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Direct high-pressure gas-phase oxidation of natural gas to methanol and other oxygenates

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Abstract. The published experimental data on the direct gas-phase oxidation of natural gas (methane) to methanol are surveyed. The results of kinetic modelling of the process, its mechanism, and its most characteristic features are considered. Prospects of the industrial use of the process and the most important directions for further studies are discussed. The bibliography includes 146 references.

I. Introduction

Direct oxidation of natural gas (methane) to methanol (DMTM) is a promising way of solving the problem of conversion of natural gas into more easily transportable fuels and chemicals. This process can be carried out both in the presence of a heterogeneous catalyst and under homogeneous conditions. In the latter case, pressures higher than 50 atm are needed to achieve a sufficiently high yield of the target products. The extensive literature devoted to the high-pressure gas-phase oxidation of methane,[1–65] including numerous papers published in recent years, makes it possible to speak of a branch of science dealing with the study of the chemical fundamentals of this process and having a long-term task of developing a competitive method for the direct processing of natural gas.

Since the possibility, in principle, of obtaining valuable oxygen-containing chemical products (oxygenates) by the direct oxidation of methane had been established,[1–3] it was reported[4–7] that direct gas-phase oxidation of methane at high pressures can yield methanol with a high selectivity. Efforts were made to increase the yields of these products and to develop industrial processes for their production. As early as 1905, one of the first patents[8] dealing with the catalytic oxidation of methane to oxygenates (formaldehyde, methanol, formic acid, etc) was obtained, and in 1929 and 1930 the first catalytic process carried out at high pressures was patented.[9,10] At present, there are no operating industrial units for the direct oxidation of natural gas to methanol; however, during World War II more than one fourth of the annual output of formaldehyde and methanol in the USA was produced in this way.[11,12]

Currently, interest in this process has revived because the role of natural gas in the world energy balance has increased, because of the urgent need for environmentally clean motor fuels in leading industrial countries, and, the publication of experimental data[66] indicating the possibility of achieving a very high selectivity in the formation of methanol.[65]

The problem of partial gas-phase oxidation of methane to methanol at high pressure has been considered in a number of reviews, beginning with a monograph[20] that summarised more than fifty years of research on the mechanism of the oxidation of hydrocarbons and ending with more up-to-date, though not fully comprehensive, reviews.[65–67] A detailed and competent survey of the studies dealing with the DMTM problem and published before 1991 is given in a difficultly accessible publication.[68] However, the time is ripe for the analysis of all the accumulated results in terms of the modern views on the kinetics of this process in order to identify the most significant lines for further research.

We shall not consider here the numerous studies dealing with the oxidation of hydrocarbons at low pressures and with the catalytic oxidation of methane to methanol and other oxygenates, particularly since a number of detailed up-to-date reviews devoted to this problem have been published.[69–75] The conclusions concerning the technological prospects of the direct gas-phase oxidation made in the present review retain their validity for the heterogeneous catalytic oxidation of methane, which does not afford higher yields of valuable oxygen-containing compounds than the gas-phase oxidation.

II. The current state of natural gas processing technology

The high strength of the C–H bonds in a molecule of methane, which is the main component of natural gas, substantially hampers its use in technological processes. As a rule, these processes require rather high pressures and temperatures. Therefore, until recently, only a few processes involved natural gas as a raw material. The proportions of natural gas used as a raw

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material and a motor fuel in Russia are extremely low (2.0% – 2.5% and 0.5%, respectively).[76]

Natural gas is used mainly in the production of synthesis gas or hydrogen. It is the possibility of producing these valuable intermediate materials that makes natural gas a very important source of various organic compounds. Among other processes, the production of chlorinated derivatives of methane, hydrogen cyanide, and ethyne are noteworthy.[77]

Liquefiable components of natural gas find much more extensive applications. At present, approximately 750000 m^3 of liquefied hydrocarbons per day is obtained from natural gas in the world, which constitutes about 7.3% of the overall world production of liquid hydrocarbons. In the USA, the gas condensate and other liquefied components of natural gas account for 18% of the overall production of liquid hydrocarbons and 70% of the raw material for the production of ethene and other basic petro-chemical products. In view of the current trends in the development of oil and natural gas production, liquid components of natural gas will amount to 25% – 30% of the total quantity of liquid hydrocarbons produced in the USA by the late 90s.[78]

Apart from liquefied hydrocarbons, motor fuels, methanol, and other oxygenates including high-octane components of motor fuels, are the target products of gas processing. However, at present there are only a few operating industrial processes in the world for the conversion of natural gas into motor fuels, based on its initial transformation into synthesis gas. It is at present the most advanced technology for producing chemicals from natural gas. However, optimistic views on the conversion of methane into synthesis gas and then into methanol or the products of the Fischer – Tropsch synthesis are difficult to justify, since synthesis gas can also be obtained from cheaper carbon-containing materials. Moreover, the high cost of these processes and a number of technological problems do not promote the maintenance of a wide interest in such conversion.

The uncertainty as regards future sources of petroleum-based raw materials and the introduction of more severe laws concerning environmental protection create a real prospect of using the enormous natural gas resources for producing traditional petrochemical products. It would be desirable to learn how to convert this gas, which is relatively difficult to handle, into a more versatile raw material. Methanol is the most probable candidate for a raw material of this kind. Therefore, the preparation and utilization of methanol is now one of the main aspects of the research in the field of industrial chemical synthesis.[79]

Despite the predicted vigorous increase in the consumption of methanol for the synthesis of *tert*-butyl methyl ether and other ethers, industrial companies still refrain from building new large plants for the production of methanol. This is mostly caused by the fear of creating excess capacities and financial stringency.[80] In our opinion, this restraint of the manufacturers is to a large extent explained by the complexity of the existing technological processes,[81] by their large capital requirements, and by the fact that they are highly power-consuming and have low profitability; this results in the obvious disinclination of the manufacturers to risk large investments, taking into account the possible underemployment of industrial capacities, as was already the case in 1988 – 1990. This actually reflects the already existing and clearly perceptible demand for a change in the basic technological processes.

At present, substantial efforts are concentrated on the perfection of technological processes for the catalytic synthesis of hydrocarbons and alcohols from synthesis gas. However, even a breakthrough in this field can hardly change the situation fundamentally, since the energy-consuming steam reforming of methane to synthesis gas accounts for approximately 75% of the prime cost in the production of methanol.[82] Only an increase in the degree of conversion of synthesis gas into methanol from the present-day ~25% to a level close to 100%, the abandonment of the circulation of synthesis gas, and the use of much cheaper air instead of oxygen, could influence strongly the economic parameters of the process.[83] Therefore, the possibility of achieving large-scale processes based on natural gas and competitive with petroleum processing, apparently depends to a large extent on the success in the development of a technology for the direct conversion of methane without the prior production of synthesis gas.

Three promising methods for the direct conversion of natural gas into chemical products have been outlined:[84]

(1) direct partial oxidation of natural gas into methanol and other oxygenates,

(2) oxidative condensation of natural gas to ethane and ethene,

(3) oxyhydrochlorination of natural gas.

Each of these methods has its own attractive features and their combination allows the production of a broad range of the most important chemical intermediate products. Hence, they supplement one another, rather than compete, though at present, the first route is certainly the most thoroughly developed and is close to practical implementation.

The development of a profitable process for producing methanol from natural gas would permit the solution of three important world-wide problems, namely, the problem of transportation, the problem of providing the chemical industry with a very valuable intermediate compound, and the problem of the mass production of environmentally clean high-octane motor fuels.

III. The main experimental data on the direct high-pressure oxidation of methane

Studies of the high-pressure gas-phase oxidation of methane and other hydrocarbons, carried out in the 1930s in order to elucidate the role of alcohols in the mechanism of the oxidation of hydrocarbons,[4-6] which was of fundamental importance in the scientific views of that time, showed for the first time that alcohols and aldehydes can be obtained in fairly high yields directly from alkanes. It was found that methanol is formed also at atmospheric pressure under conditions including the induction period of the oxidation reaction.[85] Although under these conditions the selectivity of the formation of methanol in individual stages of the oxidation of methane can reach 20%, the overall selectivity apparently does not exceed 5%.[86] Therefore, high pressure is a prerequisite for producing methanol by the direct oxidation of methane.

In fact, the range of conditions necessary for the DMTM to be accomplished had already been roughly outlined in the 1930s. They are: high pressures (100 – 135 atm),[4,5,15] moderate temperatures (400 – 450 °C),[14] and low oxygen concentrations.[13,14] The practically attainable selectivity of the formation of methanol (up to 60%) was determined,[4,5] and the main kinetic features of the process, namely the decrease in the selectivity of the formation of methanol with increase in the oxygen concentration [13,14] and high CO/CO_2 ratios in the products,[3] were identified. Until now, the main aim of the studies has been to find the conditions that would permit stable high-output production of valuable compounds in sufficiently high yields, so that the process under consideration could compete successfully with other technological processes. According to estimates,[87] this requires that the selectivity of the formation of methanol (or the sum of organic products) be higher than 75%. In the majority of studies,[4,5,19,23-26,31,39,40,46,48,60,62] for methane conversions of more than 2%, the selectivity of the formation of methanol (S_{CH_3OH}) did not exceed 50% (Table 1, Fig. 1). Some workers reported higher values up to 60% – 65%[27,45] or even 95%.[28,38,41,43,66] However, an attempt to reproduce the latter results was unsuccessful,[40] and the reasons for so great a difference are still unclear.

We shall not go into the experimental details of the investigations considered. As a rule, the researchers, who carried out this process at very high pressures (thousands of atmospheres),[23-26] used static reactors. Later, flow reactors, which are more suitable

Table 1. The selectivity of the formation of methanol and formaldehyde in the conversion of methane.

P/atm	T/°C	$[O_2]$ (%)	Conversion of CH_4 (%)	S_{CH_3OH} (%)	S_{CH_2O} (%)	Yield of CH_3OH (%)	t_r/s	Ref.
106.4	341	11.0		22.3	0.75		720	4
50	430	3.0		51.0	4.1		5	5
50	410	5.0		29.0	1.4		5	5
141	475	4.5	2.51	45.0	3.66	1.13	48	18
141	475	8.7	5.30	29.6	2.48	1.57	48	18
3500	264	7.9	6.29	40.1	0.64	2.52	600	23
40	455	2.04	2.10	59.6	17.04	1.25	~0.08	27
40	461	3.2	2.90	54.4	17.0	1.58	~0.08	27
40	483	7.2	6.10	34.6	13.83	2.11	~0.08	27
65	310	3.85	7.5	95		6	2–1000	28
65	410	7	21	80		17	2–1000	28
100	410–450	2.8		46.0	9.1	~2.8[a]	~1[a]	31
100	410–450	4.0		37.0	11.1	~3.4[a]	~1[a]	31
65.3	456	5.1	8.0	83.0		6.6	~150[a]	38
65.4	456	7.4	11.0	66.5		7.3	~150[a]	38
40	474–498	2.35–3.14	1.3–2.2	43.6–52.1	6.4–13.8	0.73–1.0[a]	1.2–2.1	39
50	425	4.9		43			100–300	40
70	448	3.3	3.9	67.5	1.8	2.56[a]	~2[a]	45
20	400	5.0	>4.6	~32			10–100	48
20	440	10.0	>6.5	~32			10–100	48
30	401	2.5	3.1	47.0		1.3–1.5		51
30	407	5.0	4.5	37.7		1.5–1.7		51
30	447	9.5	9.0	23.5		1.9–2.1		51
21–41	300–500	1–5		~30		0.5–0.8	3–15	59
50	350–550	1.5		44		1.1	>10	60
50	350–550	3		32		1.26	>10	60
50	350–550	6		22		1.8	>10	60
50	350–550	12		15.5			>10	60
100	400	2.8		38–42	6.3–7.4		~100	62

[a] Estimated by the authors.

