Chemistry for Sustainable Development **13** (2005) 701–712

Ecologically Pure Engine Fuels on the Basis of Natural Gas

A. YA. ROZOVSKII

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
Leninskiy Pr. 29, Moscow 119991 (Russia)

E-mail: rozovsk@ips.ac.ru

Abstract

Properties of and methods to obtain dimethyl ether (DME), a new power supply with the enhanced ecological properties, have been considered. With the use of advanced achievements (reforming of natural gas, based on the experience in creation of rocket technologies, direct synthesis of DME from synthesis gas), one might expect that dimethyl ether will appear competitive as compared to traditional combustibles. In the same manner as methanol, DME can be readily processed to high-grade petrol; however, unlike methanol synthesis, synthesis of DME is only slightly sensitive to the composition of synthesis gas (*i.e.* to the nature of raw material), which makes it possible to consider the processing diagram “carbon-containing raw material → synthesis gas → DME → petrol” as a versatile scheme to yield synthetic engine fuels. Possible use of steam reforming of methanol to yield pure hydrogen for fuel cells has been discussed. Modern catalysts and decontamination methods are already capable to provide methanol processing to pure hydrogen with the productivity that is theoretically acceptable to arrange the appropriate devices onboard a vehicle. Macrokinetic regime of the reaction is of significant importance for a complete decontamination from CO during selective oxidation.

INTRODUCTION

Transport and communications rank among the fundamental bases of the civilization. Meanwhile, the today development of transport leads to a progressing growth of the environment pollution, especially in megacities. This problem is put more and more in the forefront in recent years. Ecological properties of engine fuels take on the increasing significance, and the importance to search for new means to abate the noxious emission level is immutably growing. In this aspect, of significant interest are synthetic engine fuels that can be produced from natural gas, specifically, dimethyl ether (DME) and petrol with higher than usual ecological quality that is available on its basis. Both the limitation of the reserves of oil, the basic raw resource to yield engine fuels, and possible use of the technologies in question to process the alternative kinds of carbon-containing raw material, namely, coal, vegetative rests, and the like, to engine fuels also offers its mite to the viability of similar processes.

In a farther prospect, application of hydrogen as an ecologically pure engine fuel is also possible. However, the problems that are related to its storage and transportation arise in this case, too.

This article discusses certain aspects of the above two directions of ecologically purposed expansion of the operational life of engine fuels. This publication, including those of the author (see, for example, [1–4]), is far from being the first one in the given field, and certain materials of the mentioned works will be inevitably duplicated here, although the article to a greater extent reflects the content of the reports that have been made at the 1st All-Russian conference “Chemistry for Highway Transport” [5, 6].

DIMETHYL ETHER IS A NEW POWER SUPPLY

The spring of this year is 10 years from the date of the first public mention about DME as diesel fuel, when a group of leading western corporations appeared at the congress-exhibition in Detroit with the relevant announcement [7–10].

The simplest DME ether (CH_3OCH_3) is known to chemists for long. It attracted rather moderate interest for a long time, which is reflected also in its output rate that is currently of about 150 thousand ton per year (an insignificant number as compared to a scale of petroleum refining and gas processing). The main DME consumer today is the manufacture of aerosols, where its properties such as nontoxicity and the lack of odour have found application, which allows the use of DME as an ideal filler. Interest to DME gained momentum in 1980–1990s, seemingly, due to its capability to be used as a substitute of freons (DME quickly degrades in the atmosphere). A significant number of patents that appeared for DME obtaining and intensive research of leading firms in this direction are dated to this period.

However, whilst the ideas of the DME employment as a power supply have been proposed (see, for example, [11]), they nevertheless have not gained the development. In fact, DME is a gas under normal conditions, and, say, ethanol that is more accessible and that shows the same heat value is much more convenient in handling. Only after the 1995 announcement, works in the fuel field have gained a powerful stimulus and they are being intensively developed both abroad, and in Russia.

An advent of a new field for (a potentially large-scale) industrial use of a known and relatively simple chemical substance happens not so often. It comes natural that the problems appear, the major of which are two of them: the prospects, to be exact, a scale of the possible DME application as a power supply and practical implementation of its large-scale production. The forecast as to the first of them is fairly shaky, since it is related to administrative decisions to be made. Although the use of DME does not require a serious reconstruction of the engine, significant investments will be needed to create an infrastructure (the pumps, filling stations, and the like).

As regards engineering capabilities to organize a large-scale DME production, they are quite favourable. Moreover, the DME obtaining can be combined with the production of methanol and petrol (through DME) in a specified ratio.

DIMETHYL ETHER AS A SUBSTANCE AND POWER SUPPLY

Dimethyl ether represents a colourless gas, and upon the liquefaction, a colourless easily movable liquid. Certain properties of DME are given below [12]:

Molecular mass	46.07
Melting point, °C	−138.5
Boiling point, °C	−24.9
Steam tension (bar) at:	
20 °C	5.1
38 °C	8
Critical temperature, °C	127
Critical pressure, bar	53.7
Vaporization heat (at −20 °C), kJ/kg	410

DME is in liquid state at a pressure $P \geq 8$ atm and at acceptable temperature (≤38 °C). In so doing, the difficulties disappear that are typical for diesel fuel to be employed and that are related to a higher than usual viscosity at low temperatures.

