and isomerization. Depending on the reaction conditions (temperature, pressure) a variety of hydrocarbon fractions can be obtained.

The formation of hydrocarbons from CO and H<sub>2</sub> is a complex catalytic process including a large number of series and parallel transformations. The process operates at high pressures and in the presence of catalysts based on group VIII transition metal (mainly Fe, Co, Ru) [3].

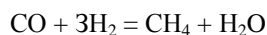
The most promising catalysts for hydrocarbon synthesis from carbon monoxide and hydrogen is cobalt system which at a pressure of 0.1-3 MPa and at a temperature of 120-130 °C makes it possible to obtain selectively allow linear alkanes [4]:



The maximum yield of liquid hydrocarbons is 208.5 g of a mixture of 1 nm<sup>3</sup> CO + 2H<sub>2</sub>.

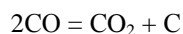
Side reactions for synthesis of hydrocarbons from CO and H<sub>2</sub> are:

a) hydrogenation of carbon monoxide to methane:

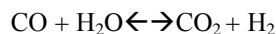


Technology, Machine-building, Geodesy

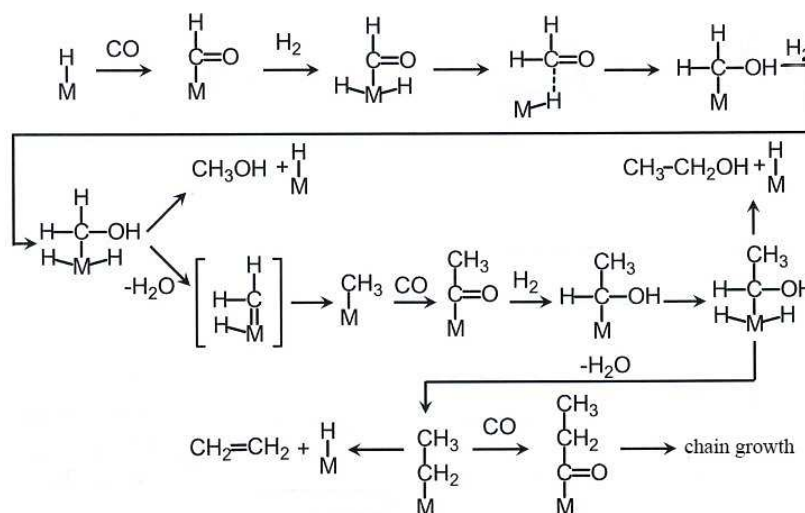
b) disproportionation of CO (Bell-Boudoir reaction):



c) the balance of water gas:



Mechanism according Henritsi-Olive [2]:



### Selectivity

The Fischer-Tropsch synthesis is considered as hydropolymerization reaction CO in which a wide hydrocarbon fraction is formed [5, 6, 7, 8].

Distribution of products is subject to polymerization kinetics, and the part of individual hydrocarbons distribution satisfies the Anderson-Schulz-Flory (Fig. 1).

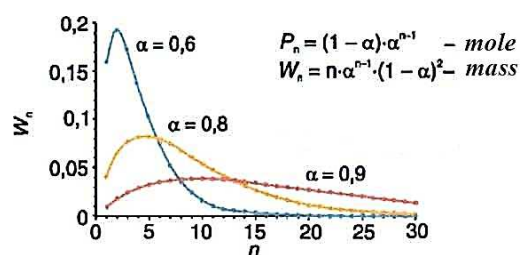


Fig. 1 The distribution of the Anderson-Schulz-Flory (ASF)

In this constant growth and chain termination  $k_1$  and  $k_2$  do not depend on the length of the intermediate chain (Flory, hypothesis). According to this model, the molecular weight distribution of products is determined by the growth of speed constants and chain termination, i.e. the value of the probability of chain growth:

$$\alpha = \frac{k_1}{k_1 + k_2}$$

The mass fraction of product with carbon number  $n$  is set by the Flory formula [5, 6]

$$W_n = n \cdot \alpha^{n-1} \cdot (1 - \alpha)^2$$

The value  $a$  is the probability of chain growth. The value  $a$  is determined by the nature of catalyst, the process temperature and pressure. For each class of products, simultaneously formed on one and the same contact of catalyst (paraffins, olefins, alcohols), the value  $a$  may be different.

