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Ecologically benign motor fuels and petrochemicals from alternative raw materials*

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Abstract: Physicochemical foundations of various processes which comprise the single stages of natural gas processing into motor fuels are considered. Among them are: novel process of syngas production by methane reforming using rocket technology, direct dimethyl ether synthesis from syngas and its conversion into the ecologically benign gasoline, an advanced technology of methanol synthesis, as well as methanol transformation into pure hydrogen, Fischer–Tropsch synthesis with increased selectivity. New developments made by the Topchiev Institute of Petrochemical Synthesis Russian Academy of Sciences (TIPS RAS) in this field are discussed. In this light, the achievement of a global goal, to make synthetic motor fuels cheaper than their oil counterparts, appears to be a solvable task for the nearest future.

INTRODUCTION

Natural gas is used mostly as a fuel nowadays. Still, its potential value as chemical raw material for production of fuels and petrochemicals is significantly higher than that of energy carrier. It may serve as a base for production of most of the organic compounds obtained by oil processing. But today's technologies are insufficient for the full use of natural gas potential, because they result in products more costly than their analogs originated from oil. This paper summarizes some of the developments in the research of natural gas processing into motor fuels made in our Institute.

The main routes of natural gas processing into motor fuels are shown in Fig. 1. There are traditional ways (methane reforming, Fischer–Tropsch, FT, synthesis, gasoline synthesis through methanol), as well as new ones (novel method of syngas production, synthesis of dimethyl ether and its transformation into gasoline).

The first stage of the natural gas processing is its reforming into syngas, a mixture of carbon oxides and hydrogen. The main ways of syngas processing into motor fuels are Fischer–Tropsch synthesis, which gives a mixture of hydrocarbons and methanol synthesis; for the upcoming years, synthesis of dimethyl ether (DME) is forecasted to be another important route. Methanol and DME after further processing give gasoline. All of these reactions are studied in detail in our Institute.

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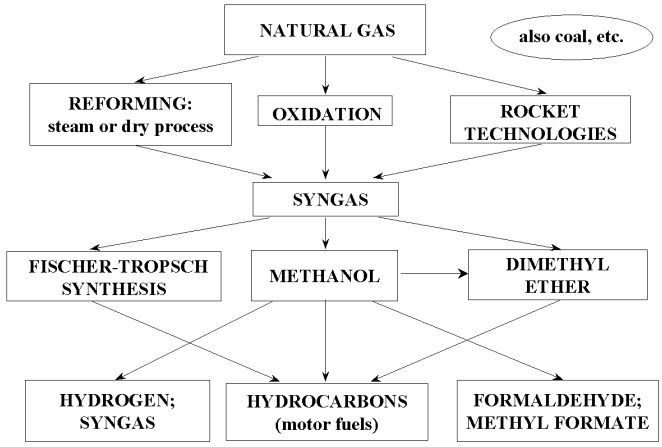

Fig. 1 Main routes of natural gas processing into motor fuels.

NATURAL GAS REFORMING

As seen from Fig. 1, a number of processes exist for the task of methane transformation into syngas. The most important ones are steam (1), dry (2) and combined (by both CO_2 and H_2O) reforming which are both highly endothermic, as well as the partial oxidation of methane (3) which is usually accompanied to some extent by the side process, full oxidation (4).

$$CH_4 + H_2O = CO + 3H_2, \qquad \Delta H^\circ_{298} = +206 \text{ kJ/mol}, \tag{1}$$

$$CH_4 + CO_2 = 2CO + 2H_2, \qquad \Delta H^\circ_{298} = +247 \text{ kJ/mol}, \tag{2}$$

$$CH_4 + {}^1\!/_2O_2 = CO + 2H_2, \qquad \Delta H^\circ_{298} = -36 \text{ kJ/mol}, \tag{3}$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O, \qquad \Delta H^\circ_{298} = -803 \text{ kJ/mol}. \tag{4}$$

Steam reforming is the process used most widely. In modern technologies it is combined with full methane oxidation (4), and this process, autothermal reforming, gives syngas of H_2:CO ratio greater than 2, which is favorable for methanol synthesis; the process is close to thermal neutrality. Nevertheless, reforming stage remains the most demanding, energy- and investment-wise. For example, investments required for this stage in methanol production make about two-thirds of the whole sum. The situation for other gas-to-liquid (GTL) processes is similar. Traditional methods of natural gas reforming are considered in detail in, for example, [1–4].

The goal of our studies was to develop a nontraditional, more efficient scheme of methane reforming into syngas using the reaction of its partial oxidation (reaction 3). Such a process could have more favorable economics than traditional ones, and in particular, could be a power-producing process of syngas production.

In methane combustion, syngas can be produced only at noticeable shortage of oxidant regarding the stoichiometry of reaction. Burning of such mixtures, known as super-rich ones, has been researched only to a small degree. Indeed, the purpose of combustion processes, as a rule, is generation of energy. In this sense, combustion of super-rich mixtures presents no interest.

We have determined the main physicochemical patterns and peculiarities in the combustion of super-rich methane–air and methane–oxygen mixtures.