TABLE 1

Certain properties of DME, propane and butane

Properties	DME	Propane	Butane
Boiling point, °C	−24.9	−42.1	−0.5
Vapour pressure (20 °C), bar	5.1	8.4	2.1
Viscosity of the liquid, cP	0.15	0.10	0.18
Liquid density (20 °C), kg/m^3	668	501	610
Relative density (to air)	1.59	1.52	2.01
Water solubility, g/l	70	0.12	0.39
Heat value, MJ/kg	28.43	46.36	45.74
Explosive limits in air, vol. %	3.4−17	2.1−9.4	1.9−8.4
Self-ignition point, °C	235	470	365

TABLE 2

Certain properties of diesel fuel and alternative combustibles

Properties	DME	Diesel fuel	Methanol	Ethanol	Methane
Heat value, MJ/kg	28.8	42.5	19.5	25.0	50.0
Density, g/cm^3	0.66	0.84	0.79	0.81	–
Cetane number	55–60	40–55	5	8	–
Self-ignition point, °C	235	250	450	420	650
Ratio air/fuel	9.0	14.6	6.5	9.0	17.2
Boiling point, °C	−25	180–370	65	78	−162
Evaporation heat (20 °C), kJ/kg	410	250	1110	904	–
Limits of explosivity (%) in air	3.4–18	0.6–6.5	5.5–26	3.5–15	5–15

Propane and butane are most similar to DME in their physical properties among habitual power supplies. The properties of these three materials are compared in Table 1 [12]. It is evident that as compared to propane and butane, DME is characterized by an elevated solubility in water and by one and a half lower heat value. Both of these are caused by the presence of oxygen atom in the DME molecule, this atom comprising about one third of the molecule mass. Other properties are close to the associated indices for the compared gases, except for a wider interval of explosive concentrations for DME, which is close to the appropriate interval for ethanol (3–15 vol. %).

Table 2 compares the properties of DME, of traditional diesel fuel (DF), and of alternative combustibles: methanol, ethanol, methane (CNG), on evidence of [12].

It can be seen that DME as a fuel for a diesel or compression engine is superior over the alternative kinds, including the traditional one. The exception is the heat value that is lower as compared to DF and methane, which is partially compensated for by a greater economy of the engine [8, 12] and the freedom from the expenses (including those of power) to clear the exhaust.

The high cetane number and the low boiling point ensure a good “cold start” of the engine; meanwhile, the main advantage of DME as a motor fuel is, certainly, the cleanliness of the exhaust in a combination with the appreciably decreased noise. According to [7–12], the exhaust is free from carbon black, and the content of CO and NO$_x$ drops drastically as compared to the diesel engine that works on traditional combustible. The exhaust of the engine that works on DME with no decontamination is suited to requirements of the standards.

Along with application as a diesel fuel, the possible use of DME as power supply in gas power stations, as a substitute of household gas, and the like is widely discussed.

SYNTHESIS OF DIMETHYL ETHER

Traditional way of DME synthesis is dehydration of methanol:

$$2CH_3OH = CH_3OCH_3 + H_2O \quad (1)$$

$$\Delta H = 23.4\ \text{kJ/mol}$$

This reaction readily proceeds practically on every dehydration catalyst, for example γ-Al$_2$O$_3$, at relatively low temperatures (250–300 °C). The original methanol is available from synthesis gas (a mixture of carbon oxides and hydrogen) that can be prepared from various raw materials, primarily from natural gas. The whole chain of the processes is as follows: natural gas → synthesis gas → methanol → DME.

The first stage, specifically, conversion, or reforming of natural gas, represents in reality partial oxidation of methane. H$_2$O (steam reforming), CO$_2$ (carbon dioxide reforming), or a combination of oxidizers (steam-oxygen reforming, steam-carbon dioxide reforming) are used as a source of oxygen. This stage in methanol synthesis takes about 2/3 capital investments and more than a half of operating costs. However, the situation may change considerably in the near future owing to the development of domestic projects that put forward new solutions of the instrumentation of the process to obtain synthesis gas from methane. These projects are based on high-temperature selective oxidation of natural gas to synthesis gas.

Among the suggested solutions, the process of interest is the one that makes use of a modified diesel or compression engine (Yu. A. Kolbanovskiy *et al.* [13, 14]) as a chemical reactor, the engine being brought up to the level of a small commercial unit. Obvious advantage of a similar process lies in the fact that it is possible to tap natural gas of low pressure, including that from the wells that are not serviceable under ordinary conditions. The use of air as an oxidizer in the process leads to a "poor" synthesis gas with nitrogen content of 50–60 %, which complicates further processing. The technology makes it possible at the same time to apply the reactor-engine for its primary purpose, to generate electric energy, which may be of interest for the remote regions.

The processes that are based on the experience in the creation of rocket technologies are thought of to be the most attractive. Particularly, V. B. Kubikov *et al.* in "Energomash" have worked out a synthesis gas generator [15], where oxygen is applied for oxidation of natural gas. A pilot setup of a greater scale that performs the oxidation by air oxygen has been created in Primorskiy Scientific and Technological Centre of the RSC "Energiya", with the TIPS, RAS, and NPKO Department involved, also by application of rocket technologies [16]. The oxidation process in the developed apparatuses proceeds at rather high temperatures, which makes it possible to obtain a high conversion level in a combination with good selectivity. The productivity of a unit volume of these devices exceeds the productivity of the known commercial analogues by tens times. Thus, both of the variations, the oxidation by air and by oxygen, are implemented in a radically new reforming of high efficiency. The high efficiency implies cutting-down capital investments, whereas the simplicity of the technology does a decrease of operating costs.