ASF distribution restricts the selectivity of the process with regard to individual hydrocarbons and their narrow fractions. Thus, the yield of the gasoline fraction C<sub>5</sub> to C<sub>10</sub> can't exceed 45%, diesel fraction C<sub>11</sub> to C<sub>18</sub> - 30%. However, selectivity for paraffin wax increases monotonically with a rise and asymptotically approaches 100%. If obtained paraffins are subjected to soft hydrocracked gas-oil fraction yield can be increased to 60% for the reacted feed [9]. The practical maximum for a published data for cobalt is 0.94 and for iron 0.94 [10]. By Shell report, their cobalt catalysts obtain a product with the value a «good for 0.9" at a pressure synthesis "slightly above 3 MPa" [11].

**Catalysts**

The reaction catalysts are group VIII metals. Ru, Fe, Co, Ni provide the highest catalytic activity. Ruthenium is already active at 100 ° C, in its presence at elevated pressure paraffins of very high molecular weight (polymethylene) are formed. However, this metal is too rare and expensive to be considered as an industrial catalyst. Nickel at atmospheric pressure provides mostly direct hydrogenation of CO to methane. With elevated pressure volatile Ni(CO)<sub>4</sub> is easily formed, so that the catalyst is washed out of the reactor. For these reasons, commercial uses only iron and cobalt catalyst systems.

Comparative analysis of iron and cobalt catalysts is shown in numerous monographs and reviews [5, 8, 12–19]. These data are summarized in Table 1.

Table 1 – Comparison of iron and cobalt catalysts for Fischer-Tropsch

Fe	Co
Cheap	Co is more expensive than Fe
Low yield of CH <sub>4</sub> even with high temperature	Yield of CH <sub>4</sub> rapidly increases with increasing of temperature
Low hydrogenating activity - products contain many olefins	High hydrogenation activity – products contain almost exclusively alkanes
Significant formation of oxygenates	Oxygenates hardly formed
Capable of operating at a low ratio of H <sub>2</sub> :CO	Requires close to the stoichiometric ratio H <sub>2</sub> :CO
Part of the CO is converted to CO <sub>2</sub> by water gas reaction	Doesn't catalyze the water gas reaction
Quickly oxidized H <sub>2</sub> O and CO <sub>2</sub>	Resistant to oxidation
H <sub>2</sub> O inhibits the synthesis of hydrocarbons	H <sub>2</sub> O has no effect on the kinetics
The short life time	The life time is limited mainly catalyst poisons in the syngas

