Analysis of Conventional and Nonconventional GTL Technologies: Benefits and Drawbacks

Viktoriia Ribun, Sergii Boichenko, Hubert Kuzhewski, and Pawel Wos

1 Introduction

Since the world's population continues to grow and national economies develop, the demand for energy increases significantly as well. At the same time, the search for clean sources of energy to reduce the impact of combustion products on the environment is increasing. Soon, natural gas demand is likely to outpace demand for other fossil fuels. The International Energy Agency (IEA) predicts an increase in demand for natural gas by more than 50% by 2035. Especially if a significant part of shale gas will be used [1]. Some countries, for example, the USA, actively produce shale gas and use GTL technologies to convert excess gas into liquid motor fuels and lubricants [2]. Ukraine also has large gas reserves. The total volume of technically recoverable shale gas resources in Ukraine is estimated at 4.8 trillion m^3 (1.75% of the world reserve), 3.6 trillion m^3 of which are concentrated in the two largest fields—Yuzivskyi field in the Donetsk and Kharkiv regions, and 1.2 trillion m^3 are concentrated in the Oleske field, which is located in the west of Ukraine. In addition, Ukraine has quite wide possibilities for the production of biogas, which contains 50–60% of methane and 30–35% carbon dioxide, and 10 billion m^3/year of biomethane [3]. Therefore, the development and implementation of technologies for motor fuel or their components production through the conversion of natural gas is a promising scientific direction for Ukraine.

V. Ribun (✉)
Chemical-Analytical Laboratory of PJSC Ukrnafta, Kyiv, Ukraine
e-mail: ribun.vika@gmail.com

S. Boichenko
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine

H. Kuzhewski · P. Wos
Rzeszow University of Technology, Rzeszow, Poland

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_14

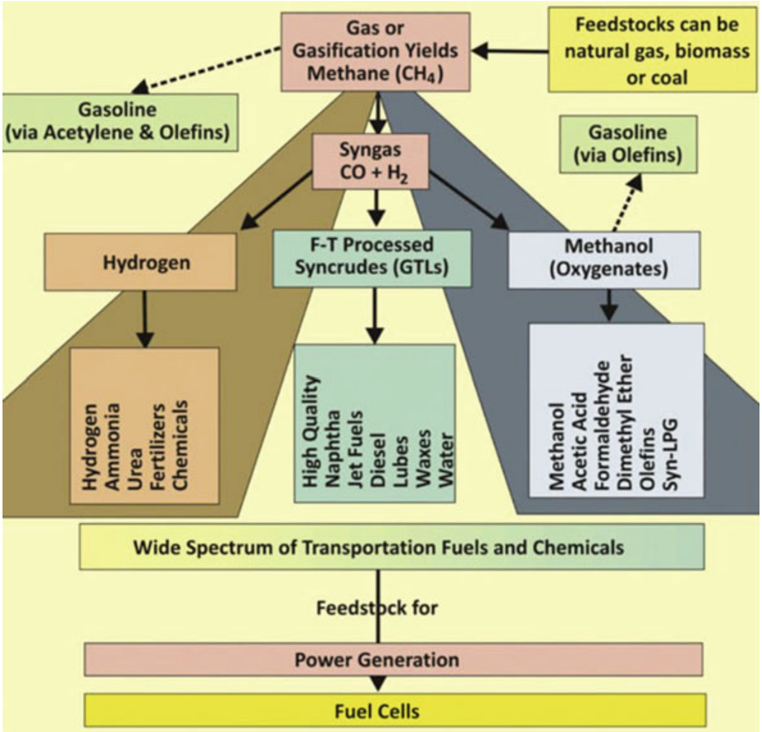

Fig. 1 Conversion of natural gas into liquid fuels and petrochemical products

The most common way of converting natural gas into liquid hydrocarbons is the Fischer–Tropsch method, that requires a pre-conversion of natural gas to synthesis gas, which is the most expensive stage of the technology. However, in recent decades, a number of alternative technologies for converting natural gas into high-quality liquid fuels have emerged, including sulfur free diesel with high cetane number, and jet fuel. Such technologies make it possible to obtain motor fuels using both ways—including the stage of synthesis gas and without conversion of natural gas to a mixture of carbon monoxide and hydrogen, which actually is synthesis gas (Fig. 1) [4].

