ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 12, pp. 2604–2610. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.G. Kiryachek, S.A. Filipchenko, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 5, pp. 70–75.

Fischer–Tropsch Slurry Process for Small- and Medium-Scale Plants Processing Associated Petroleum Gas

V. G. Kiryachek and S. A. Filipchenko

Renfors–Novyye Tekhnologii CJSC, ul. Solnechnaya 79/1, Samara, 443031 Russia
phone: +7(846)2253571
fax: +7(846)2408691
e-mail: syngaz@yahoo.com

Received June 12, 2010

Abstract—The Fischer–Tropsch three-phase synthesis (slurry process) as one of the simplest and most technologically flexible options for processing of associated petroleum gas into motor fuels and products of the basic organic synthesis is described. The process has the following advantages: a high yield of the desired products due to complete conversion of syngas; flexibility of the source syngas composition; simplicity of the equipment manufacturing; operational reliability of the equipment and non-rigid operational conditions; a stable temperature regime in the reactor; the absence of abrasive deterioration; a possibility of continuous replacement and repeated regeneration of the catalyst; and reliable heat removal together with a small area of the cooling surface.

DOI: 10.1134/S1070363211120292

INTRODUCTION

One of the first predictions of the global crisis was made in the Limits to Growth, D. Meadows' analytical report to the Club of Rome [1], which was published in 1972 on the eve of the first oil crisis and caused quite a stir. The report was based on mathematical modeling of the global development of the civilization at exponentially increasing world population, consumption of non-renewable natural resources, water, food products, and especially energy, which is the main component of the stable life of the modern society [2].

The demonstrated technical possibility of shale gas commercial production [3], which caused the United States to refuse importing natural gas, will inevitably result in global reorientation of the gas market, and first of all, the European gas market. Taking into account a strong desire of the European Union to diversify gas supply sources, it is possible to curb the growth of the Russian gas export artificially, which will increase competition on the domestic market. As a result, it can change not only the gas production and supply strategy but also the gas processing strategy. It can be expected that there will be a drastic increase in demand for small- and medium-scale block-modular complexes to satisfy local needs for chemical products and fuels using local resources. Inter alia, such local resources include associated petroleum gas (APG), cost-effective utilization of which is quite a challenge due to minor volumes.

A real possibility to process small quantities of gas, including APG, into synthetic liquid hydrocarbons is provided by the GTL technology [4], which involves a whole range of chemical processes to produce synthetic motor fuels from natural, shale, and associated petroleum gases. Diesel and jet fuels obtained as a result of this process possess unique properties as they contain almost no sulphur and aromatic compounds.

At present there is a stable growth of interest for associated petroleum gas processing. Taking into account the climatic conditions and the geographical location of Russia, as well as the presence of a large number of deposits with abundant gas resources far from the pipeline transport facilities, we can conclude that there will be a high demand for a relatively inexpensive block-modular technology allowing the companies to process APG into such an easily transportable product as synthetic liquid hydrocarbons directly on site. At the same time, manufacturing of synthetic motor fuels directly at the deposits of Siberia will solve the problem of supplying remote Russian regions with fuel, the so-called north delivery problem.

The Renfors–Novyye Tekhnologii Company is a developer of small- and medium-scale block-modular plants. We developed and tested a number of engineering solutions aimed at improving the technology for production of synthetic crude oil and synthetic motor fuels and optimizing the equipment production and operational costs. We also analyzed technologies for processing gas into other highly-liquid products described in survey [5].

History of Development of the Fischer–Tropsch Three-Phase Synthesis

One of the optimal methods to produce liquid hydrocarbons from hydrocarbon gases, which is also simple in technical implementation, is the Fischer–Tropsch three-phase synthesis (slurry process). The process of liquid hydrocarbons production from syngas obtained through conversion of natural, shale, and associated petroleum gases or through gasification of coal and biomass is performed in compliance with reactions (1)–(6) (catalytic hydropolymerization process of the Fischer–Tropsch synthesis, the FT synthesis, or FTS) [6–13].