The second stage, namely, methanol synthesis, is well mastered by industry: world productivity comprises ~30 million ton per year. Synthesis of methanol occurs as a result of two reactions passing: the synthesis itself

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (2)$$

$\Delta H = 50.1$ kJ/mol

and CO conversion by water

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

$\Delta H = 40.9$ kJ/mol

Thermodynamics of the reaction (2) is non-favourable; therefore, the process is conducted with the multiple (no less than 6 times) circulation of the reaction gas mixture through a catalyst bed, the formed methanol and water being tapped at the outlet from the reactor. Conversion "per pass" is typically insignificant and it comprises 15–16 % for an example of M-100 setups for methanol production. Meanwhile, carrying out the process under the circulation scheme facilitates heatsink for the strongly heat-intensive process of methanol synthesis.

By virtue of the fact that the temperatures of methanol synthesis and of its dehydration are close, both of the processes can be performed in the same reactor and, moreover, over the same "bifunctional" catalyst. As the latter, even a mechanical mixture of the catalysts of methanol synthesis and its dehydration can be applied. The following exothermal reactions proceed simultaneously in this case:

$$CO_2 + 3H_2 = CH_3OH + H_2O$$
$$2CH_3OH = CH_3OCH_3 + H_2O$$
$$CO + H_2O = CO_2 + H_2$$

This combination of the reactions appears uniquely favourable. Indeed, both of the products of the thermodynamically restricted reaction of methanol synthesis (2) are removed from the reaction zone, as they are converted to water by the reaction (3) and to methanol by the reaction (1). As a consequence of this, the direct synthesis of DME from synthesis gas appears to be significantly more effective than the two-stage synthesis (synthesis of methanol and its subsequent dehydration).

Table 3 lists certain indices of the direct DME synthesis on the developed copper-bearing catalyst [17] in comparison with the synthesis of methanol. It can be seen that the conversion level "per pass" and the productivity of the catalyst is much higher in the direct DME synthesis. Distinctions in technical indices, reasonably, reflect on the economy. According to an estimate of [18], the production cost of DME in the single-stage synthesis from synthesis

TABLE 3

Comparative indices of methanol synthesis and direct synthesis of DME

Reaction	Productivity, t/(t · h)	Conversion degree “per pass”, %
Synthesis of methanol (the catalyst 51-2, ICI)	0.4 at 8 MPa	10–15
Synthesis of DME (Catalyst of TIPS, RAS)	0.6–1.6 at 10 MPa	60–89

gas is 5–10 % below the cost of the equivalent quantity of methanol. Close values of the difference in the production cost (~20 %) are given in [19] calculated per a unit of energy intensity of the product. In other words, DME that has been obtained from synthesis gas in the single-stage synthesis turns out to be lower-priced than the raw material for its production (methanol) in the traditional two-stage synthesis.

The set of the reactions (1)–(3) that proceed in the single-stage synthesis of DME determines one more feature of the process: its “all-raw feature” in relation to the composition of synthesis gas. Accordingly, while synthesis gas with the ratio $H_2 : CO > 2$ is required for methanol synthesis, there are practically no similar restrictions for the single-stage DME synthesis. Moreover, the ratio $H_2 : CO = 1$ in synthesis gas is most favourable in the context of thermodynamics. Similar “all-raw feature” is caused by the reaction of the water gas (3) that exerts an influence upon the system, the reaction controlling the composition of the components of the reaction mixture and finally being crucial for the composition of the reaction products. The stoichiometry of the combined process that stems from the reaction depends on the composition of the initial synthesis gas and on the process conditions. The limiting stoichiometrical equations:

under an excess of hydrogen in synthesis gas

$$2CO + 4H_2 = CH_3OCH_3 + H_2O$$

under its limitation

$$3CO + 3O_2 = CH_3OCH_3 + CO_2$$

With no going into a detailed discussion of this feature, we will note that the list of possible raw sources to yield the initial synthesis gas, including coal, vegetative rests, and the like, is significantly extended owing to this feature.

The kinetic model of the single-stage synthesis of DME from synthesis gas on the original catalyst is designed at our laboratory with the greatest possible reliability. Schematic diagrams for the mechanism of all the proceeding reactions that have been received during independent investigations have been used for this purpose. Based on these independent investigations, theoretical kinetic models of the reactions have been developed. Their combination has led to the creation of a theoretical kinetic model of the combined process of the single-stage synthesis of DME, this model being in good agreement with experiment.

Figure 1 displays kinetic curves for one of catalyst samples at various temperatures. It can be seen that the results of the computations agree satisfactorily with the experiment.

SYNTHESIS OF DIMETHYL ETHER IN A SYSTEM OF PROCESSES TO CONVERT CARBON-CONTAINING RAW MATERIAL TO HYDROCARBON ENGINE FUEL

Currently existing and prospective processes to convert carbon-containing raw material to liquid hydrocarbon engine fuel can be simplistically reduced to a system of stages:

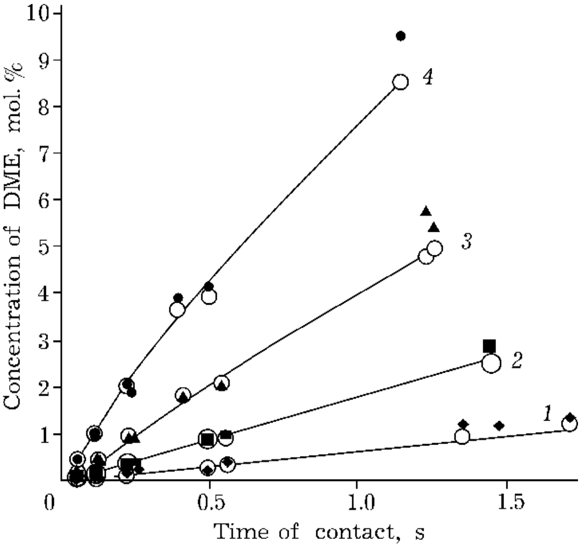

Fig. 1. Kinetics of the single-stage DME synthesis at 5 MPa from synthesis gas of the following composition, mol. %: CO 34.1, CO_2 2.7, H_2 56.3, N_2 2.7. Light points are the computation, those black are the experiment; *T*, °C: 220 (*1*), 240 (*2*), 260 (*3*), 280 (*4*).