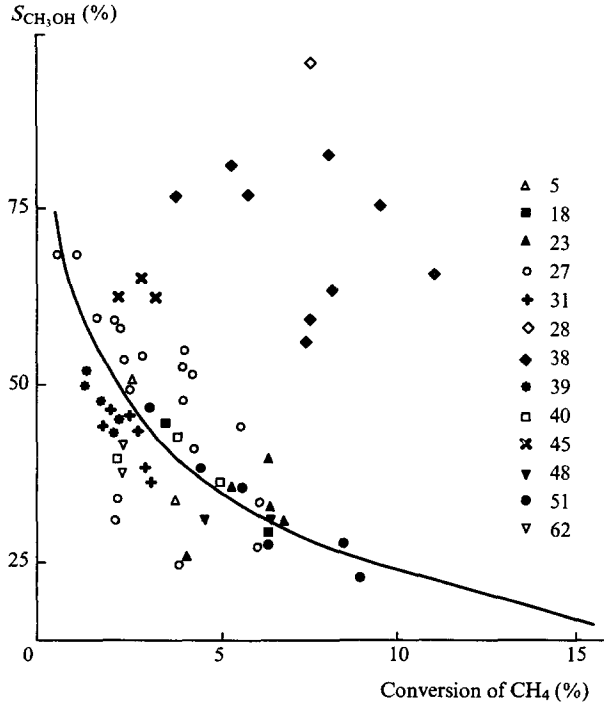


Figure 1. Dependence of the selectivity of the formation of methanol on the degree of conversion of methane. The symbols correspond to experimental data and the curve is the calculated plot (P = 100 atm, T = 420 °C).[64] The numerals denote the corresponding references.

for the practical realisation of the process, were mostly used. The experiments were carried out in broad pressure (1–230 atm) and temperature (300–500 °C and higher) ranges, with the reaction time t_r varying from fractions of a second to tens of minutes. More exotic cases can also be found. For example, the possibility of using the cylinder of an internal-combustion engine with a high compression ratio, operated by an electric motor, as a reactor for the DMTM has been investigated.[21]

1. The influence of pressure on the yields of the products of partial oxidation of methane

The high selectivity of the formation of methanol is the main characteristic feature of the high-pressure oxidation of rich mixtures of methane with oxygen. Water and formaldehyde are the two other main liquid products. The reaction always yields minor quantities of liquids such as ethanol (up to 1.5%–2%), acetone (up to 1%), and formic acid (up to 0.8%) (Table 2).[62] Small amounts of higher alcohols,[29,31,62] aldehydes,[31,68] and organic acids[25,29,31,68] have also been detected. When gases with high concentrations of ethane or other alkanes are oxidised, the yield of C_2–C_3 alcohols, aldehydes, and acids may increase considerably (see Section IV). There is some evidence that the oxidation of methane also gives methyl formate.[23,25] A GC/MS analysis of the liquid products of the partial oxidation of methane in a pilot plant[31] has shown the presence of minor quantities (fractions per cent) of dimethyl formal, dimethyl acetal, and dimethyl ether; however, it was not established whether these compounds were formed directly in the reaction or resulted from the interaction of primary liquid products after cooling. In any case, a special attempt to detect them was unsuccessful.[4] Repeated attempts to find hydrogen peroxide or organic peroxides in the reaction products have also given no positive results.[4,22] Traces of these products have been found only at atmospheric pressure.[88]

Table 2. Side products of the high-pressure gas-phase oxidation of methane.

P/atm	T/°C	$[O_2]$ (%)	H_2	HCOOH	C_2H_5OH	CH_3CHO	C_2H_6 [b]	C_2H_4 [b]	CH_3OCH_3	CH_3COOH	CH_3COCH_3	H_2O_2	Ref.
48–150	335–393	11.0		+					–			–	4
50	400–430	3.0–5.0		–									5
135	300–500	3.0–8.6	+	+									15
141–231	350–500	2.8–8.7	+	+									18
172–200	450	5.5–6.3	+	+			–	–					19
105	350	2–8	+				+	+				–	22
100–750	250–363	10		+			+			+			25
1700–3400	270–480	8.0	–	+	+						+	–	26
100	430	2.8	+		+ [a]				+ [a]	+	+		29
100	410–450	2–4		+	+ [a]	+			+ [a]	+	+ [a]		31
40	474–498	2.35–3.14	+	+			+						39
20–50	425–500	3–10		+			+	+					46
15–50	384–476	2.5–9.5					+	+					51
21–41	300–500	1–5			+	+	+	+					59
30–230	400	2.8	+	+	+ [a]						+		62
25–53	<535	2.0–4.7	+	+	+	+	+	+	+	+			68

[a] Higher homologues of these compounds have also been detected. [b] Relates to those cases where the initial gases contain no ethane or ethene or their concentration in the products is higher than the initial concentration.

The main gaseous products are carbon oxides and hydrogen, the yield of carbon monoxide at high pressures being several times larger than that of the dioxide,[62] although carbon dioxide appears earlier than carbon monoxide.[22] The yield of ethane and ethene increases with increase in temperature.

An increase in pressure intensifies the oxidation of methane by decreasing its duration or the initial temperature. For example, the pressure dependence of the delay of the self-ignition of the 8.8 : 1.2 methane–air mixture in the 60–113 atm range is described by the relation $\tau_1 \sim P^{-1.4}$ (Fig. 2),[22] and the ten-fold increase in pressure from 5 to 50 atm in a flow reactor leads to the decrease in temperature corresponding to the complete conversion of oxygen from 500 to 400 °C[40] (Fig. 3). However, the main consequence of the application of high pressures in the oxidation of rich methane mixtures is high selectivity of the formation of methanol. The increase of pressure from 10 to 106 atm increased S_{CH_3OH} by a factor of 20,[6] and when the pressure increased from 5 to 50 atm, the temperature at which methanol begins to be detected decreased from 450 to 375 °C.[40]

The results obtained by Arutyunov et al.[62] indicate that the overall yield of liquid products of the partial oxidation of methane increases monotonically as the pressure increases up to 200 atm (Fig. 4). However, the concentrations of alcohols and acetone pass through a maximum near 150 atm (Fig. 5). Consequently, the pressure dependence of the yield of methanol has a weakly defined maximum at these pressures (Fig. 6). Other data also indicate that the yield of methanol diminishes at pressures above 180 atm[18] or that the selectivity of its formation decreases at pressures above 100 atm.[65]

Despite the fact that the concentration of formaldehyde in the liquid oxidation products decreases monotonically with increase in pressure (Fig. 5), its yield remains approximately constant, since the overall yield of liquid products increases (Fig. 6). Thus, pressure is the crucial factor influencing the composition of liquid oxidation products, including the ratio of methanol to formaldehyde (Fig. 7).[62] The partial oxidation of methane under very high pressures, up to 3400 atm[26] or higher,[23] provides no real advantages. The pressure range between 75 atm (the standard pressure in gas mains) and 100 atm may apparently be considered optimal. Since the cost of gas compression is one of the major constituents of the prime costs of the products obtained by the DMTM,[87] this conclusion is important practically.

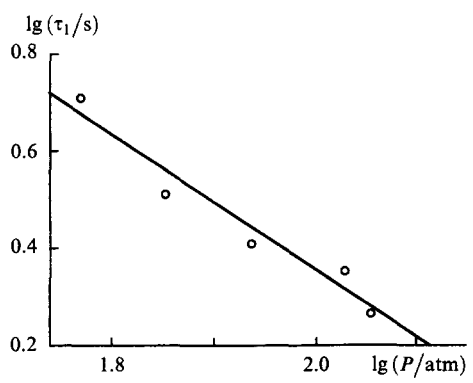


Figure 2. Pressure dependence of the delay of self-ignition of the mixture containing 88% of methane and 12% of air (T = 406 °C).[22]

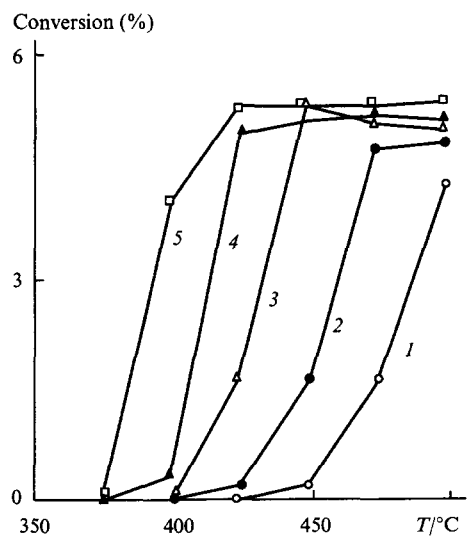


Figure 3. Temperature dependence of the conversion of methane at different pressures (atm): (*1*) 5, (*2*) 10, (*3*) 20, (*4*) 30, (*5*) 50 (reported by Burch et al.[40]).

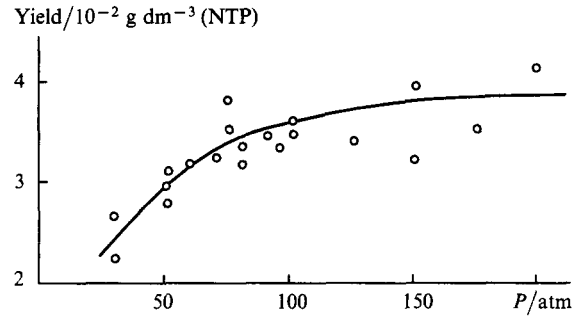


Figure 4. Pressure dependence of the overall specific yield of liquid products of the oxidation of methane (T = 400 °C).[62] Gas volumes are referred to the normal temperature and pressure (NTP).

The concentration of the main gaseous product, carbon monoxide, in the gases leaving the reactor reaches ~1.5% for an initial oxygen concentration of ~3%, and remains approximately constant in the pressure range from 30 to 230 atm (Fig. 8). The concentration of carbon dioxide is several times lower and increases with pressure, which results in the corresponding decrease in the CO/CO_2 ratio.[62] The increase in the CO_2 concentration with pressure may be partially due to the formation and subsequent decomposition of formic acid by the mechanism suggested by Vedeneev et al.[47]

At higher temperatures of 515–630 °C, when the yield of ethane and ethene is fairly high, a pressure increase from 31 to

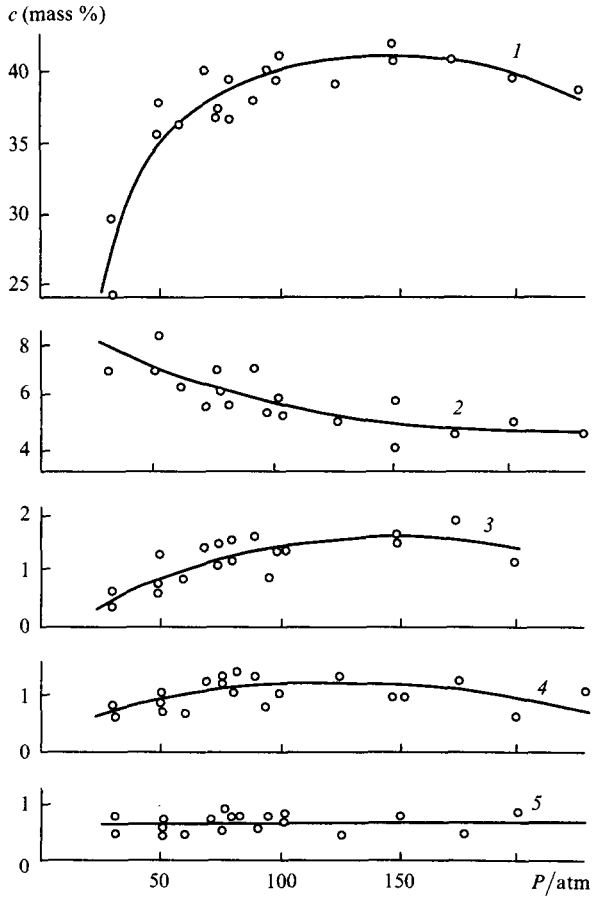


Figure 5. Pressure dependences of current concentrations of the main liquid products of the oxidation of methane (T = 400 °C):[62] (*1*) methanol; (*2*) formaldehyde; (*3*) ethanol; (*4*) acetone; (*5*) organic acids.