In this, the side task was also solved: to reach the largest possible degree of oxygen burnout in combustion, because for all known catalysts of various GTL processes, oxygen is a catalytic poison and its content in gas mixture should be less than 0.2 vol %. Otherwise, a unit for oxygen removal from syngas should be provided for the process scheme. Of course, the time of full burnout of oxygen depends

on initial conditions and the parameters of combustion process; according to our data, it is in the range 0.1–1 s.

Flame speed values for super-rich mixtures in their laminar flow through the pipes are small, usually of 8–10 cm/s order. As in common burning, turbulization of combustion zone leads to the growth of this value. But the possibilities of using this technique for super-rich mixtures are limited. It is shown in Fig. 2 that even at a relatively small level of turbulence in methane–air mixtures, flame breakdown takes place. For methane–oxygen mixtures, permissible levels of turbulence are higher, but the level at which the mixture cannot be ignited can be achieved there too easily. Nevertheless, it became possible to avoid this drawback.

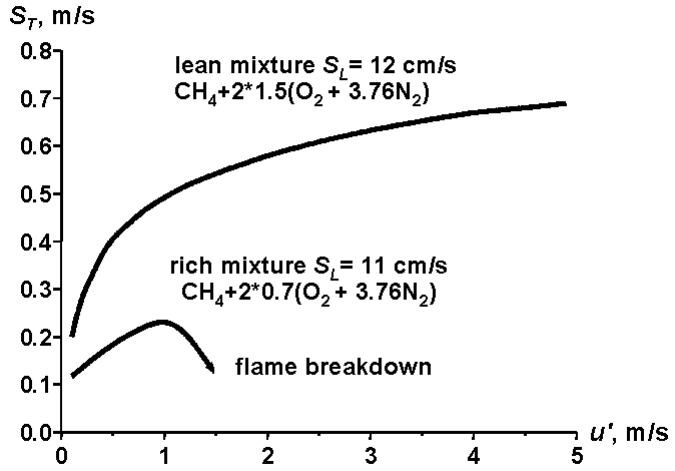

Fig. 2 Dependence of the turbulent flame speed (S_T) for rich and lean methane–air mixtures on the turbulence level (u′) under atmospheric pressure (S_L: laminar flame speed).

The mode of combustion for super-rich mixtures turned out to be highly sensitive to the method of ignition. Figure 3 shows the difference of normal burning rates with ignition by overburning wire and with prechamber ignition; the latter turned out to be efficient also in syngas production with the use of modified high-power gas engine.

As it is known, there may be different requirements to H_2/CO ratio in the produced syngas for different processing technologies. Thus, for example, methanol synthesis requires this value to be more than 2, and one-step DME synthesis requires it to be 1.0. Without special precautions, combustion of super-rich mixtures at the oxidant excess coefficient α = 0.4–0.5 gives syngas of H_2/CO ratio 1.4–1.6. Of course, H_2/CO ratio can be increased by decreasing α, say, to 0.3, but this leads to abundant soot formation, which is not predicted by thermodynamics. In methane–oxygen combustion, this process can be inhibited to a noticeable degree by adding vapor to the mixture. In the case of methane–air mixture, this technique is less efficient.

Engineering solutions in unit design are of great importance for the process of syngas production by combustion of super-rich mixtures. This is dictated by a number of circumstances: for example, one of the most important process parameters is pressure. It does not seem to make sense to reduce the pressure of natural gas which is fed from the pipe into the reformer and then to compress the resulting syngas, the volume of which is much larger than that of initial natural gas, up to the pressure 50–100 atm required for the subsequent synthesis stage. More well-rounded from all viewpoints would be the scheme where the pressure in the reformer is greater or at least equals that for the next stage. In this case, there is no need for compressing the syngas [5]. Moreover, syngas production process can be adjusted to the pressure of natural gas in the pipe. It should be noted that if the increased pressure of re-

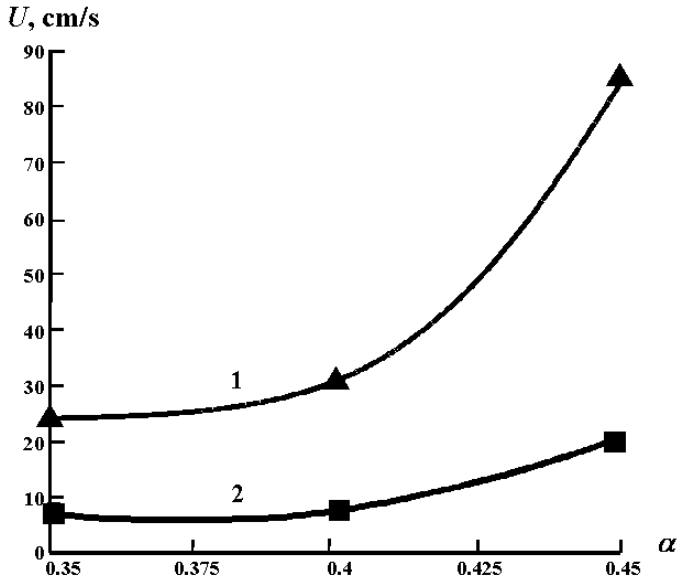

Fig. 3 Normal rates of burning in super-rich methane–air mixtures (P_0 = 70 atm, T_0 = 350 °C). 1: prechamber ignition (turbulent burning); 2: ignition by overburning wire (laminar burning).

forming is chosen, the conditions for vapor condensation and water removal from syngas are more favorable.