Synthesis of paraffin hydrocarbons:

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O},\quad (\Delta H_{500} = -165\ \mathrm{kJ\ mol^{-1}\ CO}), \tag{1}$$

$$2n\mathrm{CO} + (n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{CO_2},\quad (\Delta H_{500} = -155\ \mathrm{kJ\ mol^{-1}\ CO}). \tag{2}$$

Synthesis of olefins:

$$n\mathrm{CO} + 2n\mathrm{H}_{2n} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O},\quad (\Delta H_{500} = -165\ \mathrm{kJ\ mol^{-1}\ CO}), \tag{3}$$

$$2n\mathrm{CO} + n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{CO_2},\quad (\Delta H_{500} = -155\ \mathrm{kJ\ mol^{-1}\ CO}). \tag{4}$$

The major concurrent reactions include the water gas shift reaction (5) and the Boudoir reaction, CO pyrolysis (6):

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2},\quad (\Delta H_{500} = -40\ \mathrm{kJ\ mol^{-1}\ CO}), \tag{5}$$

$$2\mathrm{CO} \rightarrow \mathrm{C} + \mathrm{CO_2},\quad (\Delta H_{500} = -67\ \mathrm{kJ\ mol^{-1}\ CO}). \tag{6}$$

The development of the Fischer–Tropsch three-phase synthesis (slurry process) started in 1938 in Germany as an alternative to the fixed-bed process, which had a number of disadvantages. They included insufficiently fast heat removal due to the low thermal conductivity of the catalyst bed, an uneven distribution of the gas flow in the reactor, an impossibility to process gases with a high content of carbon oxides due to the Boudoir reaction, a limited flexibility in terms of changing the composition of the resulting products, a necessity to use coolers with a large specific surface area (250 $\mathrm{m^2}$ per 1000 $\mathrm{m^3}$ of syngas), and complications in loading and unloading of the catalyst.

Therefore, the Fischer–Tropsch three-phase synthesis (slurry process) turned out to be more preferable for small-scale installations. The advantages of this process include perfect removal of heat from the reactor, a possibility to process syngas with a high content of CO, stability of the process to the Boudoir reaction, a possibility to use low-calorific syngas, simplicity of manufacturing of the reactors from ordinary carbon steel, a technological flexibility and fast adaptability of the production, a possibility to combine the synthesis with the hydrocracking process, and a possibility for continuous replacement and regeneration of the catalyst.

The first research works in this area were carried out as early as in the 1930s but they were not continued [14, 15]. In 1939–1940 the Ruhrchemie Company performed a number of tests with Fe catalysts but during World War II these works were stopped [16].

The basis for the commercial slurry process was formed by H. Kolbel's and M. Ralek's works in 1938–1953. After a series of laboratory tests performed at a 6-liter reactor the results were repeated at a commercial-scale demonstration reactor produced by the Rheinpreussen-Koppers Company [17]. The production capacity of the reactor with regard to hydrocarbons reached 11.5 t $\mathrm{day^{-1}}$; the consumption of syngas amounted to 2700 $\mathrm{m^3\ h^{-1}}$; and the dimensions of the reactor were as follows: height of 8.6 m and working volume of 10 $\mathrm{m^3}$. The process parameters were as follows: catalyst content in the slurry of 10% (80 kg); synthesis temperature of 268°C; pressure of 1.2 MPa; $\mathrm{H_2/CO}$ ratio of 1/1.5; conversion rate of 89%; hydrocarbon yield of 178 g $\mathrm{m^{-3}}$ including 53.6 wt % of liquid products with t_{boil} = 180°C; methane content of 3 wt %; and specific heat-exchange surface of 50 $\mathrm{m^2}$ per 1000 $\mathrm{m^3}$ of syngas.

In 1935–1949 the BASF Company used semi-commercial pilot plants for testing of the Duftschmid process, during which the liquid phase circulated through the flooded fixed bed of the molten

Fe catalyst. The process parameters were as follows: temperature of 240–290°C; pressure of 2 MPa; H_2/CO ratio of 1/1.24; volume rate of 250 h^{-1}; conversion rate of 65–70%, hydrocarbon yield of 157 g m^{-3}; and liquid hydrocarbon selectivity of 80–90% [18].