**The block diagram and the hardware design of the reactor block**

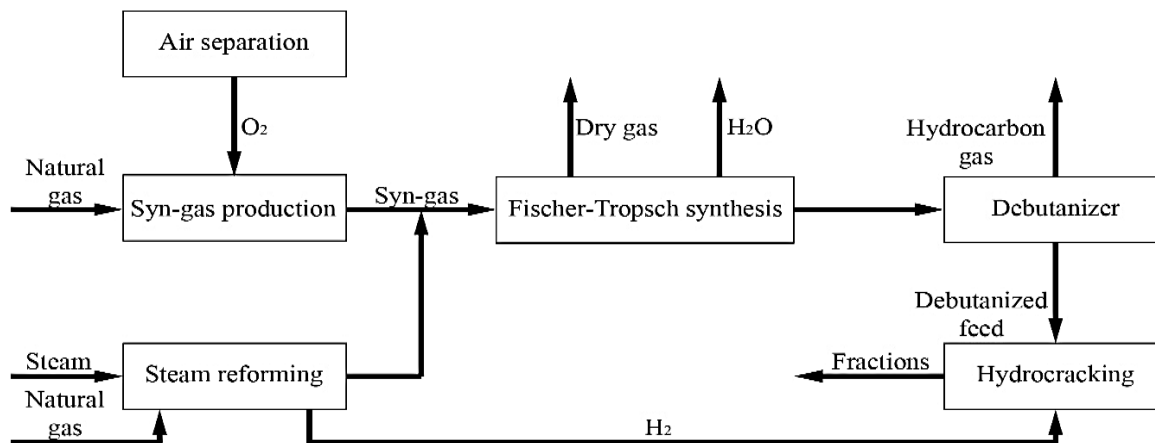


Fig. 2. The block diagram

The industrial FT synthesis reactor should provide a high rate of conversion of syngas, isothermality, effective heat dissipation, minimum loss of catalyst. Furthermore, the reactor should be structurally simple and reliable in operation. The most serious problem facing the designers is the need of a good heat removal. Local overheating is unacceptable because it leads to coking of the catalyst, and in the case of Co-catalyst - to an increased formation of methane. The reactor design is also determined by the kind of products, for which it is intended.

There are two common types of reactors for the conversion of this technology: the fixed bed type Arge reactor with tubes filled with catalyst and the liquid-based one, where the gas is blown through the movable base solid catalyst particles [20].

**Waste-free and environmentally friendly**

As known, the wide hydrocarbon fraction is obtained during the FT synthesis. Skilled use of products is possible after their separation into individual substances or narrow fractions. Separation scheme, and further processing depend on whether the plant operates the fuel or chemical route. Obviously, the relatively small production of FT is economically justified only if it is aimed at chemicals.

Because of low emissions of hydrocarbons, nitrogen oxides and sulfur, as well as less waste volume, the production of distillates plant using GTL technology is less polluting the air than refinery. Emissions do not lead to penalties for the contribution to the greenhouse effect, because they contain the same hydrocarbons, and emissions as traditional refineries.

Processed water and condensate can be reused in the plant. Gaseous light hydrocarbons collaterally displayed in small amounts of various technological installations return to the process used to generate energy. The flue gases are emitted into the atmosphere, almost without sulfur and meet the most stringent requirements in the world.

The catalyst is the only solid waste production - it returns to the manufacturer for further extraction of metals.

From the above it can be concluded that the production of hydrocarbons from carbon monoxide and hydrogen, is practically wasteless.

**The advantages of synthetic oils**

GTL technology allows a wide hydrocarbon fraction in the hydrocracking process which can obtain not only fuel, but also for the production of base oils, motor oils.

Synthetic oils obtained from GTL technology have several advantages over mineral ones.

1) Light start at low temperatures. This is possible because the base oil is made from natural gas, it has better stability on the molecular level than conventional base oils.

2) Save the properties for the entire life cycle. The base oil obtained by GTL technology has significantly greater resistance to oxidation than other base oils. Because of this it retains the original viscosity and fluidity, even after long runs.

3) Reduced cost for topping up. At high temperatures in the engine oil is vaporized, resulting in a decrease of its level in the lubrication system and reduce the engine protection. Synthetic oil has an extremely low evaporation under NOACK test results - 10% and below. This reduces its consumption, and significantly reduces the need for additional refilling.

**Conclusion.** It's obvious that the "gas to liquid" technology is a rapidly developing field of chemical industry and energy, although performance in absolute terms, is rather modest. According to forecasts, only about 2% of the world consumption of natural gas in 2015-2020 will fall on GTL-technologies. Thus, the GTL technology allows to use natural gas to produce motor fuels, basic chemicals, base oils and thereby weaken the dependence of these industries on the oil market fluctuations. In the future, it becomes possible to diversify the raw material base of energy and chemicals, more complete utilization of carbon-containing minerals of our planet.

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