$$\left.\begin{array}{l}\text{natural gas,}\\ \text{coal,}\\ \text{biogas } \textit{etc.}\end{array}\right\} \to \text{synthesis gas} \to$$

$$\to \text{methanol} \to \text{hydrocarbons} \qquad \text{(4a)}$$

Their place in the system of main processes to convert natural gas to engine fuels can be seen in the schematic diagram that is presented in Fig. 2. We do not consider here a traditional direction, the Fisher–Tropsch synthesis: it was repeatedly discussed in literature. Note is made of just the two limitations of this process that are difficult to overcome, specifically, low productivity and difficult-to-control selectivity.

Within the limits of the given schematic diagrams, dimethyl ether represents a non-extractable intermediate at the stage of methanol transformation to hydrocarbons. The possibility to produce hydrocarbons immediately from DME and, accordingly, possible "replacement" of the stage of methanol synthesis with the stage of the direct synthesis of DME from synthesis gas was *a priori* beyond question. Then, instead of the system (4a), one may write:

$$\left.\begin{array}{l}\text{natural gas,}\\ \text{coal,}\\ \text{biogas } \textit{etc.}\end{array}\right\} \to \text{synthesis gas} \to$$

$$\to \text{DME} \to \text{hydrocarbons} \qquad \text{(4b)}$$

It follows from the above-considered features of the direct DME synthesis from synthesis gas that the second stage, namely, synthesis of DME, appears to be significantly more efficient relative to methanol synthesis. It is readily apparent, for example, from the data of Table 3. However, it is important how the replacement in point will affect the other stages passing.

Transformation of DME into petrol has been studied at our laboratory (together with the laboratory of catalytic synthesis of the TIPS, RAS) on laboratory pilot plants of high pressure. A modified zeolite catalyst has been used that was prepared in the laboratory of E. S. Mortikov (IOC, RAS), and samples of our preparation. It has been demonstrated that DME is readily converted to hydrocarbons at the temperatures of 300–400 °C. We have also performed a synthesis of petrol directly from the reaction

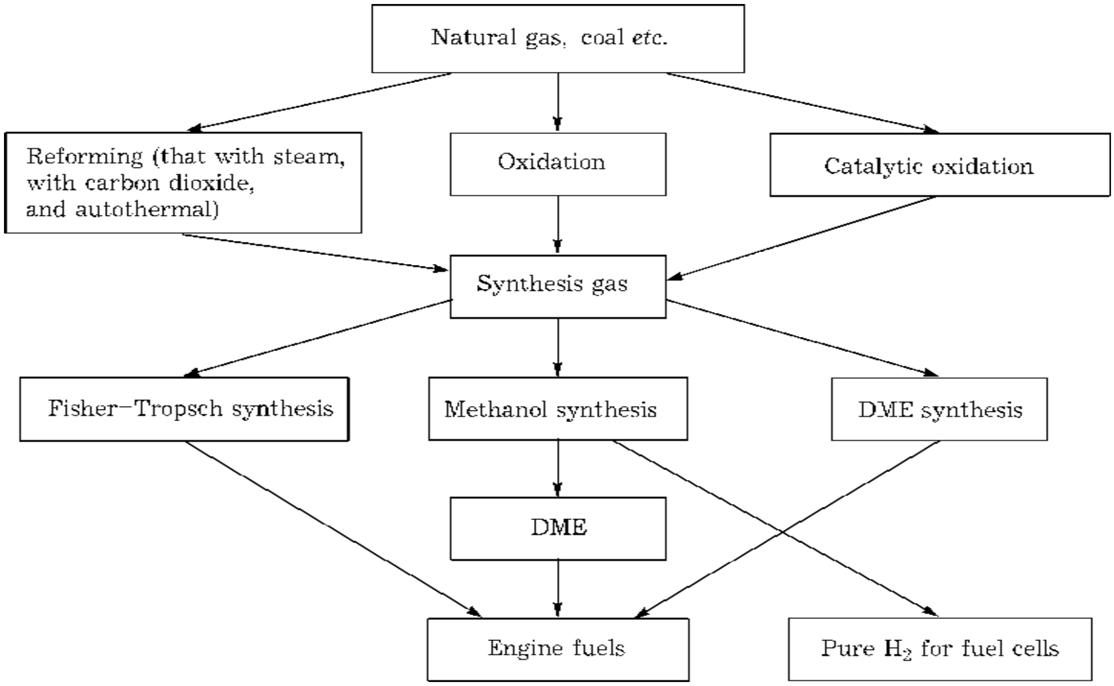

Fig. 2. Basic ways of natural gas processing to yield engine fuels.

mixture that comes out of the reactor for DME synthesis, *i.e.* petrol was produced from synthesis gas in two serial reactors as well as in a single reactor. It has been found that DME that is formed in the first reactor is converted practically quantitatively to hydrocarbons. The obtained petrol is characterized by high quality indices: the freedom from sulphur (based on the initial conditions), a low content of unsaturated hydrocarbons (~1 mass %) and benzole (tenth and hundredth fractions of percent), and by a moderate content of aromatic hydrocarbons (<30 mass %). Octane value of the petrol was at the level of 92 (IM). The synthesis products contained only hydrocarbons lower than C_{12}.