Engineering difficulties which arise from the need to conduct the process at high temperatures were overcome by cooperation of chemists with specialists experienced in rocket technologies. The reactor for syngas production under high pressure was designed, for which purpose the modified liquid propellant rocket engine was employed (its combustion chamber is designed to work under the pressure 100 atm [6]). Its schematics are shown in Fig. 4.

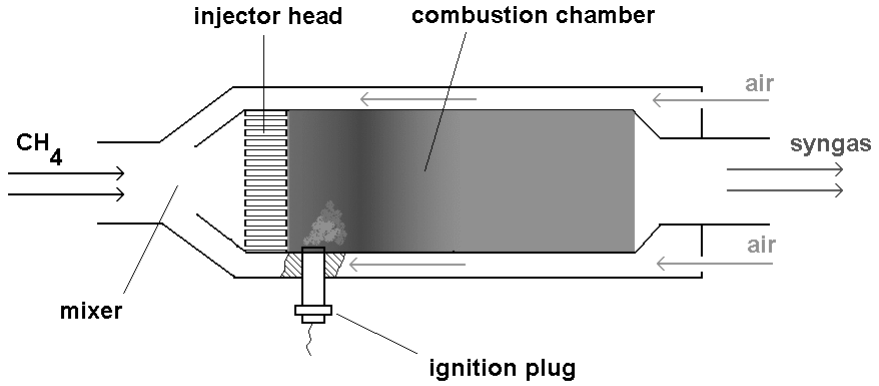

Fig. 4 Basic scheme of the chemical reactor for syngas production by methane–air mixtures combustion based on rocket technologies.

As to feeding air or oxygen into the unit, this does not represent much difficulties: either a common air compressor is used, or oxygen (preliminarily separated from air) is evaporated. It was noted above that oxygen content in syngas should be no higher than 0.15–0.2 vol %. Accordingly, to prevent catalyst poisoning or even inflammation, an on-line analyzer of oxygen content is required before the catalysis section, triggering the automatic shutdown if the emergency level is achieved.

On the basis of this research, a unit for natural gas processing was created (jointly with S. P. Korolyov's PNTTs RKK "Energiya" and "Departament NPiKO" company) of 432 kg/h capacity on methane. This unit was successfully tested in the set-up for sequential processing of methane into syngas, DME, gasoline without separation of products after intermediate stages [5].

FISHER–TROPSCH SYNTHESIS

FT synthesis is one of the most prominent pathways for syngas processing into hydrocarbons, which seems to be the most cost-efficient one, too. Still, it has a number of drawbacks, the most important being low productivity and selectivity which can be hardly controlled. The resulting mixture of hydrocarbons is characterized by a wide molecular mass distribution and requires further processing. As to productivity on liquid hydrocarbons, it is usually less than 0.1 kg/l.cat. per hour. The most widely used catalysts are Fe- or Co-based; their numerous modifications have various promoting additives to make the process parameters better.

We have set ourselves a task to design the catalysts that would have higher productivity in FT synthesis at high selectivity on target products. At that, the productivity level would have to accommodate the processing of lean syngas, obtained by air oxidation of methane, which leaves 50–60 % (or even more) of nitrogen in syngas.

The catalysts that satisfy the demands above were designed in our Institute. They consist of binary polyfunctional systems, which include a metal component (Fe- or Co-based catalyst for syngas transformation into hydrocarbons) and a zeolite-based component, which is responsible for secondary transformations of produced hydrocarbons: isomerization, cracking (the possibility of efficient cracking over zeolites under FT conditions is shown in [7]), partial aromatization and oligomerization of olefins. The use of zeolite-based component allows modification of molecular mass distribution in the direction of selective production of diesel and gasoline fuels (Fig. 5).

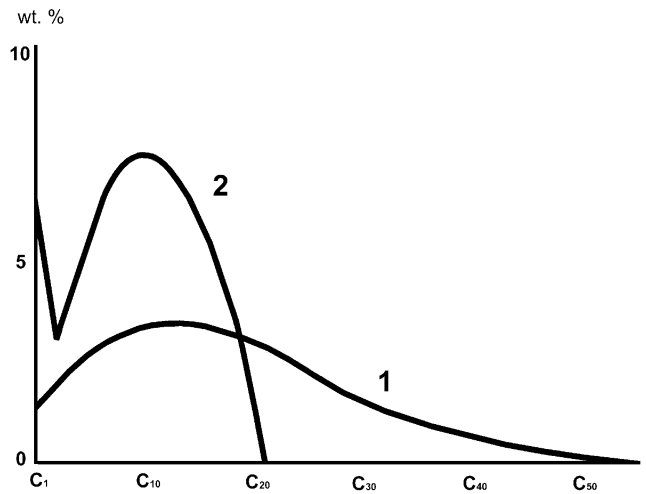

Fig. 5 Mass-molecular distributions of the products of FT synthesis over a conventional catalyst diesel type (1) and multifunctional catalyst by TIPS RAS with advanced cracking ability (2).