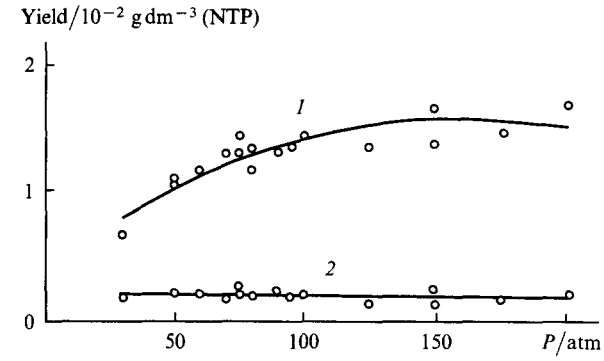


Figure 6. Pressure dependences of the yields of methanol (*1*) and formaldehyde (*2*) (T = 400 °C).[62]

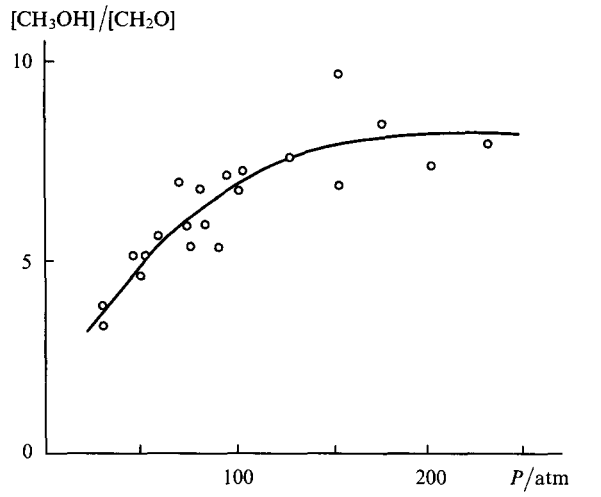


Figure 7. Pressure dependence of the ratio of the methanol and formaldehyde concentrations in the liquid product of oxidation (T = 400 °C).[62]

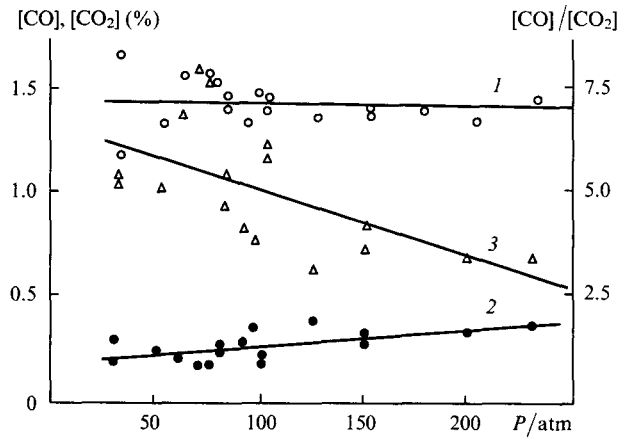


Figure 8. Pressure dependences of the yields of CO (*1*), CO_2 (*2*), and of their ratio (*3*) (T = 400 °C).[62]

102 atm leads to an increase in the yield of C_2 hydrocarbons from 8% to 36%; in addition, the temperature at which complete conversion of oxygen is achieved decreases by 100 °C.[50]

2. The influence of temperature and contact time

An increase in temperature leads to a diminution of the induction period of the reaction. As shown by Melvin,[22] $\lg \tau_I$ (τ_I is the self-ignition delay) depends linearly on $1/T$. The activation energy for

the oxidation of methane with air in mixtures having compositions from 60 : 40 to 90 : 10 at a pressure of 105 atm lies in the range of 163–188 kJ mol^{-1}.[22] However, the temperature dependence of the degree of conversion of methane for a fixed length of the reactor (see Fig. 3) is clearly S-shaped, whereupon the transition from negligibly small to maximum conversion occurs within a range of not more than 20 °C,[40,51] which reflects the critical character of the process.[58] When the temperature of the reactor walls decreases, hystereses are observed in the temperature dependences of the process parameters (heating of the mixture, conversion of methane).[51]

Once oxygen is entirely converted, further increase in the temperature within a certain range has apparently little influence on the yield of methanol.[18] Some workers have observed[40,51] that, at a pressure of 50 atm and above 425 °C (which is the temperature of the complete conversion of oxygen[40]), the value of S_{CH_3OH} already decreases monotonically (from 40% to 32% at 500 °C[40]); however, according to other data,[45] the selectivity remained practically constant between 420 and 460 °C (P = 40 atm) or passed through a maximum at ~450 °C.[18,59] (Fig. 9). Further increase in temperature may lead to a diminution of the yield of methanol due to both a decrease in the selectivity of its formation and the decomposition of a portion of the product already formed on contact with the reactor surface.[40] For the same reason, it is undesirable to increase the residence time of the mixture in the reactor for a longer period than is necessary for the complete conversion of oxygen at the given temperature.[40,59] However, if the surface of the reactor is relatively inert (quartz, Pyrex, stainless steel), the variation of the residence time of the unreacted reaction mixtures within fairly broad limits has little influence on the final yield of methanol and even on the yield of formaldehyde, although the latter is less stable under these conditions.[40,62] Attempts to increase the yield of methanol by rapid cooling of the mixture as it leaves the reactor[39] have given no significant advantage over the results of most other studies (Table 1).

When the temperature is increased to 500 °C or more, the composition of reaction products changes toward ethane, ethene, and small quantities of ethyne, the overall selectivity of their formation being as high as 37% at 515 °C and 100 atm.[49,50]

The combination of high temperatures and relatively low pressures is favourable for an increased yield of formaldehyde. When the reaction was carried out at 625 °C and 5 atm, with a methane : air ratio of 1 : 5 and a contact time of 2.3 s, the yield of formaldehyde in the gas-phase oxidation of methane was raised to 3.5% ($S_{CH_2O} \approx 50\%$ for a degree of conversion of ~7%), which is even greater than in the presence of oxide catalysts.[44]

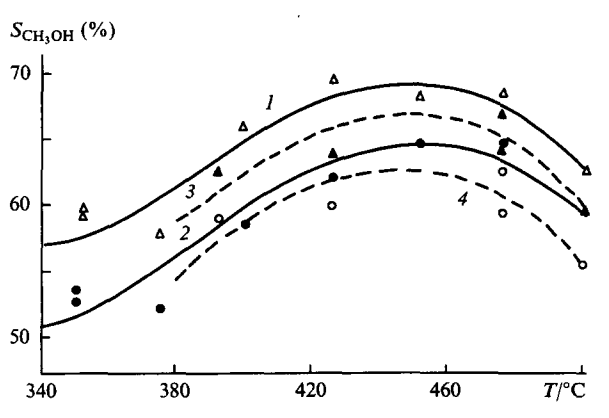


Figure 9. Temperature dependences of the selectivity of the formation of the sum of useful oxygen-containing products (*1*, *3*) and methanol (*2*, *4*) at pressures of 184 (*1*, *2*) and 231 atm (*3*, *4*).[18]

3. The conversion of methane and oxygen in the oxidation of methane to methanol

A low concentration of oxygen in the DMTM predetermines a low degree of conversion of methane after its single passage through the reactor. In virtually all experimental studies (see Table 1, Fig. 1), the degree of conversion of methane was lower than the initial percentage of oxygen. Only Gesser et al.[28] and Yarlagadda et al.,[38] who have achieved very high selectivities in the formation of methanol, reported methane conversions substantially higher than the initial oxygen contents. The reasons for this discrepancy are still unclear.

It has been noted[62] that the gas-phase reaction products always contain a small amount of oxygen {~5% of its initial concentration $[O_2]_0$ on average}. Special studies made it possible to rule out trivial explanations of this fact such as that oxygen entered the system after it had left the reactor or unreliability of the analysis. The fact that the oxidation of methane stops before the oxygen is entirely consumed is difficult to explain from the theoretical viewpoint.

In one of the early studies, Newitt and Huffner[4] stated that oxygen was fully consumed in this reaction. On the other hand, a careful analysis carried out in the study by Boomer and Thomas[17] indicated that the gases leaving the reactor contain oxygen almost in all cases. The authors emphasised that the material balance of this reaction with respect to oxygen is difficult or even impossible to reconcile. A review[65] cites data[89] which state that 95% of the oxygen present in the system enters into the reaction, i.e. 5% of the oxygen remains unchanged. Finally, Bauerle et al.[25] presented reliable data indicating that at 100–750 atm, 250–363 °C, for reaction times of up to 900 min, and $[O_2]_0$ = 10%, the process stops when the residual oxygen content is $(0.3-0.5)[O_2]_0$. Perhaps, the most remarkable relevant data are concerned with the existence of a limiting oxygen concentration in the oxidation of butane.[90] Appreciable amounts of unchanged oxygen have also been observed in experiments on the oxidation of methane at very high pressures of 1700–3400 atm.[26] In other papers, either there is no special mention of the presence of noticeable quantities of oxygen in the gas after the reaction or complete consumption of oxygen has been reported. Nevertheless, the question why the oxidation stops before all the oxygen is consumed requires an additional analysis.

4. The influence of mixture composition on the kinetics of the process and the yield of products

The kinetics and the yield of products of the DMTM are very sensitive to the composition of the mixture, especially, to the methane : oxygen ratio. As the oxygen concentration increases, the degree of methane conversion also increases, but at the same time, the selectivity of the formation of methanol rapidly diminishes[5,13,18,31,38,39,45,60] (Table 1, Fig. 10). Since S_{CH_3OH} is governed by the methane : oxygen ratio,[60] the decrease in $[CH_4]/[O_2]$ at a constant oxygen concentration leads to diminished yields of methanol and other liquid oxidation products (Fig. 11).[63] The optimal proportion of oxygen in methane is about 3%–5%; however, at this concentration, the degree of conversion of methane in a single pass through the reactor is inevitably low.

An increase in the oxygen concentration has an inhibitory effect on the reaction rate. For example, the delay of the self-ignition of mixtures of methane with air at 72 or 83 atm increases with increase in the oxygen concentration[22] (Fig. 12).

Dilution of the reaction mixture with nitrogen,[40,63] helium,[60] or other inert gases does not influence the proportions of the products, if the methane : oxygen ratio remains constant. Therefore, the results are identical no matter whether oxygen or air is used as the oxidant.