In 1944–1953 the Burean of Mines Company, the United States, [19, 20] carried out a series of laboratory tests of the process based on the BASF methodology. The process parameters were as follows: Fe catalyst; $h = 3.1$ m; $d = 7.6$ cm; $T = 230–260°C$; $P = 1$ MPa; $H_2/CO = 1/1$; volume rate of 200–300 h^{-1}; conversion rate of 80%; hydrocarbon yield of 170 g cm^{-3}; and liquid hydrocarbons content of 55–80% including 40–50% of gasoline fraction, 15–30% of diesel fraction, and 20–45% of high-molecular paraffins. One of the unusual catalysts applied was fine metal cuttings from the metal turning lathe.

In 1949–1961 a series of tests in a column reactor of the Rheinpreussen type ($h = 8.5$ m; $d = 248$ mm; $P = 2$ MPa; and internal heat exchanger of 2.5 m^2) was carried out in England [21]. The process parameters were as follows: conversion rate of 35–60%; $T \leq 280°C$; and Fe catalyst deposited from ferric sulphate.

In 1963 similar laboratory tests were performed at the Technological Institute, India [22]. The process parameters were as follows: Fe catalyst promoted with Cu, MgO, and CaO; $h = 3$ m; $d = 5$ cm; $T = 240–260°C$; $P = 1.05$ MPa; $H_2/CO = 1/0.7$; conversion rate of 91%; hydrocarbon yield of 174 g cm^{-3}; methane content of 3.5%.

In 1968 another series of tests was carried out in the University of Tokyo on the basis of a column reactor produced by the Rheinpreus-sen Company [23]. The process parameters were as follows: Fe catalyst promoted with potassium; $h = 5.5$ m; $d = 50$ mm; $T = 266°C$; $P = 1.03$ MPa; $H_2/CO = 1/1.7$; conversion rate of 80%; hydrocarbon yield of 170–190 g m^{-3} including 80% of liquid hydrocarbons; and methane yield of 5%. In work [24] the yield of C_2–C_4 olefins of 60 g m^{-3} was obtained using Fe–Mg catalyst at $T = 290°C$ and $P = 1.2$ MPa.

In 1949 the Fuel Research Station Company, England, performed a comparison analysis of the fixed-bed process, the fluid-bed process, and the slurry process and made a conclusion that due to its higher selectivity and flexibility the slurry process was the most promising [25]. A pilot plant with the capacity of 71 m^3 of syngas per hour and a daily output of 300–450 l was constructed (height of 8.5 m; internal diameter of 24.8 cm; and reaction volume of 274 l) [26]. The process parameters were as follows: $P = 1.02$ MPa; $T = 260°C$; volume rate of 197 h^{-1}; and hydrocarbon yield of 124.2 g m^{-3} including 4.2 wt % of methane and 29.7 wt % of alkanes.

The most large-scale research works of the slurry process were carried out in 1980–1990 in the Republic of South Africa by the Sasol Company [27, 28]. The commercial-scale slurry reactor commissioned in 1993 had the following dimensions: $h = 22$ m and $d = 5$ m. The process parameters were as follows: Fe and Co catalysts; $T = 200°C$; $P = 2.5–3.0$ MPa; $H_2/CO = 2/1.5$; conversion rate of 90%; and hydrocarbon yield of 178 g cm^{-3} including 80% of liquid hydrocarbons and 3% of methane.

In 2005 the NIPPON STEEL Company implemented JOGMEC project resulting in commissioning of Yufutsu pilot plant. At this plant the slurry process uses unconventional Co catalysts characterized by high efficiency and durability compared to other rival catalysts. CFD computer simulation was applied for development of this slurry reactor [29]. The process parameters were as follows: $P = 2.2–2.4$ MPa; $T = 230–240°C$; conversion rate of 87.5%; $H_2/CO = 2/1$; and linear gas speed in the reactor of 0.04–0.32 m s^{-1}. The catalyst productivity with regard to C_5^+ hydrocarbons reached 1300 g kg^{-1} of the catalyst per hour and the yield of hydrocarbons amounted to 176 g m^{-3} including 88% of liquid hydrocarbons.