With the use of the above-mentioned "all-raw feature" of the DME synthesis, a potentiality to perform petrol synthesis from synthesis gas of a variable composition has been estimated, including a "poor" synthesis gas with the volume fraction of useful components below 40 % (which corresponds to the composition that is available upon oxidation of methane by air), as well as the gas with the ratio $H_2 : CO = 1 : 1$, which simulates the products of gasification of solid raw material. In all cases, the obtained DME was converted virtually completely to hydrocarbons.

The process of natural gas remaking to yield petrol has been implemented as a whole in a pilot setup in a series of short-term runs in Primorskiy Scientific and Technological Centre of the "Energyia" RSC [16] with the involvement of BSTU, TIPS, and IOC, RAS. The results arrived at were confirmed by evidence of the laboratory pilot units. The uniqueness of the given process stems not only from the application of the new technologies, but also from carrying out all the stages of the natural gas processing at the same pressure (about 5 MPa) without any additional compression.

The modified schematic diagram of the processing (4b) that was partially unified for various kinds of raw material opens up additional opportunities to develop the processes of obtaining synthetic engine fuels of the improved ecological quality.

STORAGE AND TRANSPORTATION OF HYDROGEN AS A MOTOR FUEL

In a farther prospect, one might expect hydrogen to be applied as an ecologically pure engine fuel [20], which involves, however, solving of certain problems. The major of them appears to be the obtaining of hydrogen (including extra pure hydrogen for fuel cells), its storage, and transportation.

Hydrogen obtaining methods are refined in industry. These are, primarily, steam reforming of methane, the molecule "richest" in hydrogen:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad (5)$$

However, even an ideal variant of the complete transformation and of 100 % selectivity produces 44 g of CO_2 per each 8 g of the generated hydrogen. This ratio turns out to be even worse in alternative processes to convert hydrocarbon (or in broader terms, organic) raw material. It appears that electrolysis of water remains the unique ecologically pure way to produce hydrogen:

$$2H_2O = 2H_2 + O_2 \qquad (6)$$

The energy that is consumed in the process is recovered upon hydrogen combustion with an inevitable loss, because the efficiency factor of both processes is other than 100 %. In other words, the application of a hydrogen engine on a vehicle with ecological purposes is one of the ways to salvage electric energy with its transformation into mechanical work. Power engineers can judge what is the efficiency of this. The part of chemists is reduced, in addition to the production, to solving the problems that are related to the storage and transportation of hydrogen.

Instability of hydrides of metals in the course of multiple "absorption−excretion" cycles retards their use in hydrogen generation thus far. However, the use can be made here also of the substances, from which hydrogen can be obtained as a result of simple chemical reactions that are possible to be effected onboard a vehicle. These reactions may be a dehydrogenation of hydrocarbons and steam reforming of hydrogen-containing compounds. Both reactions proceed at acceptable temperatures (300−400 °C) and they are endothermic as well, *i.e.* their carrying out onboard a vehicle makes it possible to reclaim part of the heat of the exhaust. Their difference in hydrogen "capacity" of the raw material is significant.

Cyclohexane, dehydrogenation of which into benzene proceeds rather easily, is "the richest" in the quantity of the released hydrogen:

$C_6H_{12} = C_6H_6 + 3H_2$ (7)

We will compare the "feedback" of hydrogen in this reaction to that in the steam reforming of hydrocarbons and oxygen-containing compounds. The stoichiometrical equations for these reactions are of the following form:

$CH_4 + 2H_2O = CO_2 + 4H_2$ (8)

$C_6H_{14} + 12H_2O = 6CO_2 + 19H_2$ (9)

$CH_3OH + H_2O = CO_2 + 3H_2$ (10)

$CH_3OCH_3 + 3H_2O = 2CO_2 + 6H_2$ (11)

Table 4 gives the calculations results for the amount of raw material that is required to yield 100 l of hydrogen with the complete conversion of the stoichiometrical mixture of the reagent with water and in the absence of losses.

Making comments on the presented data, let us, first, note that from these positions, the reaction of cyclohexane dehydrogenation obviously loses competition. The situation is most favourable with steam reforming of methane; however, the necessity of using rather high temperatures for its reforming also removes it from the competitor set for "onboard" processes. The remaining substances (see Table 4) give approximately equal mass "loading". In reality, it will be unequal, since water must be taken in excess, at least 1.3 : 1, to ensure the complete transformations, so methanol gains an advantage. Furthermore, methanol is the most convenient "carrier" of hydrogen owing to the readiness of its transformation and good selectivity. Although the reforming of all the above substances yields CO_2, this is seemingly not a crucial factor for methanol, because its synthesis can be realized with CO_2 recovery [21].

STEAM REFORMING OF METHANOL

Steam reforming of methanol (reaction (10)) proceeds rather selectively on copper-bearing catalysts. However, ~1 % CO is formed as a by-product, which is poison for some fuel cells. The admissible content of CO for it to be used in many variations of fuel cells lies in an interval of 10–100 ppm. To produce pure hydrogen that is applicable to be used for fuel cells, it is necessary to combine steam reforming of methanol with clearing hydrogen from CO to reach its content specified above. On the successful solution of the given problems, methanol can be employed as a convenient "carrier" for hydrogen storage and transportation.

Accordingly, results of investigations of steam reforming of methanol, including the reaction kinetics, are rather widely presented in the literature of last years. However, even the authors of, presumably, the most detailed work [22] use an empirical, trial and error method to find the kinetic model, which typically makes it possible to describe the experiment only in the narrow studied field of the conditions.