2 The Role of Global Gas Reserves for the Development of GTL Technology Development

Global natural gas reserves are increasing faster than its consumption. An increase in unconventional gas production in North America and Australia in recent years has accelerated this trend. Indeed, taking into account the future development of unconventional gas production, such as shale gas, for energy-scarce countries, this trend is likely to continue for at least several decades. An additional resource is significant amounts of associated natural gas that is burnt or released during oil production in some countries of Africa (Nigeria) and the Middle East. Gas conversion can play a major role in reducing flaring if the technology becomes more available and cost-effective [5].

According to forecasts of the International Energy Agency (IEA), it is possible to achieve natural gas production of about 5.1 trillion m^3 in 2035, 32% of which will be unconventional natural gas. Most of this gas is currently delivered to consumers via pipelines, and approximately 30% of the gas exported from producing countries is transported as liquefied natural gas (LNG). However, a significant part of the world's natural gas reserves are either located far from consumers or are located in regions where demand for gas is limited. Transportation of natural gas by vehicles is a technologically complex process, because the gas must be compressed up to 600 times. GTL technology is an alternative and offers the chemical conversion of methane into long-chain hydrocarbon molecules that exist in a liquid state under atmospheric conditions. Methane itself can be obtained from natural gas, associated petroleum gas, gasification of coal and biomass [6].

OPEC predicts an increase in the need for diesel fuel to 37 million barrels/day by 2035 [7]. GTL technologies can make a significant contribution to the production of the necessary amount of transport fuels since demand for transport fuels increases every year (Fig. 2). The dependence on oil products for the transport sector is considered to be a threat to the energy and environmental security of country. High consumption in turn has contributed to the development of alternative fuels (biodiesel, bioreactive fuels, etc.), which can compete with GTL fuels [8]. However, GTL may benefit from increasingly stringent demands from consumers, environmentalists, governments and car manufacturers for fuel purity and efficiency. GTL diesel produced by FT processes has significantly higher quality than diesel fuel produced by typical crude oil refining processes. GTL diesel has a high cetane number (about 70 units compared to 45–55 units of petroleum diesel), low sulfur content (< 5 ppm), low content of aromatic substances (<1%), which leads to a decrease in density and improvement of low-temperature properties of diesel fuel [9].

3 Chemistry of the Fischer–Tropsch GTL Process

GTL (gas-to-liquid) and CTL (coal-to-liquid) technologies were first introduced in Germany in the 1920s using a process that became known as Fischer–Tropsch (FT) synthesis when Germany found itself short on oil, but had significant reserves of coal [10]. The need to provide liquid fuel led to the opening of factories that turned coal into gas and then into liquid using the high-temperature synthesis of FT. Despite the fact that the FT process was technically successful, it could not economically compete with the processing of crude oil, so the technology was used only to cut the lack of transport fuels. Recently, there has been renewed interest in the synthesis of

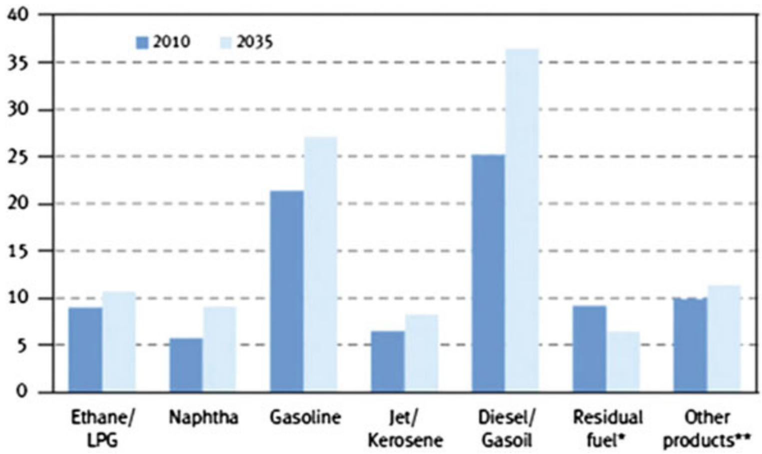

Fig. 2 Global product demand [9]

GTL fuels using low-temperature conversion of natural gas by the FT method into middle distillates [11]. It is caused by the limited supply of crude oil and the global desire to obtain cleaner high quality transport fuel.