Carbon dioxide and water vapour cannot apparently be regarded as being absolutely inert during the DMTM. In all probability, the oxygen incorporated in these compounds can participate in the formation of methanol or other oxygen-

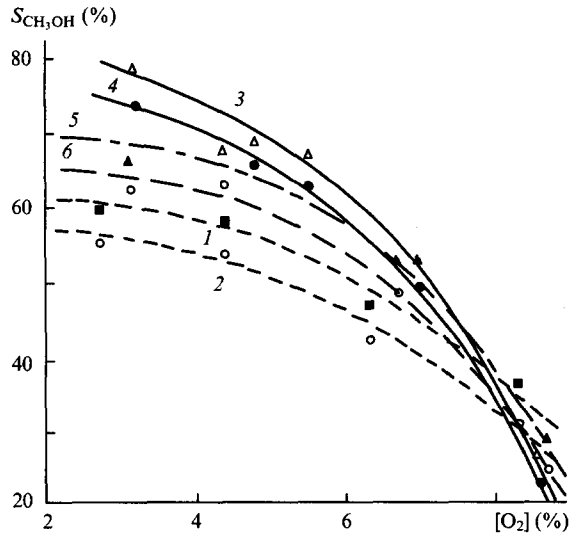


Figure 10. Dependences of the selectivity of the formation of the sum of useful oxygen-containing products (*1*, *3*, *5*) and methanol (*2*, *4*, *6*) on the oxygen concentration at pressures of 141 (*1*, *2*), 184 (*3*, *4*), and 231 atm (*5*, *6*).[18]

containing products, thus increasing their yields.[13] However, no reliable experimental data concerning this problem have been reported. When about 75% of the methane in a $8.5CH_4 + O_2$ mixture was replaced by N_2, CO_2, or H_2O (at 50 atm), apart from the reduction of the reaction rate caused by the decrease in the methane concentration, the yield of methanol also diminished (by approximately 40%).[5] This is most probably due to the decrease in the methane : oxygen ratio. The yield of formaldehyde was almost unchanged on dilution of methane with nitrogen or carbon

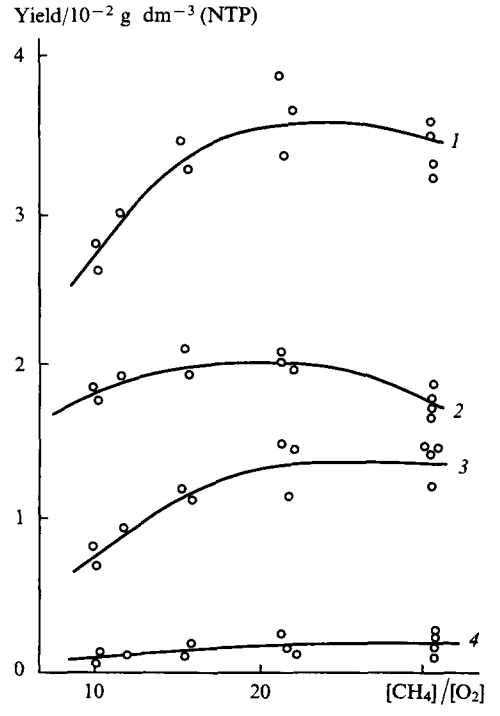


Figure 11. Dependences of the yields of liquid products of the partial oxidation of methane on the $[CH_4]/[O_2]$ ratio (P = 100 atm, T = 400 °C):[63] (*1*) the sum of liquid oxidation products; (*2*) water; (*3*) methanol; (*4*) formaldehyde.

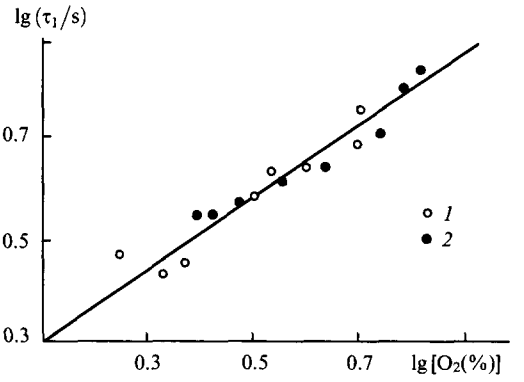


Figure 12. Dependence of the delay of the self-ignition of the mixture of methane with air at 406 °C on the oxygen concentration[22] at different methane pressures (atm): (*1*) 83.3, (*2*) 71.8.

dioxide; on dilution with water vapour, it increased almost two-fold, which confirms the suggestion that water plays an active role in this process.

In a study of the possibility of realising a recirculation scheme for the DMTM process, Arutyunov et al.[63] investigated the influence of the addition of the two main reactive gaseous products, namely, carbon monoxide and hydrogen, to the reaction system on the yield of liquid products. It was found that, if the initial concentration of these compounds does not exceed 5%, they virtually do not influence the methanol yield. However, at higher concentrations, the methanol yield may decrease by more than one half.

The influence of the addition of minor quantities of carbon dioxide (10%) or hydrogen (4%) on the DMTM process in the temperature range 400–500 °C at P = 41 atm, for $CH_4 : O_2 : N_2 = 30 : 1 : 4$, and for a contact time of 1 s has also been investigated.[59] The addition of either of these gases caused a slight (by ~ 10 °C) decrease in the temperature of the onset of the process, but the maximum yield of methanol almost did not change.

5. Homogeneous promotion of the process

Attempts to promote the DMTM process were undertaken as early as 1921, when a number of methods for the preparation of methanol and formaldehyde from natural gas were studied. These methods are: (1) oxidation over various catalysts; (2) oxidation with ozone; (3) iodination followed by hydrolysis; (4) interaction of methane with CO_2; (5) synthesis of C_2H_4 from natural gas and its subsequent oxidation; (6) oxidation of methane in solution and with liquid oxidising agents.[68]

In a study of the oxidation of a mixture of methane with air (3 : 1) at 25 atm and 300–400 °C, it was found that minor quantities of HNO_3 accelerate the reaction significantly, while small amounts of $PbEt_4$ retard it.[7] However, these additives have little influence on the composition of the products.

The possibility of initiating the partial oxidation of methane with ozone under flow conditions at P = 1 atm has been considered.[91] Although ozone appreciably promotes the reaction and increases the yield of methanol, a selectivity > 42% was achieved only when the degree of conversion of methane was no more than 1%. The use of high pressures, more favourable for the formation of methanol, requires the development of effective methods for the production of ozone under these conditions.

The presence of even minor admixtures of heavier hydrocarbons in methane is well known to decrease the reaction temperature with no substantial effect on the yields of the main products. In fact, the replacement of natural gas by methane necessitated that the temperature at the beginning of the process be increased from 350 to 425–475 °C,[18] and the addition of 5% ethane to methane led to a 50 °C decrease in the temperature.[40]

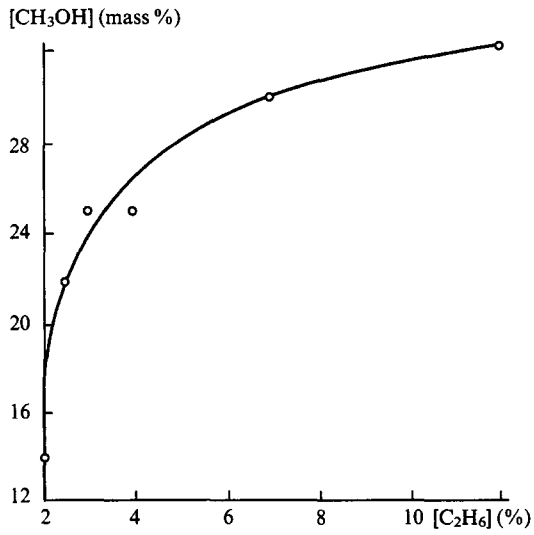


Figure 13. Influence of the addition to natural gas on the concentration of methanol in the liquid oxidation products at $P = 140.6$ atm and $[O_2] = 6\%$.[15]

Some data indicate that the yield of methanol increases substantially in the presence of large quantities of ethane (Fig. 13).[15] Unfortunately, no systematic studies on the influence of other hydrocarbons on the DMTM process have been carried out.

A decrease in the temperature of the process and an increase in the conversion of methane and the yield of methanol following the addition of 3% of ethane, propane, or isobutane have been reported ($P = 41$ atm, $CH_4 : O_2 : N_2 = 30 : 1 : 4$, contact time 1 s).[59] However, in view of the magnitude of this effect, it is difficult to determine unambiguously whether or not the added hydrocarbon itself acts as a source of the additionally formed methanol.

The most systematic study of the influence of promoters on the DMTM process has been carried out by Hunter et al.[41] at a pressure of 10 atm. About 30 different compounds, including saturated, unsaturated, cyclic, and aromatic hydrocarbons, ethers, alcohols, ketones, aldehydes, water, peroxides, sulfur-containing compounds, and amines, were tested as promoters. Many of these promoters decrease noticeably the temperature of the process. Diethyl ether exerts the greatest influence; the addition of 3.9% of diethyl ether decreases the reaction temperature from 402 to 225 °C. Another obvious consequence of the action of some promoters is a significant increase in the yield of formaldehyde, probably at the expense of the corresponding decrease in the yield of methanol. In some cases, the selectivity of the formation of methanol or/and formaldehyde increases, compared with a system containing no promoters. However, this requires the addition of fairly large amounts of promoters, which cancels the economic prospects of thus increasing the yield of methanol in a real technological process.

6. The influence of catalysts and the material of the reactor surface

The question whether the effectiveness of the DMTM process can be significantly increased by using catalysts has remained unsolved throughout the period of its study. An investigation of the influence of certain metals and alloys on this process [19] did not reveal any significant advantages of the catalytic reaction over the purely gas-phase transformation. The use of metallic reactors or catalysts at relatively low pressures favours the formation of products of the complete oxidation of methane.[40] However, at higher pressures catalysts exert no significant influence on the selectivity of the formation of methanol. Similar conclusions were based on other data.[41,56]

Analysis of the results of the reactions conducted under catalytic conditions [69–75] and in a series of recent comparative studies [40,41,56] makes it possible to conclude almost unambiguously that the catalytic process has no real advantages over the gas-phase reaction carried out at high pressures.[40,71] The same conclusion follows from the kinetic analysis of the reaction mechanism (Section V). The only obvious positive result of using catalysts in the DMTM is the possibility of lowering the reaction temperature.

The question how the material of the reactor surface influences the stability of the products of the partial oxidation of methane is of great importance. A study of the stability of methanol in reactors made of Pyrex, stainless steel, and copper [40] has shown that, in the case of copper, methanol decomposes almost completely even at 375 °C. Stainless steel is much more inert. In a Pyrex reactor, decomposition of methanol cannot be observed even at 500 °C; nevertheless, up to 15%–18% of the methanol added to the reaction mixture decomposes, probably through being involved in the reaction.[40] Quartz and Teflon are also among the best materials for reactors used for the DMTM.[41] When light paraffins are oxidised in copper or steel reactors, especially at atmospheric pressure, the yields of both alcohols and aldehydes decrease.[92] The decomposition of methanol on some surfaces affords dimethyl ether.[93] Ultimately, the reactor material exerts no crucial effect on the selectivity of the formation of methanol and other organic products, because the reaction is homogeneous and the rate of diffusion of radicals to the surface at high pressures is low. The results of pilot tests indicate [31] that the relatively low temperature of the process, which does not exceed 600 °C at the reactor outlet for an initial oxygen content of ~3%, and the low concentration of the organic acids formed can hardly create serious problems in the choice of the material of the reactor.