Obtained fuels have relatively high characteristics: the octane number of gasoline is up to 80–82 (by engine method), the cetane number of diesel fuel exceeds 50. At this, the content of aromatic compounds in fuels does not exceed, as a rule, 5 %, which allows additional possibilities for increasing the octane number of gasoline by adding aromatics. Developed catalysts are highly stable; for example,

after 1500 h on-stream, a Fe-zeolite catalyst has not shown noticeable changes in productivity and selectivity.

Table 1 shows data that characterize FT selectivity for various catalysts designed by A. V. Topchiev Institute of Petrochemical Synthesis (TIPS), aimed at the prevailing production of gasoline or gasoline-diesel fractions. As seen, despite the low content of "useful" components in lean syngas, productivities of catalysts per volume unit are sufficiently high at almost full CO conversion. Catalysts based on Fe possess smaller productivity on target products and work at somewhat higher temperatures, the main side product in this case is CO_2. Co-based catalysts function at lower temperatures, their main side product is methane.

Table 1 Space/time yield and selectivity of metal-zeolite catalysts (TIPS RAS) in FT synthesis from lean syngas (50 % N_2). CO conversion was 90–95 %.

Catalyst	Synthesis conditions	Total HC space/time yield, g/l*h	Selectivity on fractions, %					
			C_1	C_2	C_3-C_4	C_5-C_{10}	C_{11}-C_{20}	C_{21}^+
Fe/zeolite, sample 1	250–270 °C, 3 MPa, H_2/CO = 1.5/1, ~3 000 h^{-1}	180–200	20–24	10–12	22–28	30–36	6–10	1–2
Fe/zeolite, sample 2	250–260 °C, 3 MPa, H_2/CO = 1.5/1, ~2 500 h^{-1}	140–150	18–20	8–9	18–20	30–34	12–15	3–4
Co/zeolite	220–240 °C, 3 MPa, H_2/CO = 2/1, ~4 000 h^{-1}	300–350	35–40	4–6	10–12	30–35	10–14	2–3

Aside from the production of fuels, FT synthesis can be also used for production of olefins, the most important petrochemical raw materials. They preferably form, as a rule, over Fe-containing catalysts; Co-based ones are not good for this purpose (Fig. 6). Fe-zeolite catalysts developed by TIPS allow us to obtain olefins in substantial amounts (50–60 % and more). Also notable is the fact that olefins are present to a larger degree in neighboring fractions of gaseous hydrocarbons and diesel fuel than in gasoline fraction (see Fig. 6). The content of C_3-C_4-olefins in gaseous products forming over the TIPS-designed Fe-zeolite catalysts is high enough to consider them an independent and valuable product.

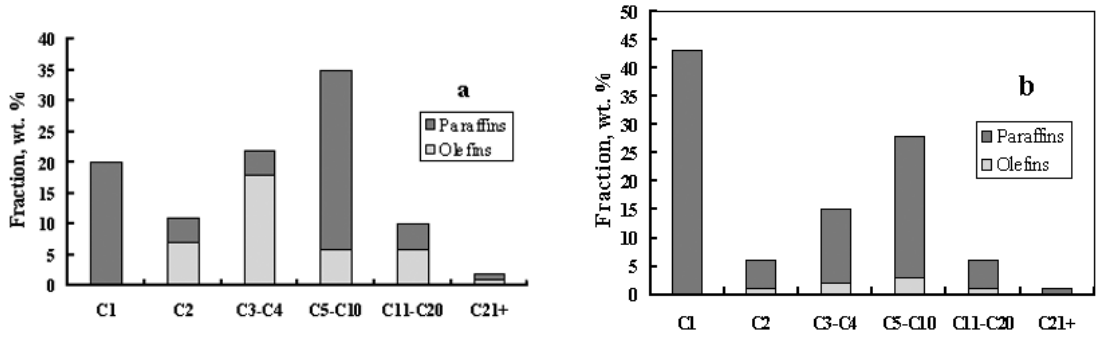

Fig. 6 Selectivity on hydrocarbon fractions and olefin content in FT synthesis over TIPS catalysts: (a) Fe-zeolite, (b) Co-zeolite.

METHANOL SYNTHESIS

Synthesis of methanol, one of the technologies of syngas processing with the largest capacities, was realized first on an industrial scale by BASF 80 years ago; since the 1960s, it is performed according to

the innovations made by ICI. Currently, the total capacity of methanol plants is more than 30 million t annually worldwide.

This reaction proceeds over Cu-based catalysts with high selectivity, so the content of impurities does not exceed hundredths of 1 %. Fundamentals of methanol synthesis were recently discussed elsewhere ([8], see also [9,10]), so we will only summarize the main points here.