The conversion of natural gas into liquid hydrocarbons can be accomplished through several chemical transformation steps leading to a variety of products. Currently, GTL technology based on Fischer–Tropsch synthesis is the most common. The process consists of three main stages, which require significant supporting infrastructure and a safe supply of natural gas for highly efficient synthesis [12].

1. Synthesis gas production. Natural gas is treated with steam and/or partial oxidation. The produced syngas consists mainly of carbon monoxide and hydrogen [13–17].
2. Catalytic (FT) synthesis. Depending on the technology, syngas is converted in reactors of various designs, into a variety of paraffinic hydrocarbons (crude synoil) with a long carbon chain ($\approx$ 100 carbon atoms in the molecule) [18–20].
3. Cracking of FT synthesis products. Crude synoil is cracked as in a traditional oil refinery to produce diesel fuel and commercial lubricants. Cracking of long-chain hydrocarbons can be adjusted to obtain products that market demands. The highly profitable target products of FT synthesis usually are middle distillate diesel fuel, jet fuel, and lubricating materials. Modern facilities are designed to obtain target products [21–26].

Fischer–Tropsch processes are not limited only to the use of conventional natural gas. Coal seam gas, associated gas, coal or biomass can be also processed using FT technologies by changing the catalyst, pressure and temperature conditions of synthesis [27]. A constant and safe supply of feed gas, regardless of origin, is essential to the commercial viability of large-scale FT GTL plants. The integration of mining and processing processes allows developers of GTL projects to earn profits with less potential risk [28].

4 Syngas Syngthesis

Syngas is usually obtained by the method of partial oxidation or conversion with water steam [29]. Syngas production is an intermediate step for many petrochemical processes, including a number of alternative GTL technologies.

Production of syngas by partial oxidation of methane (1) requires separation stage to remove nitrogen from the air and obtain oxygen of high purity [30].

$$CH_4 + 1/2O_2 \rightarrow CO + 3H_2. \tag{1}$$

Typical schemes of partial oxidation usually include:

- section for burning gas with pure oxygen. It contains a combustion chamber and operates at high temperatures (1200–1500° C) without catalysts;
- heat removal section, since the reaction is exothermic;
- carbon removal section [31].

The steam reforming process is widely used to obtain synthesis gas as a feedstock for a number of petrochemical processes and to produce hydrogen used in hydrocracking refineries. Reforming occurs according to reaction (2).

$$CH_4 + H_2O \rightarrow CO + 3H_2. \tag{2}$$

Steam reforming is usually carried out in the presence of a catalyst and under operating conditions that include temperatures of 850–940° C and a pressure of approximately 3 MPa. The process, as a rule, is carried out in tubular reactors using the heat of flue gases to preheat the source gas or to obtain steam in boilers [32].

In the autothermal reforming (ATR) synthesis gas production combines steam reforming with partial oxidation. The heat generated as a result of partial oxidation is used to heat the steam reforming reaction. The gases from the combustion chamber are mixed with steam and directed to the steam reformer, which makes the process autothermal. In autothermal processes, the heat is produced only by the reaction [33].

5 Fischer–Tropsch Synthesis

The The Fischer–Tropsch synthesis is one of the common technologies for increasing the carbon chain to obtain long-chain hydrocarbon molecules:

$$CO + 2H_2 \rightarrow -CH_2 - + H_2O(\text{exotermic}). \tag{3}$$

However, in practice, the process occurs according to Eq. (4).

$$2CO_{(gas)} + H_{2\,(gas)} \rightarrow (-CH_2-)_{nliquid} + CO_{2\,(gas)} + H_2O. \quad (4)$$

Carbon dioxide and water are formed as by-products. The FT reaction competes both the methane forming reaction (reverse steam reforming reaction 5) and reaction leading to the formation of propane and butane.

$$\mathrm{CO} + 3\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O}. \quad (5)$$

To promote the FT reaction and limit the methane forming reaction, the synthesis is carried out at low temperatures (220–350 °C), pressure 2–3 MPa and using cobalt-based catalysts [34].