7. Physical initiation of the process

Attempts to use various physical methods for controlling the rate and selectivity of the DMTM have been undertaken since the 1920s. The effects of an electric discharge, radiation, and ultraviolet light on this process were then studied.[15]

In the 1980s, studies on the initiation of the DMTM by laser radiation were carried out in the Los Alamos National Laboratory (USA).[94,95] From the results obtained, one can judge that, at 450 °C, 2.04 atm, and an oxygen concentration of 11%, only the rate of the reaction could be really increased, while S_{CH_3OH} and the proportions of products do not change noticeably. However, kinetic analysis of the system showed that at elevated temperatures (530–730 °C), a pressure of 60 atm, and for the $CH_4 : O_2 = 2 : 1$ ratio one may expect a 50% selectivity of the formation of methanol with a degree of conversion of about 25%. The time scale of the reaction (3 ms) dictated the use of a reactor with a supersonic nozzle.[94] Nevertheless, the authors were apparently unable to solve the problem of the quick removal of the heat of reaction and to achieve quick 'quenching' of the reaction products, without which a high selectivity of the formation of methanol at a relatively high oxygen concentration cannot be ensured.

Among the physical methods for stimulating the oxidation of methane, the use of an ultra-high frequency, glow discharge and thermal initiation by a heated wire have also been considered.[96] It has been shown [97] that, in a methane plasma, methane dimerises to C_2 hydrocarbons with a selectivity of more than 95% for a degree of conversion from 30% to 90%. However, the energy efficiency of this thermodynamically unfavourable process is only 0.2%–3.3%. An attempt to use an ultra-high frequency discharge for oxidising methane to methanol [98] has shown that the features of the reactor design are also significant. The introduction of methane behind the area of plasma induction allowed the yield of C_2 hydrocarbons to be significantly diminished, but the selectivity of the formation of methanol was still extremely low.

8. Cool-flame and periodic phenomena in the oxidation of methane

The existence of cool-flame and related periodic and critical phenomena has been observed in the oxidation of many hydrocarbons with various structures, including alkanes up to propane and ethane.[20,99,100] In the vast majority of studies, cool flames have not been detected in the oxidation of methane. However, the authors of some studies have noticed phenomena that could have been interpreted as cool-flame phenomena. These situations have also been found in the high-pressure oxidation of methane to methanol.[23,42,45] Only Vanpee [101] and Egret et al.,[102] who worked at atmospheric pressure, obtained fairly convincing experimental evidence for this phenomenon. Recently it was confirmed once again:[103] cool flames were detected in a $2CH_4 + O_2$ mixture at 650–740 Torr and about 500 °C. The dependence on time of the temperature of the reaction mixture exhibited two maxima, the temperature rise in the first one being 100–120 °C. A region of a negative temperature coefficient of the rate of oxidation of methane has been found.[104]

Since there is a theoretical possibility of the appearance of cool-flame regimes in the high-pressure oxidation of methane,[61,105] which may lead to the yields of products, differing fundamentally from those reached in other known oxidation regimes, we present here the published experimental data.

In a process carried out at a pressure of 3360 atm, an oxygen concentration of 8%, and an initial temperature of 262 °C in a static reactor, two temperature peaks with amplitudes of 6 and 14 °C, accompanied by corresponding pressure increases, have been observed against the background of a slow temperature rise.[23]

Temperature oscillations typical of the cool-flame phenomena have been observed during the oxidation of methane in a flow reactor at 25–35 atm and an oxygen concentration not less than 5%.[42] At oxygen concentrations of 8% or more and temperatures of about 410 °C, these oscillations were steady. An increase in the temperature to 450 °C led to a decrease in the amplitude of the oscillations and an increase in their frequency. At 475 °C, the oscillations disappeared. The amplitudes and the frequencies of the oscillations at various points along the reactor axis were very different. The maximum S_{CH_3OH} was achieved at the lowest temperatures at which oscillations no longer occurred; however, the selectivity remained lower than that observed at the optimal oxygen concentrations ($\leqslant 3\%$). It was suggested that, under the conditions in which these oscillations occur, the process in the reactor can be controlled in order to achieve the highest selectivity.

9. The role of other factors

Among other factors which can, in principle, influence the kinetics and the yield of products of the partial oxidation of methane, one should mention the rate at which the reagents are introduced into the reactor, the conditions in their mixing, the heat transfer conditions, and features of the reactor design.

The fact that the yield of products depends substantially on the ratio between the diameter of the reactor, through which a slow (1.6 m s^{-1}) stream of methane is passed, and the diameter of the coaxial nozzle, through which oxygen is passed at a high velocity (60–300 m s^{-1}), and on the velocity of the oxygen supply through the nozzle has been reported in a patent.[27]

There is evidence that it is necessary to ensure the maximum homogeneity of the mixture entering the reactor. For this purpose, a premixing chamber filled with Teflon turnings has been mounted before the reactor.[28] However, an attempt[40] to reproduce the high yields of methanol obtained by Gesser et al.[28] by using the same premixing device gave no noticeable positive results. The composition of the gas, the mixing conditions, as well as the reactor size and the constructional materials used[28,40] were approximately the same and could not account for the large difference between the selectivities of the formation of methanol (~80% and ~40%, respectively). It was concluded[40] that some slight, but perhaps significant, differences in the reactor design may account for this difference, and that the essential influence of this factor is due to the cool-flame reaction regime.

The influence of the reactor design (the way in which oxygen is supplied into the stream of methane) on the process has been studied.[60] The improvement of the conditions in the mixing of the reactants by introducing oxygen through a spiral nozzle or into a narrow zone of the reactor did not lead to a substantial increase in the yield of methanol. The best results were achieved by distributing the oxygen supply along the whole reactor.[30,60] In this connection, it was suggested[60] that the high yields attained in some experiments reported in a patent[27] were due to the great distance of the flow of oxygen, before it was mixed with methane, the oxygen being injected into the reactor through a narrow coaxial nozzle, which is equivalent to a distributed supply. The best results were achieved at moderate rates of supply of oxygen. At high rates, the degree of turbulence might increase, and, hence, the mixing area might diminish, which could cause a decrease in the yield of methanol.

Theoretical calculations predict the possibility of increasing the yield of methanol by an order of magnitude by using a fundamentally different scheme for conducting the process.[95,106] In conformity with these calculations, conducting the reaction at 730 °C with rapid quenching of the products may ensure $S_{CH_3OH} = 57\%$ with an oxygen concentration of 25%, which corresponds to a methanol yield of about 13%.[106]

IV. High-pressure oxidation of methane homologues

Data on the oxidation of rich mixtures of methane homologues with air or oxygen at high pressures are quite scarce and are presented in a very small number of papers.[5,6,13,15,90,107–109] Most of these papers have been considered in detail in a review.[20]

When gases containing large proportions of higher hydrocarbons are used, the process parameters such as the pressure and the temperature needed decrease sharply. As the concentration of higher hydrocarbons grows, there is an increase in the degree of conversion of natural gas, for which the selectivity of the formation of alcohols still remains high; in addition, higher alcohols, including iso-alcohols, aldehydes, and some other compounds, are also formed.

1. Ethane

Since ethane is oxidised much more readily than methane, it follows that, as mentioned in Section III, even a slight increase in the proportion of the ethane admixture in methane (natural gas) decreases the reaction temperature by approximately 100 °C and increases the yield of alcohols (Fig. 13). The most comprehensive studies of the oxidation of ethane have been carried out by Newitt and coworkers.[5,6,107] The oxidation of mixtures with the approximate composition $C_2H_6 : O_2 = 9 : 1$ under static conditions at 15–100 atm,[6,107] afforded methanol, ethanol, formaldehyde, acetaldehyde, formic acid, and acetic acid apart from carbon oxides, methane, and water. On the basis of the results obtained, it has been concluded[6] that an increase in pressure, with approximately the same reaction time (2.5–4.5 min), leads to an increase in the yield of C_2 products (ethanol, acetaldehyde, and acetic acid) and to a decrease in the yields of methanol and formaldehyde. However, maintenance of a constant reaction time does not ensure the maximum yield of alcohols. In any case, examination of the full set of experimental data[107] shows (Table 3) that the maximum yields of alcohols and acetaldehyde depend only slightly on pressure, at least in the range above 50 atm. The role of pressure is more clearly manifested by an increase in the yield of acetic acid, the maximum selectivity of its formation reaching 27.2% at 100 atm, and a monotonic decrease in the yield of formaldehyde. Apparently, one can also conclude that the selectivities of the formation of ethanol and acetic acid increase as the oxygen concentration in the mixture decreases. In the oxidation of a

Table 3. Pressure dependence of the selectivity of the formation of the products of the oxidation of ethane.[107]

P/atm	T/°C	Selectivity of the formation (%)[a]											CO/CO_2	t_r/min
		EtOH	CH_3OH	CH_3CHO	HCHO	AcOH	HCOOH	CO	CO_2	CH_4	Σ_l	Σ_g		
15[b]	315	16.0	19.4	1.9	4.5	0	0	–	–	–	41.8	–	–	3.0
50[c,d]	286	24.4	14.1	8.3	2.0	1.7	0.9	34.8	10.0	0	51.4	44.8	3.48	10.7
75[b]	279	18.0	16.6	6.8	0.4	3.6	0.6	–	–	–	46.0	–	–	2.5
100[c,d]	266.5	23.7	11.2	6.0	0.05	23.8	0.6	9.3	14.2	8.6	65.3	32.1	0.65	34.5

[a] Based on the combusted ethane. [b] Initial mixture composition: 88.2% C_2H_6 + 11.8% O_2. [c] Initial mixture composition: 88.4% C_2H_6 + 11.6% O_2. [d] The results of the experiments in which the highest ethanol yields were achieved. Σ_l and Σ_g are the sums of liquid and gaseous products respectively.

mixture with the composition $C_2H_6 : O_2 : N_2 = 90 : 3 : 7$ in a flow reactor at $P = 50$ atm, $T = 360$ °C, and for a contact time of 4 s, the selectivity of the formation of ethanol was 63%.[5] When the contact time increased to 20 s, the selectivity of the formation of ethanol decreased to 14.5%, while S_{CH_3OH} increased from trace amounts to 7.8%. When portions of oxygen were successively added to the mixture which had already reacted, the quantities of ethanol, aldehydes, and acids formed and the quantity of methane remained virtually constant, and only the contents of methanol and carbon oxides increased monotonically.[107]

In a more recent study,[108] in which the process was carried out under flow conditions at 27–37 atm, a high selectivity of the formation of alcohols (more than 70%) was also observed. However, whereas at the relatively low pressures mentioned above the ethanol : methanol ratio in the reaction products was less than unity, with increase in pressure to 90 atm this ratio increased to 6. In the experiments under consideration, the time the mixture spent in the reactor also increased from ~1 min at 15 atm to 7 min at 90 atm. Therefore, it is difficult to distinguish the influence of the linear velocity of the reactant flow in the reactor from the influence of the pressure itself. It should be noted that in another study,[5] the opposite influence of the residence time of the mixture in the reactor has been observed: at 50 atm, the increase in the residence time from 7 to 20 s reduced the ethanol : methanol ratio from 19 to 2. It has also been reported[109] that this ratio increases as the oxygen concentration decreases.