Two reactions take place in the course of methanol synthesis from carbon oxides and hydrogen over Cu-based catalysts: methanol synthesis itself, which proceeds from CO_2 and H_2 (5):

$$CO_2 + 3H_2 = CH_3OH + H_2O, \qquad \Delta H^\circ_{298} = -49.4 \text{ kJ/mol} \tag{5}$$

and water gas shift reaction (WGSR)–CO conversion by water (6):

$$CO + H_2O = CO_2 + H_2, \qquad \Delta H^\circ_{298} = -41.2 \text{ kJ/mol}. \tag{6}$$

This macroscopic mechanism was proven first in our Institute in 1975 [11]. Because it was in contradiction with the common viewpoint then, the proofs were obtained by different independent experiments. Two most vivid results of these studies will be touched upon here. The first conclusion was made using the radioactive label ^{14}C. Methanol synthesis was conducted over a commercial Cu-based catalyst at 250 °C under ~5 MPa in a set-up with stream circulation, with constant freezing-out of methanol and simultaneous uninterrupted sampling of the integral sample of the gas phase. Syngas had 30 vol % of CO and 4 vol % of $^{14}CO_2$, so that CO was present in excess. The results of this experiment were as follows: carbon monoxide gained the label 430 au in the result of molecular exchange; carbon dioxide lost most of its radioactivity, so its average integral specific label became 1480 au as opposed to the initial value 5900 au; the radioactivity value for formed methanol was 1500 au. From these results, it is completely clear that the only possible source of carbon for methanol is CO_2.

For the ultimate check of this result, the experiment was set on methanol synthesis in flow reactor where the initial syngas could be thoroughly cleaned of CO_2 and H_2O, which produces CO_2 by WGSR. When the removal system was on, methanol synthesis stopped, resuming on turning the system off.

Further studies [10] showed that methanol synthesis and WGSR proceed as conjugated reactions. A kinetic scheme of the process mechanism was built; on this basis, it became possible to develop the theoretical kinetic model.

In turn, this allowed us to propose more efficient two-stage technology of methanol synthesis, which makes it possible to increase the productivity per unit of catalyst volume twice while cutting energy consumption [9]. It was found that methanol synthesis is severely retarded by water forming: its concentration in reaction zone, resulting from the balance of reactions 5 and 6, defines the productivity per unit of catalyst volume. This is a good example of how the technology can be advanced by fundamental research.

Thus, kinetic limitations of methanol synthesis can be overcome. Still, limitations imposed by thermodynamics remain in force—as methanol synthesis is not favored by thermodynamics, all technological schemes require multiple circulation of gas mixture through the reactor. The value of conversion per pass in common technologies is not higher than 16 %; in a newly developed two-stage scheme the situation is better, but not by much. The most promising way to overcome thermodynamic limitations lies in direct synthesis of DME from syngas, which is discussed below.

DIRECT SYNTHESIS OF DIMETHYL ETHER AND GASOLINE FROM SYNGAS

At the 1995 SAE Congress in Detroit, DME was promoted by a number of reknown companies as a prospective replacement for diesel fuel, remarkable for its clean exhaust which easily abides current and forthcoming standards. Its potential as the raw material for chemical syntheses is not yet understood fully due to little knowledge of DME chemistry. As for today, it is expected that DME can be a feasible raw material for ethylene (and other olefins) synthesis [12], for syntheses of gasoline, acetic acid

[13], pure hydrogen, etc. Of course, its use in the fuel industry would be in itself a good guarantee of large demand for DME.

The main method of DME industrial production today is methanol dehydration (~150 000 t annually); as methanol synthesis is far from ideal (see previous section), it does not seem to be an expedient way. Direct synthesis of DME from syngas is much more efficient. This route is chosen by almost all contemporary developers (e.g., [14–17]). In our Institute, the physicochemical foundations of direct DME synthesis from syngas were studied in detail, resulting in the development of the appropriate catalyst and process technology [18].

Catalytic system for direct DME synthesis should be active as in methanol synthesis, so in its dehydration. Cu-based catalyst was used as the component accelerating methanol synthesis, and γ-Al_2O_3 was used for dehydration. Because temperatures of two processes are close, they can be united in one reactor. The system of reactions is as follows: first is methanol synthesis (5), then its dehydration (7), and finally WGSR (6).

$$2CH_3OH = CH_3OCH_3 + H_2O \quad (7)$$

Reactions 6 and 7 remove correspondingly water and methanol from the reaction zone, which allows us to surpass the thermodynamic limitations of methanol synthesis (5). Reaction 6 exerts a favorable effect on the process rate, too, because water is its main inhibitor. To illustrate this, the comparison is given in Table 2 between methanol and direct DME syntheses over a well-worked Cu-based catalyst (51-2 by ICI). As seen, both productivity and conversion per pass are higher in the latter case. In fact, as the productivity value is given per total catalytic system, of which the catalyst of methanol synthesis is just a part, the observed difference in activity is even more drastic.

Table 2 Direct DME synthesis from syngas in comparison with methanol synthesis.