Key Features of the FT Process in the Slurry Reactor

The FT synthesis is a highly exothermic reaction. The significant heat liberation (up to 25% of syngas combustion heat) is a crucial problem largely responsible for the choice of the reactor type. One of the major technological tasks is to organize removal of heat from the reaction zone in order to avoid overheating of the catalyst bed, an increase in the methane yield, and carbonization of the catalyst due to the Boudoir reaction.

The main advantage of the FT synthesis in the liquid phase is a possibility to achieve the composition of products meeting the consumer requirements. Ample opportunities to vary the product composition are illustrated by the following three examples of synthesis aimed at producing high-molecular paraffins, obtaining low-molecular paraffins, and combining the FT synthesis with the hydrocracking process, respectively.

(1) A possibility to obtain low-molecular compounds at elevated temperatures of 280–320°C is described in work [30]. The resulting fraction with a boiling point reaching 200°C contains 85% of olefins.

(2) A possibility to produce high-molecular paraffins at temperatures of 216–232°C removing the dispersed catalyst from the slurry using a filter with a high-gradient magnetic field is demonstrated in work [31].

(3) In works [30–33] the FT synthesis is combined with the hydrocracking process, when within a temperature range of 290–320°C an impregnating mixture is added and high-molecular hydrocarbons (with a boiling range of 290–400°C) crack into low-molecular compounds.

(4) Flexibility with regard to the source syngas composition and a possibility to vary the composition of products of the three-phase synthesis are demonstrated in work [34].

In reactors with a fixed-bed catalyst the reaction heat is removed from the catalyst tubes using a cooling agent fed into the inter-tube space. Despite the intensive heat exchange on the outer surface of the tubes, a temperature gradient at the center of the tube can exceed 15–20°C, which makes it impossible to increase the tube diameter or the production capacity of the unit. A great pressure differential in the tubes resulting from close packing of the catalyst grains and a high labor intensity of the catalyst reloading are other disadvantages of fixed-bed reactors [7].

In reactors with a two-phase fluid-bed catalyst the reaction heat is removed through direct contact of hot particles with gas, which results in an insignificant temperature differential in the reaction zone (1–2°C). The disadvantages include attrition of the catalyst particles and their adhesion resulting from deposition of carbon and high-molecular paraffins, as well as erosive wear of the chemical equipment.

Three-phase slurry reactors are represented by simple columns with highly dispersed catalysts (particles below 50 μm in size) suspended in a liquid, as a rule, in high-molecular paraffin, through which syngas is bubbled upwards. Thus, there is no problem of mechanical stability of the catalyst particles floating in the liquid, which also ensures good removal of heat from the surface of the catalyst.

The temperature gradient in the reactor does not exceed 1°C; therefore, the process can be performed at higher temperatures with no risk of local hot spots and the resulting high methane concentrations. The removal of heat from the slurry reactor is performed at the heat-exchanger tube bundle, the specific area of which amounts to 50 m^2 per 1000 m^3 of syngas, which is 4–6 times smaller than the specific heat-exchange surface in the fixed-bed reactor. The lower limit of the temperature range is determined by the optimal viscosity of the carrier liquid, while the higher limit (approximately 280°C) is dictated by the undesirability of secondary hydrocracking reactions. The reaction temperature is regulated by controlling the pressure of the superheated steam in the heat-exchanger tubes.