2. Propane

Data on oxidation of propane at high pressures have been reported by Newitt and coworkers[6,109] (static conditions) and Wiezevich and Frolich[15] (flow conditions). These data are partly presented in Tables 4 and 5. Qualitative analysis showed that, among aldehydes, propanal and acetaldehyde are formed, among normal alcohols, methanol, ethanol, and propanol are produced, while carboxylic acids are mostly represented by acetic acid with minor amounts of propionic and formic acids.[109] An increase in pressure results in a substantial increase in the yields of 2-propanol, acetone, and organic acids, some reduction of the yields of aldehydes and normal alcohols, an increase in the yield of CO_2, and a decrease in the yield of CO; when the pressure is 20 atm or more, propene is no longer present in the reaction products. In addition, increase pressure appreciably diminishes the temperature of the process (Table 4) and leads to a change in the content of normal alcohols in the reaction products. The proportions of methanol and ethanol decrease with increasing pressure, while the proportion of propanol increases (Table 5). From the data presented, one can see that the most significant changes in almost all the process characteristics occur when the pressure increases to 20 atm. Further increase to 100 atm[109] or 200 atm[15] gives no fundamental advantages, except for an increase in the yield of 2-propanol.

It is necessary to take into account the fact that the data[109] concerning the pressure dependences of the yields of the propane oxidation products, presented in Tables 4 and 5, have been obtained at temperatures ensuring an approximately constant rate of the process rather than under the conditions ensuring the optimal yields of the alcohols. Since according to the same study an increase in temperature increases the overall yield of normal alcohols (at 30 atm, it increases from 21% to 40% as the temperature increases from 260 to 286 °C), one should expect that, under the optimal conditions, the yield of the alcohols would be appreciably higher. As in the oxidation of methane or ethane, a decrease in the oxygen concentration in the mixture leads to an increase in the selectivity of the formation of the alcohols.[109] However, in the oxidation of propane, a relatively high selectivity of the formation of the alcohols (more than 30%–40%) can be achieved even for the propane : oxygen ≈ 1 : 1 ratio. The optimal conditions for the formation of the alcohols are ensured by the highest possible safe oxygen concentration.[15]

Table 4. Selectivity of the formation of the products of the oxidation of the propane : air = 1 : 3.6 mixture (according to Newitt[6,109]).

Products	Selectivity (%)[a]			
	A	B	C	D
The sum of aldehydes	20.5	21.8	13.5	13.7
The sum of normal alcohols	19.7	21.0	17.5	15.2
Isopropyl alcohol	1.3	2.8	6.2	16.0
Acetone	0.5	4.3	12.5	7.9
The sum of acids	4.3	17.0	19.0	18.9
Carbon dioxide	7.3	17.1	21.4	20.6
Carbon monoxide	21.3	16.0	9.9	7.7
Propene	25.1	0	0	0

[a] Reaction conditions: A — 1 atm, 373 °C; B — 20 atm, 281 °C; C — 60 atm, 252 °C; D — 100 atm, 250 °C.

3. Butane, pentane, and heptane

There are only scattered data on the gas-phase oxidation of butane, pentane, and heptane at high pressures,[15,90] permitting only a general idea about the expected yield of the alcohols and their proportions. The oxidation of n-butane, pentanes, and heptanes was studied[15] using the same equipment and under approximately the same flow conditions as were used for the oxidation of propane. The following conditions are optimal for the formation of higher alcohols from alkanes: pressure from 130 to 200 atm, the lowest possible temperature, a reaction time less

Table 5. Relative yields of alcohols in the oxidation of the mixture propane : air = 1 : 3.6 (according to Newitt[6,109]).

Alcohol	Yield (%)			
	5 atm	30 atm		65 atm
CH_3OH	76.3	58.0	55.3	50.1
C_2H_5OH	19.1	17.6	13.2	9.8
n-C_3H_7OH	4.6	4.3	7.3	12.2
iso-C_3H_7OH	–	20.0	24.2	27.9

than 10 s in a heated reactor, and the highest possible safe concentration of oxygen.

Apart from the compounds found also in the products of the oxidation of propane, the oxidation of n-butane with oxygen at a pressure of 33–160 atm yields also butanols, their proportion increasing with increase in pressure. In general, low pressures during the oxidation of alkanes are likely to be favourable for the formation of lower alcohols and organic acids, while high pressures promote the formation of higher alcohols and aldehydes.[15] In addition, increasing the pressure decreases the temperature of the process: the temperature of the oxidation of n-butane decreases from 255 to 210 °C as the pressure increases from 33 to 160 atm. The composition of the products of the gas-phase oxidation of butane differs greatly from that in its liquid-phase oxidation at high pressures, the latter yielding mostly acetic acid and ethyl methyl ketone with minor amounts of alcohols.[110]

The oxidation of a mixture of 60% n-pentane and 40% isopentane, saturated beforehand with oxygen up to its concentration of 5%–6%, gives mostly alcohols, aldehydes, acetone, and acids containing 2–3 carbon atoms. Conversely, the products of the oxidation of heptane (the fraction boiling at 70 to 97 °C and containing almost all of the heptane isomers present in the head of the petrol fraction) contained mainly hexanols and heptanols with boiling points from 140 to 180 °C. The fact that these results differ from those obtained with pentane has been tentatively attributed to the occurrence of the reaction in the liquid phase.

In another study,[90] the oxidation of n-butane, carried out at 385 °C, 3.5–12.5 atm, with reaction times from 1.0 to 4.5 s, and under turbulent flow conditions in order to minimise the transverse concentration and temperature gradients, was rapidly quenched by cooling with water. The butane and oxygen concentrations varied between 1.5 mol % and 6 mol % each, and the rest was nitrogen. The pressure dependence of the yield of useful products (alcohols, aldehydes, acetone, and acids) passed through a maximum at $P = 8.8$ atm. No appreciable variations of the ratios between various products were observed. The most surprising finding was that there are limiting oxygen concentrations for the onset and termination of the process. The reaction did not proceed if the starting oxygen concentration was less than 1.5% and stopped when the concentration of O_2 fell below this value. Although incomplete conversion of oxygen has also been noted in other studies (Section III, 3), the existence of concentration limits in the high-pressure oxidation of alkanes was pointed out in none of them. The maximum yield of useful products was achieved for an oxygen concentration of 4.5%.[90]

Under the optimal conditions ($P = 8.4–9.8$ atm, reaction time 1.2–1.8 s, concentrations of n-butane and oxygen mixed with nitrogen 4–5% each), 20% of the hydrocarbon taken was converted into useful products. The selectivity of the formation of these products was about 50%.

4. General features of the high-pressure oxidation of alkanes

On the basis of the experimental data considered in Sections III and IV, some general conclusions concerning the features of the oxidation of methane homologues at high pressures can be drawn (Table 6).

1. In the oxidation of all the $C_1–C_5$ alkanes under optimal conditions, a selectivity of the formation of liquid organic products not less than 50% can be achieved.

2. An increase in the oxygen concentration reduces the selectivity of the formation of liquid organic products, but, on passing from methane to pentane, the hydrocarbon : oxygen ratio for which a high selectivity is still achieved decreases sharply (~30 for methane, ~10 for ethane, and ~1 for propane, butane, and pentane). The degree of conversion of hydrocarbons into useful products increases in the same series (up to ~2% for methane, ~5% for ethane, and ~20% for propane, butane, and pentane).

3. The pressure and the temperature optimal for the production of liquid hydrocarbons decrease monotonically in the methane–pentane series (100 atm and 450 °C for methane, 50 atm and 360 °C for ethane, 20 atm and 280 °C for propane, and 9 atm and 260 °C for butane). As a rule, these data correspond to a process conducted under flow conditions with a reaction time of several seconds.

4. The influence of pressure on the product composition decreases in the methane–pentane series.

Table 6. The optimal parameters of the high-pressure oxidation of alkanes for the formation of liquid organic products (averaged published data).

Hydrocarbon	P/atm	T/°C	$[C_nH_{2n+2}]/[O_2]$	Degree of conversion into useful products (%)[a]
CH_4	100	450	30	2
C_2H_6	50	360	10	5
C_3H_8	20	280	1	20
C_4H_{10}	9	260	1	20

[a] The maximum overall selectivity of the formation of liquid organic products from all the alkanes exceeds 50%.

V. The mechanism of the high-pressure oxidation of methane

The understanding of the mechanism and, consequently, the optimisation of the conditions in a process as complex as the oxidation of methane, which has been one of classical objects of study in chemical kinetics for decades,[111] are impossible without the creation of an adequate kinetic model. Several theories which make it possible to explain the experimentally observed characteristic features have been suggested;[20] however, at present, the radical-chain mechanism of the gas-phase oxidation of alkanes is generally accepted.[112] In view of the complexity of the methane oxidation process, one can hardly expect that a universal model, suitable for the quantitative analysis of all cases of practical interest, will be developed in the near future. Therefore, the existing quantitative models have as a rule limited applicability. In conformity with the subject of our review, we shall consider only those models which involve the modelling of the oxidation of methane at high pressures and moderate temperatures.

1. The principles of the construction of quantitative kinetic models of complex gas-phase processes

One can hardly expect that a mathematical description (kinetic model) of a complex chemical reaction will be in complete quantitative agreement with the real process. This is due to both the unavoidable inaccuracy of the kinetic parameters of a model and the errors of the real experiment. The kinetic parameters of complex models are mainly selected using the experimental rate constants for the elementary reactions, and it is desirable to have available also the results of theoretical calculations or empirical or semiempirical estimates for all the key elementary stages as well as those elementary stages, which have not been studied or have been poorly studied. The experience in modelling complex gas-phase reactions indicates that, if there is no confidence in the reliability of the available experimental rate constants for any elementary reactions or if these data deviate significantly from the theoretical estimates or calculations, the latter should be preferred.[64]

Models adequately describing a whole set of reliable and noncontradictory experimental data are the most valuable. The adjustment of a model to make it describe accurately a group of results by manipulating the rate constants for individual reactions is not very promising. Kinetic analysis indicates[36] that the yields of products often depend strongly on the parameters of those elementary reactions in which these products are neither formed nor consumed. Moreover, a rather complex kinetic model possesses certain 'internal stability'. In some cases, several parallel pathways to the formation of particular products exist, and

attempts to attain a specified change of their yield by varying the parameters of 'obvious' reactions may fail.

2. Characteristic features of the oxidation of methane at high pressures and moderate temperatures

The rise in pressure influences the course of gas-phase reactions for several reasons. As the pressure grows, the frequency of intermolecular collisions and hence the rate of the process increase, which decreases the reaction temperature. This, in turn, leads to the possibility of the 'survival' of certain intermediates, which would decompose or undergo further transformations at a higher temperature. Pressure can also shift the equilibria of reversible reactions, and in the oxidation of hydrocarbons at moderate temperatures the most important are reactions of the type [113,114]

$$R + O_2 \rightleftharpoons RO_2 .$$

Pressure changes can also result in a redistribution of the contributions of various paths in multipath reactions (for example, in the reactions of biradicals with unsaturated hydrocarbons),[115] in an increase in the yields of the products of radical recombination, and in the deactivation of excited molecules.[111] Finally, pressure is a critical factor for chain reactions.[112]

The possibility that, even at pressures of several hundreds of atmospheres, fundamentally new reaction paths may appear, due to the manifestation of the cage effect, when a short-lived molecular complex formed during the process has time to react with other reactants before it decomposes, has been discussed.[116]

At the same time, modelling of kinetic processes occurring at pressures of tens of atmospheres is facilitated in the vast majority of cases by the possibility of neglecting the pressure dependences of the rate constants for unimolecular and termolecular reactions and of using their values obtained for the infinite pressure limit.[111] The heterogeneous destruction of radicals and intermediates at these pressures is limited by the rate of their diffusion to the surface and plays a relatively small role, which also facilitates the modelling.