In connection with the above, steam reforming of methanol and clearing of the produced hydrogen from CO traces by means of catalytic oxidation of CO [3, 23–25] has been investigated at our laboratory. By virtue of the fact that the research is not completed yet, some of the given results can be adjusted subsequently.

The purpose of the research was to obtain the theoretical kinetic model of the reaction, the model being based on the reaction

TABLE 4

Minimal consumptions of raw materials to obtain 100 l of hydrogen, g

Raw material	Reaction	Quantity	Water consumption	Total
Cyclohexane	Dehydrogenation (7)	125	–	125
Methane	Steam reforming (8)	18	40	58
Hexane	« « (9)	20	51	71
Methanol	« « (10)	47	27	74
DME	« « (11)	34	40	74

mechanism. Steam reforming of methanol was studied in flow-through setups on copper-bearing catalysts with various water/methanol ratios (the mixture 1.3 : 1 was used as the basic one) in an interval of pressure of 0.1–2.1 MPa. The reforming itself on copper-bearing catalysts can be accompanied by the reverse reaction of water gas (3) and by the formation of methyl formiate and its subsequent decomposition to yield a mixture of $CO + H_2$ [26]:

$$2CH_3OH = CH_3OCHO + 2H_2 \qquad (12)$$
$$\downarrow$$
$$2CO + 2H_2$$

At the temperatures over 200 °C, the last reaction typically proceeds to a complete decomposition of methyl formiate.

Passing of both the reactions, (3) and (12), results in that CO impurity appears in hydrogen; therefore, their role in the combined process has been estimated at the first investigation stage.

It has been demonstrated that the reaction of water gas is close to equilibrium under conditions of steam reforming of methanol at the temperatures of 250–300 °C, and the reaction (12) is suppressed virtually completely when water is present in significant concentrations. Under conditions of steam reforming at high concentrations of water, practically all active sites are filled with adsorbed water or with its transformation products, i.e. the initial state of an active site in reforming corresponds to the final state ZH_2O in the schematic diagrams of the methanol synthesis mechanism (the reaction that is reverse to reforming). Then, according to the principle of microscopic reversibility, when the reverse reaction occurs, all the stages that are included into the mentioned schematic diagrams will be realized, so extensive information on the mechanism of methanol synthesis will be available to construct a schematic diagram of the mechanism for its steam reforming. On this basis, a theoretical kinetic model of the reaction of steam reforming of methanol has been developed.

The works [3, 27] compare experimental data on the kinetics of the reaction of steam reforming of methanol on copper-bearing catalysts with those calculated, received on the basis of the mentioned model. In so doing, quite satisfactory agreement of the computation with the experiment was evidenced. Moreover, it has been possible to describe both methanol synthesis and its steam reforming based on the same equations with the same parameter values. The relevant computations and comparison with the experiment have been performed in the work [27] on the basis of the literary data [28].

As a result of the investigation, particularly in the course of experiments, the productivity of a copper-bearing catalyst during steam reforming of methanol has been received that is more than 10 l/(l of catalyst · h) with a satisfactory selectivity, which makes possible the application of the devices of rather small dimensions for its processing. To take an illustration, ~1–2 l of the catalyst are required to process the methanol equivalent (with respect to the energy content) of petrol consumption at a level, say, 10 l/h.

A question is still urgent as to what will be an energy consumption to conduct steam reforming of methanol. In fact, it is necessary to heat the reaction mixture to reach the reaction temperature (~20 kcal/mol), and to this must be added the heat quantity that is necessary for the heat-absorbing reaction of reforming to be implemented (~10 kcal/mol). On the other hand, more than 170 kcal are generated upon the oxidation of three moles of hydrogen that are formed in reforming. Hence it follows that an energy consumption for reforming is relatively insignificant, all the more so because, at least, part of the consumption can be compensated for due to a heat exchange of the reaction mixture with the exhaust gases.

CO OXIDATION WITH AN EXCESS OF HYDROGEN

Oxidation of CO with an excess of hydrogen (selective oxidation of CO, PROX) is intensively studied in recent years in connection with the necessity to solve the problem of hydrogen decontamination for fuel cells (see, for example, [29, 30]). However, the judgements about the mechanism and kinetics of the reaction are characterized by diversity and they are inconsistent with each other. However, we may assume it to be reliably established that the selectivity of oxygen consumption (the fraction of the reacted oxygen that is consumed for the CO oxidation) declines with the increase in temperature.

Most attention during the investigation of the reaction, reasonably, is being concentrated on the selection of the catalysts. Unexpectedly, it was found that macrokinetics of the process could play a considerable part in selective oxidation of CO [25]. Many researchers observed a fast growth of CO conversion with the rise in temperature. This phenomenon is often referred to with the "ignition" term. It is worth noting that ignition, as a rule, cannot be implemented in heterogeneous catalysis because of the intensive heterogeneous breaking the chains. Spontaneous transition of a reaction in a long-range diffusion field (that D. A. Frank-Kamenetskiy named as "ignition of a catalyst surface") [31], however, can be observed. The transition is observed in the case when a positive heat flow q^+ that is caused by an exothermal reaction becomes equal to a negative heat flow q^- that is related to the heatsink, in a combination with the condition $dq^+/dT > dq^-/dT$. Then, as the temperature rises, the reaction abruptly changes over to a long-range diffusion field, which is followed by a spontaneous jump of temperature in the catalyst bed (and by the associated change of the apparent reaction rate). Theoretically, varying conditions of the heatsink, we can conduct the same reaction either under the surface ignition conditions, or in a usual regime, without ignition.