There are two types of FT technologies based on natural gas: high-temperature (HTFT) and low-temperature (LTFT) Fischer–Tropsch synthesis. As a result of HTFT synthesis, if the process conditions are chosen correctly and are used the appropriate catalysts, obtained crude syn-oil contains a high percentage of short-chain hydrocarbons (<10 carbon atoms) and significant amount of propane, butane and other olefins (for example, propylene and butylene). These short-chain hydrocarbon gases are usually extracted from tail gases using cryogenic separation. The resulting tail gas is returned to the technological process for further processing. The high-temperature (HT) process of FT GTL based on an iron catalyst allows to obtain such fuels as gasoline and diesel, which are quite similar to traditional fuels obtained by refining conventional oil. The resulting GTL fuel is sulfur free, but contains some aromatic hydrocarbons. Typical operating conditions of the HTFT process are a temperature of about 320° C and a pressure of about 2.5 MPa. The HTFT process can be quite efficient (conversion > 85%), but not all products are ready for use. As a rule, high-temperature Fischer–Tropsch synthesis is carried out in reactors with a circulating fluidized bed [35].

The low-temperature Fischer–Tropsch process (LTFT) is carried out at a low temperature with cobalt based catalyst in slurry reactors with a bubbling column (for example, the Sasol) or in tubular reactors with a fixed bed (for example, the Shell). A synthetic diesel fuel (GTL diesel) obtained during LTFT process does not contain sulfur and aromatic substances. Typical operating conditions of the LTFT process are temperature of approximately 220–240 °C and pressure of approximately 2.0–2.5 MPa. The LTFT conversion is usually only about 60%. The main direction of most large-scale projects based on FT synthesis in the current market conditions is the production of high-quality GTL diesel fuel with low emissions, jet fuel and synoil (as petrochemical feedstock or gasoline addition) [36].

6 Alternative GTL Technologies

The problem of developing a chemical process for obtaining liquid fuels from natural gas without the most expensive stage of obtaining synthesis gas (60% of the cost price), has been raised for a long time. The most common way to obtain gasoline from natural gas is the conversion of methane to methanol, and methanol, in turn, to gasoline. Moreover, the production of methanol takes place without the synthesis gas stage. Currently, several technologies for converting natural gas into methanol have been developed. They do not include the synthesis gas stage – direct oxidation of methane to methanol (OMM) (6) and oxidative coupling of methane (OCM) [37]. OMM is conducted under high pressure (70–80 atm) and relatively low temperatures (400–450 °C). The main products with the same selectivity (40–50%) are methanol and carbon monoxide.

$$CH_4 + O_2 \begin{cases} \nearrow & 0.9\ CH_3OH + 0.1\ (CH_2O + H_2) \\ \searrow & 0.9\ (CO + 2H_2O) + 0.1\ (CO_2 + H_2O + H_2) \end{cases} \tag{6}$$

Recently, scientists have been developing the OCM method, the main products of which are olefins, mainly ethylene, carbon monoxide and a small amount of hydrogen. The technology is based on the cracking of heavy components of natural and associated gases (C3 +). The process is carried out under atmospheric pressure and high temperatures (≈750 °C). The interaction of methanol or olefins with CO makes it possible to obtain a wide range of GTL products. Direct partial oxidation with simultaneous oligomerization can be an alternative way of GTL technology, which does not include the step of synthesis gas obtaining (7), (8) [38].

$$CH_3OH \rightarrow CH_3{-}O-CH_3 \rightarrow C_nH_{2n}(\text{olefins}); \tag{7}$$

$$C_nH_{2n} \rightarrow \text{polymerization, cyclization} \rightarrow C_nH_{2n+2},\ \text{cycloparaffins, arenes.} \tag{8}$$

The Mobil company has developed the first plant, where the technology of conversion of methanol into gasoline is implemented. The plant produces sulfur-free gasoline (octane number 92 units). Methanol is converted into diethyl ether, and then into light olefins C5 + and further into paraffins, naphthenes and aromatic compounds (8). Catalysts used in the process promote the synthesis of hydrocarbons containing less than ten Carbon atoms. The product contains 53% paraffins, 9% naphthenes and 26% aromatichydrocarbons. Methanol is loaded into a system of reactors with a fixed catalyst bed, where it is completely converted into hydrocarbons and water, which are separated into a propane-butane mixture, crude gasoline and water. Crude gasoline is divided into liquefied automobile gas (C3–C4), light gasoline, and heavy gasoline. Heavy gasoline is hydrotreated to reduce duren (1,2,4,5-tetramethylbenzene) content, and then recombined with light gasoline into a finish product that contains no sulfur. The yield of gasoline is usually only 38% [39].