Since the DMTM process occurs at moderate temperatures, its modelling is simplified, because a large number of elementary reactions requiring high activation energies as well as processes involving CH, C, C_2, and other species, formed only at high temperatures, can be excluded from the kinetic scheme. Moreover, when rich mixtures are employed, some reactions that are significant only at relatively high oxygen concentrations can also be ignored.

3. The model of the high-pressure oxidation of methane

The development of a quantitative model of the high-pressure oxidation of methane is a complicated problem in spite of the above possibilities of simplifying the kinetic scheme. Models developed for other conditions cannot be applied directly to the DMTM process; at best, they can serve as the starting point for such work. The most logical and comprehensive programme for the modelling of the DMTM has been reported by Vedeneev and coworkers.[33-37,64] An extensive study on the modelling of the DMTM has been carried out at Trondheim University and the Norwegian Technological Institute.[39,68] Several other research groups have also presented their results.[45,54,61,94] Unfortunately, these publications are either difficult to obtain[68,94] or give no detailed description or justification.[45,54]

Detailed analysis and comparison of various models is beyond the scope of our review. We shall consider only the first model suggested for the DMTM process,[34] since it has been most fully described and tested in the modelling of a wide range of experimental results by the same workers and by other research groups.[48,60] In addition, the base model[34] and its modifications[37,64,117,118] have proved suitable for describing various processes ranging from the DMTM[34,37,64] to the oxidative condensation of methane[118] or the oxidation of methane below atmospheric pressure.[117]

The base model[34] (Table 7) takes into account all the main reliably established elementary reactions that play a significant

Table 7. The mechanism of the oxidation of methane[34] and the parameters of the equation $k = AT^n\exp(-E/RT)$.

Reaction	A[a]	n	E/kJ mol^{-1}
1. $CH_4 + O_2 = CH_3^{\cdot} + HO_2^{\cdot}$	1.00×10^{-10}	0	234.30
2. $CH_3^{\cdot} + HO_2^{\cdot} = CH_4 + O_2$	1.00×10^{-12}	0	0
3. $CH_3^{\cdot} + O_2 = CH_3OO^{\cdot}$	2.00×10^{-12}	0	0
4. $CH_3OO^{\cdot} = CH_3^{\cdot} + O_2$	8.90×10^{13}	0	130.96
5. $OH^{\cdot} + CH_4 = H_2O + CH_3^{\cdot}$	1.32×10^{-17}	1.9	11.25
6. $CH_3OO^{\cdot} + CH_3OO^{\cdot} = CH_3O^{\cdot} + CH_3O^{\cdot} + O_2$	1.71×10^{-13}	0	0
7. $CH_3OO^{\cdot} + CH_3OO^{\cdot} = CH_2O + CH_3OH + O_2$	0.74×10^{-13}	0	0
8. $CH_3OO^{\cdot} + CH_3^{\cdot} = CH_3O^{\cdot} + CH_3O^{\cdot}$	4.50×10^{-11}	0	0
9. $CH_3OO^{\cdot} + HO_2^{\cdot} = CH_3OOH + O_2$	7.70×10^{-14}	0	−10.88
10. $CH_3^{\cdot} + HO_2^{\cdot} = CH_3O^{\cdot} + OH^{\cdot}$	3.00×10^{-11}	0	0
11. $HO_2^{\cdot} + HO_2^{\cdot} = H_2O_2 + O_2$	2.20×10^{-13}	0	−5.15
12. $CH_3^{\cdot} + CH_3^{\cdot} = C_2H_6$	4.00×10^{-11}	0	0
13. $CH_3O^{\cdot} + HO_2^{\cdot} = CH_3OH + O_2$	1.70×10^{-11}	0	0
14. $CH_3O^{\cdot} + CH_4 = CH_3OH + CH_3^{\cdot}$	1.00×10^{-12}	0	46.02
15. $CH_3O^{\cdot} + O_2 = CH_2O + HO_2^{\cdot}$	1.00×10^{-13}	0	10.88
16. $CH_3O^{\cdot} = CH_2O + H^{\cdot}$	1.00×10^{14}	0	125.52
17. $CH_3OO^{\cdot} + CH_4 = CH_3OOH + CH_3^{\cdot}$	1.00×10^{-12}	0	89.96
18. $CH_3OO^{\cdot} + CH_2O = CH_3OOH + CHO^{\cdot}$	4.70×10^{-13}	0	50.21
19. $HO_2^{\cdot} + CH_2O = H_2O_2 + CHO^{\cdot}$	2.00×10^{-12}	0	46.02
20. $CH_3^{\cdot} + CH_2O = CH_4 + CHO^{\cdot}$	1.40×10^{-12}	0	29.10
21. $CH_3O^{\cdot} + CH_2O = CH_3OH + CHO^{\cdot}$	1.00×10^{-12}	0	15.06
22. $OH^{\cdot} + CH_2O = H_2O + CHO^{\cdot}$	1.25×10^{-11}	0	0.73
23. $H^{\cdot} + CH_4 = H_2 + CH_3^{\cdot}$	1.30×10^{-10}	0	49.90
24. $H^{\cdot} + O_2 + M = HO_2^{\cdot} + M$	1.00×10^{-32}	0	−4.18
25. $H^{\cdot} + CH_2O = H_2 + CHO^{\cdot}$	3.27×10^{-11}	0	15.35
26. $CHO^{\cdot} + O_2 = CO + HO_2^{\cdot}$	5.50×10^{-11}	−0.4	0
27. $CHO^{\cdot} + M = CO + H^{\cdot} + M$	4.00×10^{-10}	0	71.13
28. $CH_3OOH = CH_3O^{\cdot} + OH^{\cdot}$	4.00×10^{15}	0	179.91

Table 7 (continued).

Reaction	A [a]	n	E/ kJ mol^{-1}
29. $H_2O_2 = OH^{\cdot} + OH^{\cdot}$	3.00×10^{14}	0	207.94
30. $OH^{\cdot} + H_2 = H_2O + H^{\cdot}$	1.06×10^{-17}	2.0	6.23
31. $HO_2^{\cdot} + H_2 = H_2O_2 + H^{\cdot}$	5.60×10^{-12}	0	93.30
32. $CH_3OO^{\cdot} + H_2 = CH_3OOH + H^{\cdot}$	3.60×10^{-12}	0	93.30
33. $CH_3O^{\cdot} + H_2 = CH_3OH + H^{\cdot}$	3.60×10^{-12}	0	41.80
34. $CH_3^{\cdot} + H_2 = CH_4 + H^{\cdot}$	3.60×10^{-12}	0	45.20
35. $CH_3OO^{\cdot} + CH_3O^{\cdot} = CH_3OOH + CH_2O$	1.50×10^{-12}	0	0
36. $CH_4 + HO_2^{\cdot} = CH_3^{\cdot} + H_2O_2$	3.00×10^{-12}	0	89.96
37. $CH_3^{\cdot} + CH_3OH = CH_4 + {}^{\cdot}CH_2OH$	3.30×10^{-13}	0	41.00
38. $CH_3OO^{\cdot} + CH_3OH = CH_3OOH + {}^{\cdot}CH_2OH$	5.00×10^{-13}	0	60.25
39. ${}^{\cdot}CH_2OH + O_2 = CH_2O + HO_2^{\cdot}$	2.00×10^{-12}	0	0
40. $HO_2^{\cdot} + CH_3OH = H_2O_2 + {}^{\cdot}CH_2OH$	1.50×10^{-12}	0	60.25
41. $OH^{\cdot} + CH_3OH = H_2O + {}^{\cdot}CH_2OH$	5.70×10^{-12}	0	5.86
42. $OH^{\cdot} + CH_3OH = H_2O + CH_3O^{\cdot}$	1.70×10^{-11}	0	13.81
43. $CH_3O^{\cdot} + CH_3OH = CH_3OH + {}^{\cdot}CH_2OH$	6.60×10^{-13}	0	22.17
44. $H^{\cdot} + CH_3OH = H_2 + {}^{\cdot}CH_2OH$	2.16×10^{-11}	0	22.00
45. $H^{\cdot} + H_2O_2 = OH^{\cdot} + H_2O$	3.00×10^{-10}	0	26.36
46. $OH^{\cdot} + H_2O_2 = H_2O + HO_2^{\cdot}$	3.70×10^{-12}	0	2.16
47. $H^{\cdot} + H_2O_2 = H_2 + HO_2^{\cdot}$	1.70×10^{-11}	0	20.92
48. $CH_3OO^{\cdot} + H_2O_2 = CH_3OOH + HO_2^{\cdot}$	2.50×10^{-13}	0	54.39
49. $CH_3O^{\cdot} + H_2O_2 = CH_3OH + HO_2^{\cdot}$	2.50×10^{-13}	0	16.74
50. $CH_3^{\cdot} + H_2O_2 = CH_4 + HO_2^{\cdot}$	2.50×10^{-13}	0	11.71
51. $OH^{\cdot} + CO = H^{\cdot} + CO_2$	2.50×10^{-17}	1.3	−3.20
52. $HO_2^{\cdot} + CO = OH^{\cdot} + CO_2$	1.70×10^{-10}	0	96.20
53. $CH_3O^{\cdot} + CO = CH_3^{\cdot} + CO_2$	2.60×10^{-11}	0	49.37
54. $CH_3O^{\cdot} + CH_3O^{\cdot} = CH_3OH + CH_2O$	3.00×10^{-11}	0	0
55. $CH_3^{\cdot} + CH_3O^{\cdot} = CH_4 + CH_2O$	2.80×10^{-11}	0	0
56. $CH_3^{\cdot} \xrightarrow{\text{heter.}}$ radical destruction	5.00×10^{-3}	0	0
57. $CH_3OO^{\cdot} \xrightarrow{\text{heter.}}$ radical destruction	5.00×10^{-3}	0	0
58. $HO_2^{\cdot} \xrightarrow{\text{heter.}}$ radical destruction	5.00×10^{-3}	0	0
59. $CH_3OOH \xrightarrow{\text{heter.}}$ radical destruction	5.00×10^{-3}	0	0
60. $H_2O_2 \xrightarrow{\text{heter.}} H_2O$	1.50×10^{-3}	0	0
61. $H_2O_2 \xrightarrow{\text{heter.}} H_2O + O_2$	1.50×10^{-3}	0	0

[a] Preexponential factors are expressed in s^{-1} for unimolecular reactions, cm^3 molecule^{-1} s^{-1} for bimolecular reactions, or cm^6 molecule^{-2} s^{-1} for the termolecular reaction 24.

role at high pressures and moderate temperatures, including heterogeneous destruction of radicals and peroxides on the reactor surface. Some reactions, discussed in the literature but not properly justified, have not been included in the model.

a. The main stages of the process

In a kinetic analysis of a complex process, the possibility of identifying the minimum number of elementary stages necessary and sufficient to describe the process and also the identification of the elementary stages the variation of the rate constants for which influences most appreciably the process kinetics or the product composition (the rate-limiting stages), are of prime importance. This problem is solved by analysing the sensitivity of the process kinetics, the rate of product accumulation, and other characteristic features to the variation of the rate constants for individual reactions.[35]

Analysis of the process kinetics indicates[35] that the rate-determining stages include the decomposition of methyl hydroperoxide (stage 28 in Table 7) and of hydrogen peroxide (29) and also the formation of methyl hydroperoxide (17, 18, 38, 48) and hydrogen peroxide (36, 40). All the above stages of the peroxide formation and decomposition reactions belong to the group of reactions responsible for degenerate branching. The hydrogen peroxide formation (stage 19) is not included in the set of rate-determining stages, since at low temperatures the effectiveness of branching associated with the decomposition of hydrogen peroxide is low and the effective consumption of formaldehyde, one of the main degenerate-branching agents, exerts a greater influence.