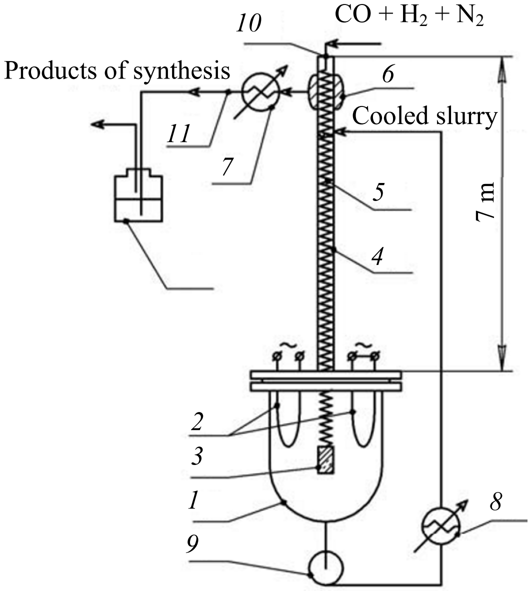

Fig. 1. Laboratory unit for Fischer–Tropsch three-phase synthesis: (*1*) bottom of the column; (*2*) heating elements; (*3*) spraying device; (*4*) bubble column; (*5, 8*) heat-exchangers; (*6*) gas-liquid separator; (*7*) cooling condenser of light hydrocarbons; (*9*) circulation pump; (*10*) incoming syngas; and (*11*) products of synthesis.

The optimal liquid medium is a fraction of hydrocarbons with a sufficiently high boiling point obtained as a result of the FT synthesis. The limiting stage of the FT synthesis process is the external diffusion resistance of the reactants flow through paraffin to the surface of the catalyst particles [6].

Distribution of hydrocarbons formed in the process of the FT synthesis is described by the Anderson–Schulz–Flory equation [35]:

$$m_n = (1 - \alpha)\alpha^{n-1},$$

where (m_n) molar content of the product; (n) carbon number of the product; (α) chain growth probability, and