A small Texas company, Synfuels International, has developed a process in which methane at high temperature is converted to acetylene (C_2H_2). Then acetylene is converted using a specially designed catalyst (acetylene conversion ≈98%) into ethylene, which in turn is converted into a number of different types of fuel, in particular gasoline. A small demonstration plant was also created [40]. Other companies are also looking for ways to convert gas into gasoline.

7 Experience in Small-Scale FT Plants Operation

Some companies have developed small-sized modular plants for the processing of associated petroleum gas, for example, the British company Compact GTL. This approach consists of such steps as processing of feedgas into a steam methane reformer to produce synthesis gas, feeding it to a FT reactor that converts the feedstock into synthetic crude oil, water, and “tail gases” containing hydrogen, carbon monoxide, and light hydrocarbons gases. Then, the synoil is exported to a conventional oil refinery for further processing. Petrobras’ CENPES research and development center has successfully completed a three-year qualification test program for the small-scale GTL technology. This approach enables expansion of GTL technology opportunities [41].

Another company that deals with small-scale FT GTL processes is Velocys. It owns a modular system with a capacity of 1,000 barrels per day. The system is designed to obtain acetylene for the production of diesel and synthetic oil [42].

Although small-scale GTL technologies exist and are commonly used, most of the capital investments in GTL remain concentrated in large-scale FT GTL technologies. Most built capacities that based on FT GTL technologies are owned by two companies. Sasol has developed its GTL technology, which uses autothermal reforming to produce syngas, a slury FT reactor and Sasol’s patented cobalt catalyst. The resulting products are subjected to isocracking that is developed by Chevron. Sasol has implemented its technology by building the Oryx plant in Qatar, which has a design capacity of 32,400 barrels per day. Water produced as a byproduct of the GTL plant is used for irrigation in Qatar [43]. Sasol is planning a project to build GTL factories in Uzbekistan, the USA and Canada.

In 1993, Shell put into operation the first commercial GTL plant in the world in Malaysia, and later the Pearl plant in Qatar. Synthesis gas is obtained by partial oxidation with oxygen, and FT synthesis is carried out in a reactor with a fixed layer of cobalt catalyst. Varying the conditions of FT synthesis, the company manufactures a wide range of GTL products: motor fuels, high-quality oils and lubricants, and a number of chemicals that are raw materials for organic synthesis [44].

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9 Comparison of FT GTL Products with Conventional Oil Refining Products

Installations basing on FT GTL technology can be desined to produce a wide range of products, from base oils and lubricants to transport fuels and special chemicals. Most of developed technological lines are aimed at production of diesel fuel (C14–C20) along with jet fuel (C10–C13), gasoline (C5–C10), lubricants (>C50) and small amounts of liquefied petroleum gas (C3–C4). Choosing the operating conditions in the Fischer–Tropsch reactor, the mixture of the obtained products can be adjusted. So, GTL products are obtained in such quantities that allow them to complement the market of traditional oil products produced at conventional oil refineries [45].

However, typical FT GTL products are quite different from refinery products, which are obtained as a result of catalytic cracking (Fig. 3). As a rule, the yield of FT GTL diesel fuel is about 70%, that is rather higher than in oil refineries, where diesel fuel yield is usually about 40% [46]. In most oil refineries, the final product is low quality fuel oil and the yield depends on the quality of the processed crude oil, the type and capacity of the plants. In contrast to traditional plants, the products of FT GTL are high-value (compared to crude oil) light and middle distillates. Moreover, the yield of middle distillates is higher in comparison with typical oil refinery [47].