Reaction	Space/time yield, t/t/h	Single-pass conversion, %
Methanol synthesis over catalyst 51-2 (ICI)	0.4 (under 8 MPa)	5–16
DME synthesis over TIPS RAS catalyst	0.6–1.6 (per sum of catalysts, under 10 MPa)	60–90

By choosing the components of the catalytic system, their ratio, and spatial arrangement, it is possible to change the composition of the end-product, from almost pure DME with a small admixture of methanol (1–2 %) to a DME-methanol mixture with regulated ratio. There is a side-product in this process, in which an excess oxygen is bound—CO_2 and/or water. Their amount depends on the composition of initial mixture and the activity of catalytic system in reaction 6. The more the hydrogen in syngas, the more the water in products, and the opposite is true for CO_2. In this, the coefficient of carbon binding in useful products grows, but at the same time, rectification costs more. The process can be summarized by the equation lying somewhere between two extreme cases—eq. 8a at hydrogen deficiency and eq. 8b at hydrogen excess:

$$3CO + 3H_2 = CH_3OCH_3 + CO_2 \quad (8a)$$

$$2CO + 4H_2 = CH_3OCH_3 + H_2O \quad (8b)$$

In order to obtain a justified kinetic model of direct DME synthesis from syngas, the mechanism and kinetics of methanol dehydration over γ-Al_2O_3 were studied. It was shown that the reaction product, water, strongly binds to the active centers, but can be easily removed by interacting with methanol from the gas phase in the adsorption substitution reaction. DME is formed over an active center by the

interaction of the methoxy group with methanol molecule from the gas phase. The research of reaction mechanism has allowed the building of the kinetic scheme of reaction mechanism and, on this basis, the development of a theoretical kinetic model. By combining this model with the ones for methanol synthesis reaction and WGSR, we obtained the theoretical kinetic model for direct DME synthesis from syngas. Figure 7 shows the comparison of experimental data with the ones calculated by the model to a good agreement.

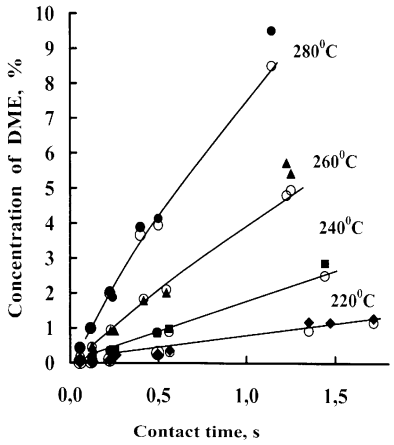

Fig. 7 Direct DME synthesis from syngas in flow reactor under 5 MPa. Comparison of calculated (hollow points) and experimental (blackened points) DME concentrations.

In conclusion of this section, let us note that direct DME synthesis from syngas can be used to process the various types of carbon-containing raw material. In this scheme, DME is the intermediate nonseparated product in the production of liquid synthetic fuels.

natural gas
coal → **syngas** → **methanol** → **DME** → **hydrocarbons**
renewable raws

Together with an overall improvement of the process characteristics, direct DME synthesis has an important advantage in allowing the use of syngas of arbitrary composition ($H_2/CO \geq 1$), while, say, methanol synthesis requires this ratio to exceed 2. This fact lays down the foundations for successful employment of direct DME synthesis in the processing of coal, lumbering rejects, and theoretically, of any carbon-containing resource to be transformed into syngas.

In DME transformation into olefins and/or gasoline, zeolite catalysts of the same type as in the gasoline synthesis from methanol are used. This transformation should proceed more easily than that of methanol. Therefore, in choosing an appropriate catalyst it is important to pay the attention to its selectivity rather than activity, for the former controls the ratio of hydrocarbons in products. Developed catalysts provide almost complete conversion of DME into gasoline of advanced ecological quality. At a sufficiently high octane number (92 by research method) the content of aromatics is 20–30 wt % (for different catalysts), olefins ~ 1 wt %, iso-paraffins – 60 wt %, benzene is in trace amounts, and sulfur compounds are, naturally, absent. The content of lighter hydrocarbons in the mixture can be maintained on the level 10–20 wt %.

Two circumstances make the discussed synthesis even more attractive. First, the whole process chain from syngas to gasoline can be conducted in the series of reactors without DME separation at an intermediate stage. Second, gasoline synthesis can be performed using even lean syngas obtained by air oxidation of methane. Such a process was successfully tried in the pilot set-up mentioned in the section on natural gas processing. About one-tenth of syngas obtained from air oxidation of methane in this set-

up was used in the DME/gasoline synthesis unit, and the results were in agreement with calculations by the theoretical kinetic models developed.

METHANOL STEAM REFORMING AND DECOMPOSITION

Hydrogen and syngas are considered to the promising energy carriers from only the fairly recent times. Both can be produced from methanol correspondingly by its steam reforming and decomposition. This makes methanol a convenient medium for their storage and transportation. Most often, Cu-based catalysts are used for these processes, having sufficient activity and high selectivity.