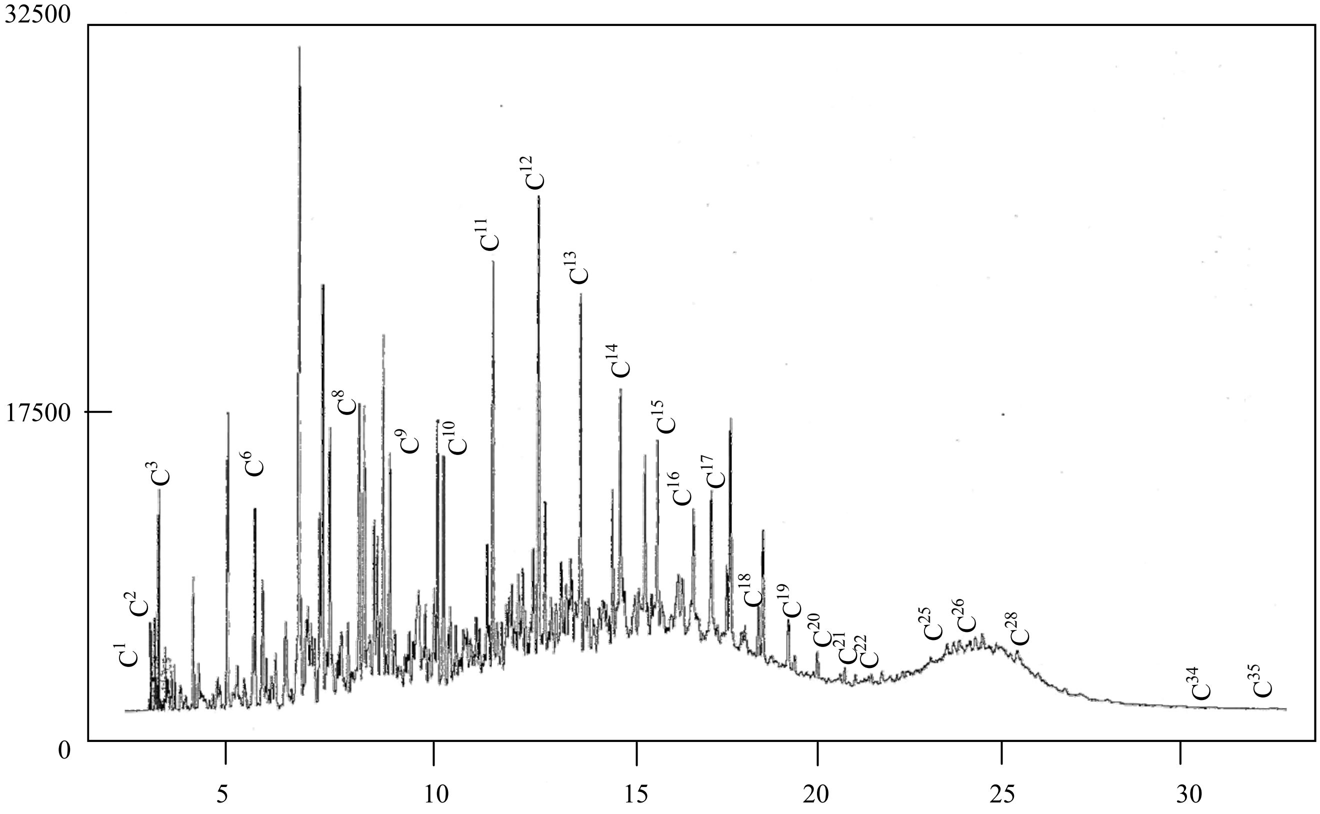

Fig. 2. Typical chromatogram of liquid products of synthesis.

$$P_n = n(1 - \alpha)^2\alpha^{n-1},$$

where P_n weight content of the product.

The slurry process catalysts can be represented by group VIII transition metals, i.e. Fe, Co, and Ni. Moreover, the major role in industrial processes is played by the first two metals as, in general, nickel is active only in the methane formation reaction.

The process was developed for Fe catalysts, which are optimal for production of petrochemical materials. The main characteristics of Fe catalysts applied in the FT synthesis are as follows: operation at high temperatures of 250–300°C; formation of more low-molecular hydrocarbons (α = 0.6–0.7); an increased content of olefins in the reaction products (up to 80–90%); higher selectivity in formation of iso-hydrocarbons (up to 5–10%) compared to the value of 2–5% for cobalt; a significant activity in the water gas shift reaction (5) (for this reason $H_2/CO = 1/1.3$ is recommended for Fe catalysts to avoid a drop in the target hydrocarbon yield); and formation of significant quantities of alcohols, aldehydes, and CO_2.

Potassium carbonate is used as a promoting additive [36]. Alkali metals suppress methane formation and promote the formation of long-chain hydrocarbons; however, in a combination with copper they contribute to the formation of hydrogen under the Boudoir reaction. In order to regulate selectivity of the liquid-phase synthesis it is possible to add potassium carbonate directly into the slurry. Fe catalysts can be regenerated through air oxidation. After regeneration the catalyst activity is fully restored and its selectivity is increased.

The key features of cobalt catalysts for the slurry process are a high hydrogenating activity and a possibility to function at relatively low temperatures (200–240°C) and pressures of 0.1–5 MPa; the volume rate in syngas is as follows: $CO/H_2 \sim 1/2$. Under such conditions 90% formation of alkanes takes place. Like Fe catalysts, Co catalysts can be repeatedly regenerated.

Catalysts of the Fischer–Tropsch synthesis are extremely sensitive to sulphur poisoning. Therefore, it is necessary to preliminarily desulphurize syngas, at least, to the level of 2 mg m^{-3}. Residual sulphur is adsorbed at the surface of the catalyst deactivating it; as a result, products of the FT synthesis contain almost no sulphur. This fact makes synthetic fuels manufactured on the basis of the FT technology quite attractive due to the modern strict environmental requirements to motor vehicles.

Laboratory Unit for the Slurry Process

As a prototype laboratory unit for the slurry process we used a laboratory unit (h = 7 m and d = 50 mm) simulating a plug-flow reactor manufactured by the Rheinpreussen Company. The layout of the unit is given in Fig. 1.

The structure and operating principles of the laboratory unit are described below. Syngas consisting of a mixture of $CO/H_2/N_2$ with a ratio of 1/2/2.88 is fed into the upper part of the column 10, heated in a spiral heat-exchanger 5 going along the entire column, and enters a spraying device 3 at the bottom of the column 1. The whole unit is filled with a catalyst slurry consisting of deposited Fe catalyst (92.3%) and promoting agents (ZrO_2 4.2%, CuO 2%, and K_2CO_3 1.5%). We used TP-22 turbine oil as a liquid phase. The optimal weight of the catalyst in the slurry in terms of active metal amounted to 78 g l^{-1}. An increase in the catalyst concentration resulted in a higher viscosity of the liquid-phase system.