As noted above [9], the world demand for diesel fuel is growing by about 3% per year faster than for other refined products. Produsers face significant challenges in

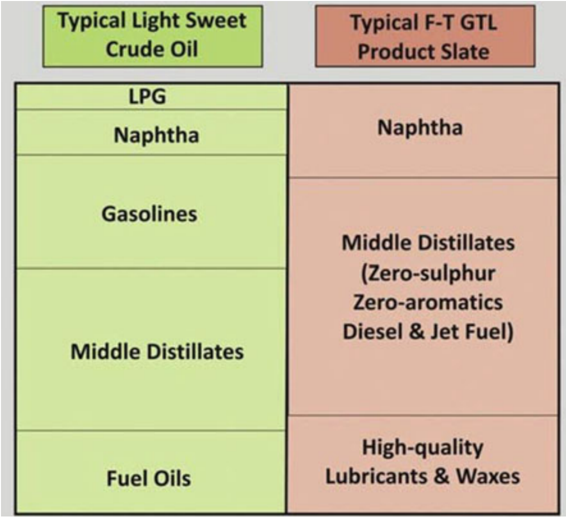

Fig. 3 Refinery volume yield versus FT GTL yield

meeting demand and requirements of diesel fuel, as the supply of crude oil becomes more difficult due to resource exhaustion of resources. Forecasts for the next decades show that demand for diesel fuel will continue to grow (Fig. 2).

10 SWOT-Analysis of GTL Technologies

The current state of development of GTL technologies involves a number of challenges and treas. The main challenges are the high technological complexity of the process, significant capital investments in expensive equipment and investment risks. However, despite the mentioned threats, there are certain opportunities to overcome them. For example, the integration of mining processes and small-scale processing plants, the development of cheap catalysts that increase the selectivity of target products, etc. In order to stimulate innovation and enable new technology, one should consider following points that provide opportunities and prospects for GTL technology:

– reduce complexity. Robust technology can be optimized, but it is difficult to make already complex technology robust;
– reduce capital by innovation. Develop new technology based on improving common GTL process, e.g. small-scale GTL plants;
– explotation of smaal deposits of natural gas and unconventional gas. Use biogas and biomethan as feedstock for GTL process;

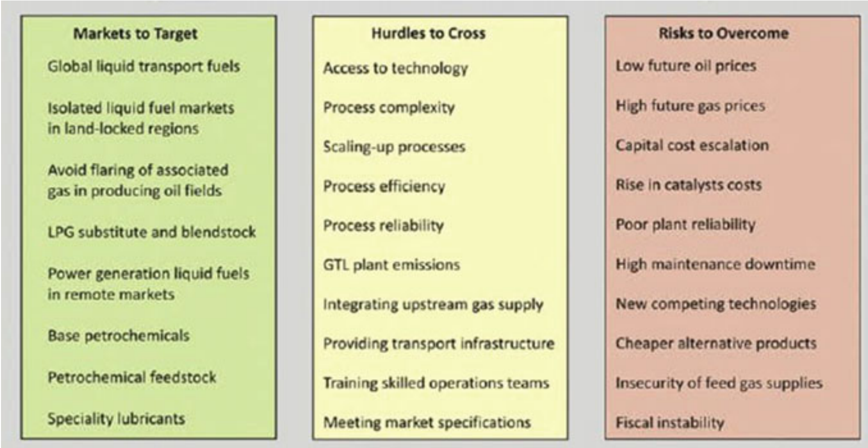

Fig. 4 The GTL industry: opportunities and chelrnges

– improve FT synthesis developing new catalysts to reduce costs of process and its complexity.

The main challenges and risks of GTL technologies are shown in Fig. 4 [48].

11 Conclusions

GTL technologies can contribute to reducing global dependence on transport fuels produced from crude oil. They offer significant opportunities for the development of unconventional natural gas deposits, in particular shale gas and biogas, which is quite promising for Ukraine.

However, the technologies are complex, expensive, patents for key processes are held by several companies. Therefore, the development of simple small-scale GTL installations is an important scientific and technological problem.

Currently, large GTL plants are operating using FT syntesis. However, alternative GTL technologies for converting methane into methanol or olefinic hydrocarbons with their subsequent conversion into gasoline without obtaining syngas are developing quite quickly. Such technological installations can replace traditional oil refineries and petrochemical plants and significantlly reduce the cost of common GTL process.

The GTL industry is influenced with oil and gas prices. Market price fluctuation for crude oil and natural gas complicate capital investment calculations for new GTL projects. While refineries are only affected by oil prices, GTL operations are affected by both oil and natural gas prices. Therefore, the future is in small-scale hybrid installations, which allow to reduce capital investment and monetize natural gas into more expensive, high-quality, cleaner and demanded transport fuels.

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