Methanol steam reforming is relatively easy to deal with, as this reaction proceeds as the one reverse to methanol synthesis (5). The difference between its conditions and these of methanol synthesis does not amount to much, with the exception of catalyst stability, because water is already present on the surface as the result of methanol synthesis, and its presence on the catalyst surface is a crucial factor. Therefore, mechanism and kinetics of methanol steam reforming can be determined on the basis of methanol synthesis, which is a well-researched reaction.

The applicability of such approach was illustrated by the example of methanol steam reforming over commercial Cu-Zn-Al-oxide catalyst SNM-1 under atmospheric pressure [8]. Figure 8 depicts the comparison between calculated and experimental data for methanol steam reforming under increased pressure (0.6 and 2.1 MPa) in flow reactor over Cu-based catalyst 51-2 (ICI). As seen, calculated data match experimental ones. It can be expected that the mechanism and, correspondingly, the reaction kinetics stay the same in the wide range of pressure for various Cu-based catalysts.

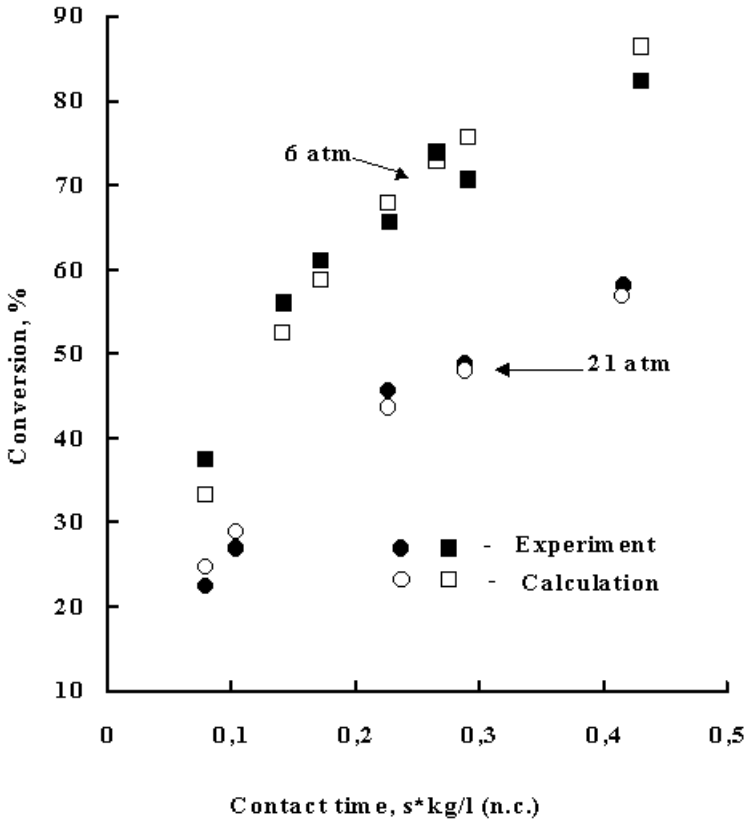

Fig. 8 Methanol conversion in steam reforming over Cu-based catalyst 51-2 (ICI) at 275 °C (comparison of experimental and calculated data).

Hydrogen obtained by methanol reforming has an admixture of CO, the content of which is usually close to the equilibrium value for WGSR (~1 vol %). In order to use such hydrogen for fuel cells, it must undergo an exhaustive CO removal procedure. The studies conducted in our Institute showed that this task can be solved successfully in the mode of catalyst surface ignition [19]; fundamentals of surface ignition have been dealt with in refs. [20,21]. CO oxidation was performed in flow reactors over a Pt-based catalyst using a feed containing CO – 0.85, O_2 – 0.85, H_2 – 33, H_2O – 17, CO_2 – 17 vol % (the rest – N_2). In Fig. 9, the gas temperature dependence of residual CO content is shown for the case of a Pt-based catalyst in an isothermal flow reactor and in a flow reactor where surface ignition mode is realized. In the latter case, the gas temperature directly at the exit from the catalyst bed is given. For both modes, the temperature interval shown in Fig. 9 corresponds to the minimum of residual CO content; it is seen that the latter value is lower in the case of surface ignition mode by a whole order of magnitude. Using this technique, residual CO content in hydrogen can be decreased to as low as 10–20 ppm without any noticeable difficulties.