Heating elements *2* maintained the reaction temperature at 275°C. Mixing and cooling were performed using a circulation pump *9* and an air-cooling heat-exchanger *8*. The level of the slurry was kept at a height of 6 m; the pressure of the synthesis process amounted to at 1.2 MPa. The sprayed syngas was bubbled through the liquid layer containing the catalyst, where synthetic hydrocarbons were formed as a result of the reaction. Products of the reaction were removed from the column through the separator *6*, where they were separated into liquid and gas phases. After that the gas phase was sent to the condenser *7* and then gathered in the condensate tank. A typical chromatogram of the reaction liquid products is given in Fig. 2.

The analysis demonstrated that the chain growth probability was $\alpha = 0.75$. In Fig. 2 a chromatographic peak is observed within a period of 27–31 min. This peak is related to the removal of the liquid phase from the source slurry of C_{23}–C_{30}.

CONCLUSIONS

The GTL technology is a dynamically developing area of gas chemistry. One of the simplest and most flexible options under the GTL technology that makes it possible to process minor volumes of associated petroleum gas for production of motor fuels and products of the basic organic synthesis is the Fischer–Tropsch three-phase synthesis (slurry process). The advantages of the FT three-phase synthesis are as follows: economic effectiveness; a high yield of target products due to a sufficiently complete conversion of syngas; a high selectivity of the synthesis and the maximal yield of valuable components; flexibility with regard to the source syngas composition; simplicity of the equipment manufacturing, its operational reliability, and non-rigid operating conditions; stable temperature conditions in the reactor (±1°C); nonoccurrence of erosive wear of the reactor; a possibility of continuous replacement and repeated regeneration of the catalyst; and reliable heat removal together with a small area of the cooling surface (50 m^2 per 1000 m^3 of syngas).

All the above-listed points allow us to count on the development of cost-effective small- and medium-scale block-modular plants for conversion of minor quantities of APG and natural gas into synthetic hydrocarbons, at the same time, solving the vital environmental and economic problem of hydrocarbon gas flaring.

REFERENCES

1. Meadows, D., *The Limits to Growth, Report to the Club of Rome*, 1972.
2. Arutyunov, V.S. and Lapidus, A.L., *Ross. Khim. Zh.*, 2003, vol. 47, no. 2.
3. *Modern Shale Gas: Development in the United States, A Primer*, Katelyn, M.N., Ed., 2009.
4. Eliseev, O.L., *Ross. Khim. Zh.,* 2008, vol. 52, no. 6, pp. 53–62.
5. Slivinskii, E.V., Kuz'min, A.E., Abramova, A.V., Kliger, G.A., and Loktev, S.M., *Neftekhimiya*, 1998, vol. 38, no. 4, pp. 243–268.
6. Uchkin, M.S., *Candidate Sci. (Econ.) Dissertation*, Moscow, 2005, p. 178.
7. *Khimicheskiye veshchestva iz uglya* (Chemical Compounds from Coal), Fal'be, Yu.M., Ed., Moscow: Khimiya, 1980, p. 614.
8. Radchenko, M.N., Kagan, D.N., and Krechetova, G.A., *Synthetic Hydrocarbon Motor Fuel from Natural Gas*, Moscow: IVTAN, 1998, p. 233.
9. Kagan, D.N., Krechetova, G.A., and Shpil'rain, E.E., *Malostadiinyi protsess polucheniya sinteticheskikh*

motornykh topliv iz prirodnogo gaza na malogabaritnykh ustanovkakh nizkogo davleniya: tekhnologiya, ekonomika (Few-Stage Process of Production of Synthetic Motor Fuels from Natural Gas at Low-Pressure Small-Size Units: Technology, Economy), Preprint OIVT RAN no. 8-473, Moscow, 2004, p. 59.