This feature taken into consideration, A. M. Kipnis *et al.* at our laboratory have studied selective CO oxidation with an excess of hydrogen on the Pt-containing catalyst in flow-through reactors with sharply disparate conditions of the heatsink [25].

Reactor 1 (with a high rate of heat abstraction) was close to isothermal. The reaction was conducted in a metal cylindrical reactor with a coaxially arranged metal tube. A batch of a catalyst was diluted with an inert in the 1 : 10 ratio and loaded into a radial gap between the tube and the walls of the reactor. A quartz cylindrical reactor 2 (with a low rate of heat abstraction) approximated to an adiabatic one, so the temperature of the gas mixture increased, as the mixture was moving along the axis of the reactor. A batch of a catalyst was placed in the reactor without dilution by inert. The temperature of the gas mixture was measured at the inlet and near to the outlet from the catalyst bed with an accuracy of 0.1 °C (the thermocouples in a thin metal cover have been arranged in the catalyst bed). The temperature of the furnace was set by means of a special programmator.

A residual CO content in the dehydrated gas mixture was measured (and recorded) *online* by means of an IR analyzer BINOS 100 (error <1 ppm). To model the mixtures that were obtained in steam reforming of methanol, the reaction was performed in the presence of CO_2 and steam.

In the reactor 1, CO oxidation occurred in a kinetic field; the same was observed in the reactor 2 at a low temperature. Once the temperature in the catalyst bed in the reactor 2 reached the critical temperature of the surface ignition, it spontaneously increased, with the temperature of the furnace being constant and with a simultaneous drop of the residual CO content. The reaction abruptly changed over to a long-range diffusion field. Under surface ignition regime, it is possible to decrease the temperature of the furnace, without leaving the diffusive field, until the critical temperature of the surface quenching is attained. Once the temperature reaches this critical value, the temperature in the catalyst bed intermittently drops and the CO content increases, both of the parameters coming to the level that was before the ignition. As it does so, hysteresis that is typical of the surface ignition phenomena is observed.

To check the reasonableness of the interpretation of the observed effects, two independent methods to determine the activation energy have been used, specifically, from the dependence of the critical temperature of ignition on the rate of volume flow of the gas stream (see [32], p. 123), and by the conventional method, for the data that have been obtained in the isothermal reactor. Both values have been practically coincident (13 and 14 kcal/mol).

The circumstance that the residual content of CO under optimum conditions in the surface ignition mode was essentially less than in the isothermal reactor, where the reaction proceeded in the kinetic field (Fig. 3) [25], is seen to be the most important of the acquired results. With the temperature and the rate of

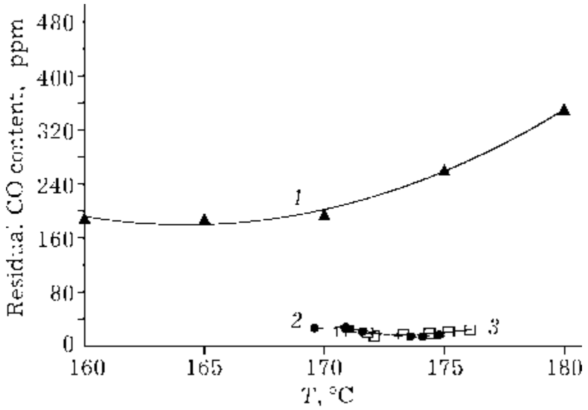

Fig. 3. Dependence of residual CO content on gas temperature in the isothermal reactor 1 (*1*) and in a "hot point" at the outlet from the catalyst bed in the reactor 2 (*2*, *3*). The composition of the initial mixture, vol. %: CO 0.85, O_2 0.85, CO_2 17, H_2 33, H_2O 17, N_2 is the rest; the rate of volume flow, h^{-1}: 13 500 (*1*), 12 800 (*2*), 14 200 (*3*).

volume flow being identical, the residual content of CO is less by an order of magnitude in the regime of the ignition of the catalyst surface.

Thus, the regime of ignition of the catalyst surface appears to be significantly more favourable for selective oxidation of CO with an excess of hydrogen. This stems from a distribution of temperature over the catalyst bed that is more favourable for selective oxidation: in a frontal part of the reactor, the reaction proceeds at lower temperatures, and in addition, at rather high concentrations of oxygen.

The examination of the presented data demonstrates that under conditions of ignition of the catalyst surface, rather low concentrations of residual CO become accessible that are required for hydrogen to be used in fuel cells. As regards the productivity of the appropriate device, it follows from Fig. 3 that the use of 1 l of the catalyst can provide a decontamination of more than 10 000 l H_2/h, including the process in the presence of H_2O and CO_2 for a gas stream after steam reforming of methanol.

CONCLUSIONS

Thus, we have at hand all prerequisites to create the manufacture of ecologically pure diesel fuel, dimethyl ether, from natural gas. With the use of advanced achievements (reforming of natural gas on the basis of the experience in creation of rocket engineering, a single-stage synthesis of DME from synthesis gas), one might expect that the produced dimethyl ether will appear competitive as compared to traditional combustibles as regards the economy too. As we keep in mind the high cost of pipelines, it appears to be reasonable to estimate also the possibilities to process natural gas of the remote deposits *in situ* and to transport it to the consumption areas in the form of DME or petrol that is produced from it.

Mention should be also made that with the single-stage synthesis of DME from synthesis gas, the $H_2:CO$ ratio in synthesis gas is no longer critical. The modified schematic diagram for the processing is characterized not only by appreciably improved technical and economic indices, but also it allows the use of synthesis gas of a variable composition. This significantly expands, in its turn, also the list of potential sources of the raw material, and a set of methods for their processing. The schematic diagram as a whole becomes a versatile way for processing diversified raw material to yield engine fuels.