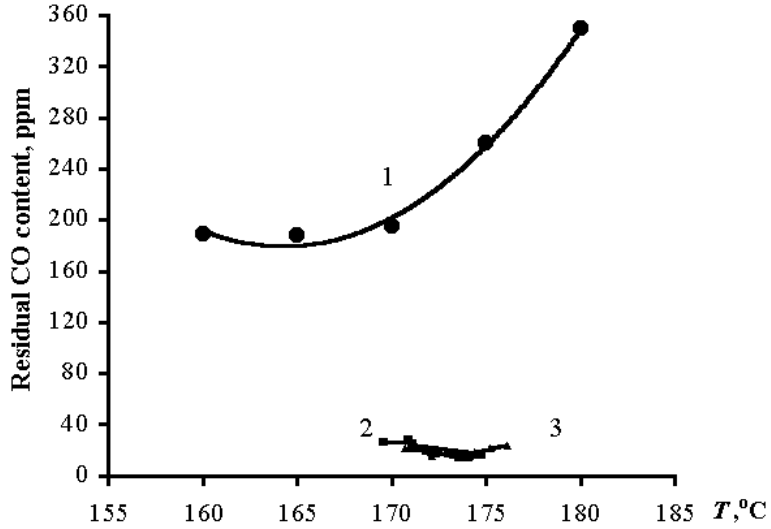

Fig. 9 Dependence of outlet CO content on gas temperature: in isothermal reactor (1) and at the bottom of catalyst bed in surface ignition mode (2,3). Feed composition (vol %): CO – 0.85, O_2 – 0.85, CO_2 – 17, H_2O – 17, rest – N_2. GHSV (h^{-1}): 13 500 (1), 12 800 (2), and 14 200 (3).

Though it may seem strange, methanol decomposition appears to be a more complicated reaction than its steam reforming. As found in [22,23], the reaction of methanol decomposition ($CH_3OH = CO + 2H_2$) does not proceed at all over Cu-based catalysts if the temperature is moderate: methanol has to be dehydrogenated to methyl formate (MF) first (9) and only after this MF gives CO and H_2 (10):

$$2CH_3OH = CH_3OCHO + H_2 \qquad 2CH_3OH = CH_3OCHO + 2H_2 \tag{9}$$

$$CH_3OCHO = 2CO + 2H_2. \tag{10}$$

Detailed study of proceeding individual reactions [23] (see also [24]) showed that almost all carbon-containing components of the reaction mixture form strong bonds with the surface active centers. It was found also that MF decomposition requires a free surface center adjacent to the center of its adsorption. In the absence of such a center MF decomposition is suppressed. Reaction route is shown below (11), where I is hemiacetal, z is an active site (Cu) on the catalyst surface:

$$2CH_3OH + z_2 \xleftarrow{(-H_2)} 2CH_3Oz \longleftrightarrow I$$
$$\xleftarrow{(-H_2)} CH_3OCHO \xrightarrow{(+z)} 2CO + 2H_2 + 3z \quad (11)$$

It should be noted that under the conditions of methanol steam reforming, this reaction is suppressed almost completely at moderate temperatures if water is present in sufficiently high concentration.

Reaction 11 is a consecutive reaction, which can be used both for methanol decomposition into CO and H_2 and for obtaining the intermediate product, MF. Nevertheless, MF production by this method meets the difficulties, because unfavorable thermodynamics of its formation requires the choice of relatively high temperatures (220 °C and higher), while MF decomposition over Cu-based catalysts starts to proceed actively at lower temperature, 170 °C.

These difficulties can be overcome by using the peculiarities of reaction mechanism, namely, the requirement of a free adjacent center. Under conditions of strong adsorption of reacting components on the active centers of the catalyst, the concentration of free centers can be minimized by increasing, say, methanol concentration, as was done in [23]. Indeed, at as high a temperature as 240 °C it became possible to conduct methanol dehydrogenation into MF with high selectivity (Table 3). It is seen from the data presented there that at 240 °C, selectivity on MF reached 95 % at almost equilibrium methanol conversion. Moreover, selectivity on MF did not diminish with the temperature increase from 170 to 240 °C. To our knowledge, these characteristics surpass any known ones.

Table 3 Highly selective MF synthesis by methanol dehydrogenation over a Cu-based catalyst.

T, °C	Feed rate, l/g/h	Pressure *P*, MPa	$P_{methanol}$, MPa	Conversion *x*, %	Conversion into MF, %	x/x_{eq}, %	Selectivity *S*, %
190	21.7	0.85	0.14	21.5	20.7	73	96
240	20.3	0.85	0.13	44.1	42.0	99	95

From the data given, it follows that in syngas production by methanol decomposition it would not be desirable to perform the process under increased pressure, as this will lead to MF appearance in products. MF formation and decomposition can reveal itself also in methanol steam reforming at high temperatures (300 °C and higher), increasing CO concentration in products above the equilibrium level for WGSR.

CONCLUSION

Thus, we have considered briefly the results of studies concerning separate stages of natural gas processing into motor fuels (see the scheme in Fig. 1). By employing new scientific developments, the technology of almost each stage can be bettered, in some cases in a radical way. It can be expected that the use of new developments in the field will allow production of synthetic motor fuels from natural gas in an economically viable way to rival its oil counterparts—in the nearest future, if not today.

It should be noted also that of all stages of natural gas processing, the one most dependent on the type of carbon-containing raw material is syngas production. Thus, syngas produced by processing carbon and lumbering rejects is characterized by decreased H_2:CO ratio, being unacceptable for use in methanol synthesis; nevertheless, it presents a quite feasible raw material for DME synthesis, as thermodynamics gives the optimal value H_2:CO = 1. This increases the stimulus for involving new types of raw materials (including renewables) into the production of motor fuels on a sound basis.

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