10. Kagan, D.N., Krechetova, G.A., and Shpil'rain, E.E., *Parameters of Few-Stage Technology for Processing of Natural Gas into Synthetic Diesel and Jet Fuels at Low-Pressure Small-Size Units*, *Topical Problems of Gas Chemistry*, Moscow: Izd. Neft' i Gaz, 2004, pp. 63–77.
11. Kagan, D.N., Lapidus, A.L., and Shpil'rain, E.E., *Khimiya Tverdogo Topliva*, 2008, no. 3, pp. 6–8.
12. Kagan, D.N., Shpil'rain, E.E., and Lapidus, A.L., *Gazokhimiya*, 2008, no. 2, pp. 50–58.
13. Zhorov, Yu.M., *Termodinamika khimicheskikh protsessov: neftekhimicheskii sintez, pererabotka nefti, uglya i prirodnogo gaza* (Thermodynamics of Chemical Processes: Petrochemical Synthesis, Processing of Oil, Coal, and Natural Gas), Moscow: Khimiya, 1985, p. 464.
14. Fisher, F., *Brennstoff-Chem*., 1932, vol. 13, p. 461.
15. Fisher, F., Roelen, O., and Feist, W., *Brennstoff-Chem*., 1932, vol. 13, p. 461.
16. Roelen, O. and Schenk, P., *BIOS-Ber*., no. 447, p. 31.
17. Kolbel, H. and Ralek, M., *Catal. Rev. Sci. Eng*., 1980, vol. 21, no. 2, pp. 225–274.
18. Duftschmid, F., FIAT Final Report 1267, 1949; German Patent DRP 762.320, 1935, I. G. Farbenindustrie.
19. Shulz, J.F., Seligman, B., Shaw, L., and Anderson, R.B., *Ind. Eng. Chem*., 1952, vol. 41, p. 307.
20. Schlesinger, M., Benson, H., Murphy, E., and Storch, H., *Ind. Eng. Chem*., 1954, vol. 46, p. 1322.
21. Farley, R. and Ray, D.J., *J. Inst. Pet*., 1964, vol. 50, p. 27.
22. Mira, A.K. and Roy, A.N., *Indian Chem. Eng*., 1963, p. 27.
23. Konugi, T., Sakai, T., and Negishi, N., *Sekiyu Gakkaishi*., 1968, vol. 11, p. 636.
24. Deckwer, W.-D., Sepremen, Y., Ralek, M., and Schmidt, B., *Ind. Eng. Chem. Proc. Des. Dev*., 1982, vol. 21, p. 222.
25. Hall, C.C. and Gall, D., *J. Inst. Petroleum*, 1952, vol. 38, p. 845.
26. Farley, R. and Ray, D., *J. Inst. Petroleum, London*, 1964, vol. 50, p. 27.
27. Jager, B. and Espinosa, R., *Catal. Today*, 1995, vol. 23, p. 17.
28. Jager, B., Dry, M.E., and Steynberg, A.P., *Cat. Lett*., 1990, vol. 7, pp. 293–302.
29. *Development of GTL (Gas to Liquid) Technology*, Nippon Steel Technical Report, 2005, vol. 62, no. 62, pp. 2–7.
30. Kolbel, H. and Ackermann, P., German Patents DBP 973384, 1960; DRP 755822, 1953, Rheinpreussen.
31. Kolbel, H. and Ackermann, P., German Patent DRP 914374, 1954, Rheinpreussen.
32. Kolbel, H. and Ruschenburg, R., *Brenston-Chem*., 1954, vol. 35, p. 161.
33. Kolbel, H. and Ackermann, P., *Chem.-Ing.-Tech*., 1956, vol. 28, p. 381.
34. Kolbel, H., Ackermann, P., and Engelhardt, F., *Erdol und Kohle*, 1956, pp. 9, 153, 225, 303.
35. Henrizi-Olive, G. and Olive, S., *Khimiya kataliticheskogo gidrirovaniya CO* (Chemistry of Catalytic Hydrogenation of CO), Moscow: Khimiya, 1987, p. 248.
36. Kolbel, H. and Ackermann, P., German Patents DRP 763307, 1952; 764705, 1953; 766025, 1953; DBP 907648, 1954, Rheinpreussen.