Meanwhile, a concise discussion of the possible use of steam reforming of methanol to yield hydrogen for fuel cells demonstrates that modern-day catalysts and decontamination methods already can provide processing of methanol into pure hydrogen with the productivity that is theoretically acceptable to arrange the appropriate devices onboard a vehicle.

Acknowledgements

The author considers it a pleasant duty to express his thanks to academician N. A. Platae for his attention and support of the given direction of research, as well as to the Russian Foundation for Basic Research (grants No. 98-03-32186 and 02-03-32202), MKNT (grant No. 1.1.233), NEDO (grant 98EA4) and to Haldor Topsoe A/S for the financial support of particular sections of the research.

REFERENCES

1 A. Ya. Rozovskii, Dimetilovy efir – dizelnoye toplivo XXI veka, Mezhdunar. shk. "Inzhenerno-khimicheskaya nauka dlya peredovykh tekhnologiy" (Treatises), Kazan', 1997, pp. 110–133.

2 A. Ya. Rozovskii, *Ros. Khim. Zh.*, 47, 6 (2003) 53.

3 A. Ya. Rozovskii, G. I. Lin, *Izv. RAN*, 11 (2004) 2352.

4 A. Ya. Rozovskii, E. V. Slivinskii, G. I. Lin *et al.*, *Pure & Appl. Chem.*, 76 (2004) 1735.

5 A. Ya. Rozovskii, E. V. Slivinskiy, G. I. Lin *et al.*, 1 Vseros. konf. "Khimiya dlya avtomobil'nogo transporta" (Thesises), Novosibirsk, 2004, p. 7.

6 M. A. Kipnis, E. A. Volnina, P. V. Samokhin *et al.*, *Ibid.*, pp. 199−202.

7 T. Fleisch, C. McCarthy, A. Basu *et al.*, *SAE Paper,* 950061 (1995).

8 P. Kapus, H. Ofner, *Ibid.*, 950062 (1995).

9 J. B. Hansen, B. Voss, F. Joensen, I. D. Sigurdardottir, *Ibid.*, 950063 (1995).

10 S. C. Sorenson, S.-E. Mikkelsen, *Ibid.*, 950064 (1995).

11 J. Haggin, *Chem. Eng. News*, 69, 29 (1991) 20.

12 T. H. Fleisch, P. C. Meurer, DME. The Diesel Fuel for the 21st Centure*,* Presented at AVL Conf. "Engine and Environment 1995", Graz, 1995.

13 Pat. 2096313 RF, 1997.

14 Pat. 2120913 RF, 1998.

15 V. B. Kubikov, Novye promyshlennye tekhnologii proizvodstva sinteticheskikh toplivnykh productov iz alternativnogo prirodnoy nefti syrya (Doklad na soveshch. po novym toplivno-energeticheskim tekhnologiyam), Moscow, 1997.

16 S. K. Petrov, S. M. Andryushkin, V. P. Khomutnikov *et al.*, XVII Mendeleevskiy s'yezd po obshchey i prikladnoy khimii (Thesises), Kazan', 2003, p. 459.

17 Pat. 2218988 RF, 2003.

18 T. Fleisch, A. Basu, M. J. Gradassi, J. G. Masin, Natural Gas Conversion, IV. Studies in Surface Science and Catalysis, 1997, pp. 107, 117.

19 J. B. Hansen, F. Joensen, Natural Gas Conversion, Proc. of the Natural Gas Conversion Symp., Elsevier, 1991, p. 457.

20 M. Jacoby, *Chem. Eng. News*, 81, 23 (2003) 35.

21 A. Ya. Rozovskii, *Zh. Fiz. Khim.*, 70 (1996) 199.

22 S. P. Asprey, B. W. Wojciechowski, B. A. Peppley, *Appl. Catalysis. A: General*, 179 (1999) 51.

23 G. I. Lin, M. A. Kipnis, I. N. Zavalishin *et al.*, VI Ros. konf. "Mekhanizmy kataliticheskikh reaktsiy", Moscow, 2002, vol. 1, p. 96.

24 P. V. Samokhin, G. I. Lin, E. A. Volnina, A. Ya. Rozovskii, XVII Mendeleevskiy s'yezd po obshchey i prikladnoy khimii (Thesises), Kazan', 2003, p. 462.

25 A. Ya. Rozovskii, M. A. Kipnis, E. A. Volnina *et al., Kinetika i Kataliz*, 44 (2004) 654.

26 S. V. Gorshkov, G. I. Lin, A. Ya. Rozovskii, *Ibid.*, 40 (1999) 372.

27 A. Y. Rozovskii, G. I. Lin, *Topics in Catalysis*, 22, 3−4 (2003) 137.

28 V. D. Kuznetsov, F. S. Shub, M. I. Temkin, *Kinetika i Kataliz*, 25 (1984) 606.

29 M. J. Kahlich, H. A. Gasteiger, R. J. Behm, *J. Catal.*, 171 (1997) 93.

30 P. V. Snytnikov, V. A. Sobyanin, V. D. Belyaev *et al.*, *Appl. Catalysis A: General*, 239 (2003) 149.

31 D. A. Frank-Kamenetskiy, Diffuziya i teploperedacha v khimicheskoy kinetike, Nauka, Moscow, 1980.

32 A. Ya. Rozovskii, Geterogennye khimicheskiye reaktsii. Kinetika i makrokinetika, Nauka, Moscow, 1980, p. 324.