The most important quadratic chain termination reactions are stages 6, 7, and 11. Although in stage 6 two relatively inactive $CH_3O_2^{\cdot}$ radicals are converted into two reactive $CH_3O^{\cdot}$ radicals, the latter are partly converted into $HO_2^{\cdot}$ radicals (the competing stages 14 and 15), which are effectively destroyed in stage 11.

Due to the rapid decomposition of methyl hydroperoxide, stage 9 is a chain propagation reaction, though formally two

radicals are converted into molecular products in this reaction. The positive role of stage 5 is that it transforms the hydroxyl radicals into the methyl radicals, which, in turn, are converted into methylperoxyl radicals, responsible for the branching steps. The effective transformation of the methyl radicals into the $CH_3O_2^{\cdot}$ radicals is ensured by the fact that, under the DMTM conditions, the equilibrium involving the two reversible stages 3 and 4 is shifted toward the formation of the $CH_3O_2^{\cdot}$ radical throughout the process, until a negligible oxygen concentration is reached in the system.

Among the remaining reactions, the inhibiting stages 22 and 46 should be noted; here the $OH^{\cdot}$ radicals are consumed and branching agents such as formaldehyde and hydrogen peroxide are destroyed. Stage 52, in which the less reactive radicals $HO_2^{\cdot}$, effectively destroyed in stage 11, are converted into the reactive $OH^{\cdot}$ radicals, is also significant.

The limiting role of stages 14, 15, 21, and 49 can be explained by the competition between the reactions involving the conversion of the reactive $CH_3O^{\cdot}$ radicals either into the relatively inactive $HO_2^{\cdot}$ radicals or (in the subsequent stages) into $CH_3O_2^{\cdot}$ radicals, which participate in the formation of methyl hydroperoxide acting as a branching agent.

The qualitative scheme presented below,[35] which involves the most significant reactions responsible for the multiplication of active centres (28 and 29), the formation of the main branching agents (17, 18, 38, 48, 36, 19, 40, and 9), and the termination steps (6, 7, and 11), makes it possible to explain the mechanism of the self-acceleration of the reaction.

It follows from the kinetic analysis of the model[35] that stages 5, 14, 15, 21, 22, 46, 49, and 52, also contribute to the self-acceleration mechanism; since these stages are not directly related to the chain branching or chain termination steps, their role in the mechanism of the self-acceleration of the reaction would be difficult to elucidate without numerical analysis of the model.

Branching:

$$CH_3O_2^{\cdot} + \begin{cases} CH_4 \xrightarrow{(17)} \\ CH_2O \xrightarrow{(18)} \\ CH_3OH \xrightarrow{(38)} \\ H_2O_2 \xrightarrow{(48)} \end{cases} CH_3OOH \xrightarrow{(28)} CH_3O^{\cdot} + OH^{\cdot}$$

$$HO_2^{\cdot} + \begin{cases} CH_4 \xrightarrow{(36)} \\ CH_2O \xrightarrow{(19)} \\ CH_3OH \xrightarrow{(40)} \end{cases} H_2O_2 \xrightarrow{(29)} OH^{\cdot} + OH^{\cdot}$$

Propagation:

$$CH_3O_2^{\cdot} + HO_2^{\cdot} \xrightarrow{(9)} CH_3OOH + O_2$$

Termination:

$$CH_3O_2^{\cdot} + CH_3O_2^{\cdot} \begin{cases} \xrightarrow{(6)} 2\,CH_3O^{\cdot} + O_2 \\ \xrightarrow{(7)} CH_2O + CH_3OH + O_2 \end{cases}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \xrightarrow{(11)} H_2O_2 + O_2$$

b. The mechanism of the initial stage

In the initial stage of the process, the reactions involving intermediate compounds may be neglected and the mechanism of the DMTM may be therefore represented by the simpler set of stages given below.[33]

1. $CH_4 + O_2 \longrightarrow CH_3^{\cdot} + HO_2^{\cdot}$
3. $CH_3^{\cdot} + O_2 \longrightarrow CH_3OO^{\cdot}$
4. $CH_3OO^{\cdot} \longrightarrow CH_3^{\cdot} + O_2$
17. $CH_3OO^{\cdot} + CH_4 \longrightarrow CH_3OOH + CH_3^{\cdot}$
36. $CH_4 + HO_2^{\cdot} \longrightarrow CH_3^{\cdot} + H_2O_2$
28. $CH_3OOH \longrightarrow CH_3O^{\cdot} + OH^{\cdot}$
29. $H_2O_2 \longrightarrow 2OH^{\cdot}$
5. $OH^{\cdot} + CH_4 \longrightarrow H_2O + CH_3^{\cdot}$
14. $CH_3O^{\cdot} + CH_4 \longrightarrow CH_3OH + CH_3^{\cdot}$
15. $CH_3O^{\cdot} + O_2 \longrightarrow CH_2O + HO_2^{\cdot}$
57. $CH_3OO^{\cdot} \xrightarrow{\text{heter.}}$ radical destruction
6. $CH_3OO^{\cdot} + CH_3OO^{\cdot} \longrightarrow CH_3O^{\cdot} + CH_3O^{\cdot} + O_2$
7. $CH_3OO^{\cdot} + CH_3OO^{\cdot} \longrightarrow CH_2O + CH_3OH + O_2$
9. $CH_3OO^{\cdot} + HO_2^{\cdot} \longrightarrow CH_3OOH + O_2$
11. $HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$

The combination of stages 17 and 28 leads to chain branching (the branching via reaction 29 may be ignored in the analysis of the initial stage in view of the long characteristic time of this process, which exceeds 10^3 s). A characteristic feature of the high-pressure oxidation of methane is that the condition $\varphi = 2k_{17}[CH_4] - k_{57} > 0$ is always satisfied owing to the slow diffusion of radicals to the reactor walls and the high methane concentrations. Hence, in the initial stages, the reaction proceeds by a branched-chain mechanism. Since under the DMTM conditions the relation $k_{28} \gg k_{17}[CH_4]$ normally holds, the branching is limited by the interaction of the methylperoxyl radicals with methane. Thus, the kinetics of the process are essentially governed by four stages: 1, 17, 28, and 57.

However, the exponential self-acceleration of the reaction in the initial stage does not lead to an explosion, owing to the quadratic radical destruction reactions (negative chain interaction[112]). Apparently, the scheme takes into account all the significant quadratic radical interactions, since in virtually all the stages of the process the concentrations of the methylperoxyl and hydroperoxyl radicals are comparable and are many orders of magnitude greater than those of all other radicals. Analysis has shown that it is the combination of stages 6 and 7, which are two paths involving the quadratic interaction of the methylperoxyl radicals, that ensures that the reaction goes to a quasi-steady-state regime. Stage 7 plays a crucial role because reaction 6, unlike reaction 7, does not by itself ensure a quasi-steady-state regime. The individual reactions 9 or 11 also do not ensure a quasi-steady-state regime, although allowance for them influences the kinetics of the transformation of peroxyl radicals.[33]

The initial self-acceleration of the reaction occurs and is completed over a very short period when the degrees of conversion of the reactants are extremely small and cannot be detected experimentally. It follows from the above study[33] that in its initial stage, the high-pressure oxidation of methane is a branched-chain reaction, which then becomes a quasi-steady-state regime, characterised by approximately equal branching and quadratic chain termination rates.

c. Reaction paths in the formation of methanol and formaldehyde

A quantitative analysis of the model of the high-pressure oxidation of methane (Table 7) aimed at elucidating the mechanisms of the formation of the main products has been reported by Vedeneev et al.[36] Apart from the reactions in which a particular product is directly produced or consumed, the influence of other reactions was also studied.

The major contribution to the formation and consumption of methanol is made by stages 14, 38, 40, and 49, although some

other reactions also cannot be ignored. The main contribution to the formation of formaldehyde is made by stages 15 and 39, while its consumption occurs mostly via stage 19. Formaldehyde is mostly produced via independent parallel processes, primarily stage 15, rather than via a path involving the oxidation of methanol (stage 39), and the rate of its formation exceeds that of methanol. The fact that the final yield of formaldehyde in the DMTM is almost an order of magnitude lower than that of methanol (see Section III) is determined only by the higher rate of the further transformation of formaldehyde. This is properly illustrated by the experimental data,[119] indicating that in the initial stage of the process, when the degree of conversion of methane is less than 1%, the selectivity of the formation of formaldehyde (~54%) exceeds appreciably the selectivity of the formation of methanol (~36%) but falls very rapidly as the degree of conversion of methane increases to 4%–6%, which occurs in the final stage of the DMTM process.

Hydrogen peroxide plays an important role in the process kinetics and, in particular, in the self-acceleration mechanism, despite the fact that it has not been experimentally detected in the studies on the high-pressure oxidation of methane. Hydrogen peroxide is formed mostly in stages 11, 19, 36, and 40. Carbon monoxide is formed in stages 26 and 27 and carbon dioxide is produced in stages 51–53. Certain other reactions in which CO and CO_2 are formed, in particular, the addition of $HO_2^{\cdot}$ radicals to H_2CO and the addition of $HCO^{\cdot}$ radicals to O_2, should probably also be taken into account, although their mechanisms have not yet been reliably elucidated.

The model discussed above[34] has been supplemented[64] by two heterogeneous termination reactions and a set of reactions describing in more detail the kinetics of the formation and decomposition of carbon monoxide and a significant side product — formic acid. A mechanism of the formation of the latter has been suggested.[47] However, analysis has shown that allowance for this set of reactions has no appreciable influence on the kinetics of the consumption of the reactants and the formation of the remaining products.

d. Modelling of the high-pressure oxidation of ethane and methane–ethane mixtures

The quantitative models of the oxidation of the closest methane homologues suggested by various groups of researchers do not cover the region of relatively high pressures and hence they unfortunately cannot be applied directly to the analysis of the partial oxidation of methane homologues to alcohols. Therefore, Vedeneev et al.[118] have developed a preliminary model of the high-pressure oxidation of ethane based on the model of the oxidation of methane at high pressures.[34]

The recombination of the methyl radicals

$$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow C_2H_6,$$

has been regarded as the main reaction yielding ethane. At pressures above 10 atm, the values corresponding to the infinite-pressure limit were used for the pressure-dependent rate constants. The reactions of all the reactive species, namely $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$, $HO_2^{\cdot}$, $CH_3^{\cdot}$, $CH_3O^{\cdot}$, and $CH_3OO^{\cdot}$, with ethane were taken into account. The numerical values of the rate constants for these reactions were taken from the published data, except for the reactions of ethane with $HO_2^{\cdot}$ and $CH_3OO^{\cdot}$, the rate constants for which were calculated from the rate constants for similar reactions involving methane with allowance for the 8.4 kJ mol^{-1} decrease in the activation energy, in conformity with the Polanyi–Semenov rule.

The formation of ethene was described by the reactions

$$C_2H_5^{\cdot} + M \longrightarrow C_2H_4 + H^{\cdot} + M,$$

$$C_2H_5^{\cdot} + O_2 \longrightarrow C_2H_4 + HO_2^{\cdot},$$

although the latter is probably not an elementary stage. This model includes both the forward and the corresponding reverse reactions related by equilibrium constants (altogether 188 elementary stages). The model does not take into account the formation of C_3 or higher hydrocarbons.

The model under consideration[118] makes it possible to describe quantitatively a wide range of processes, from the oxidation of methane to methanol (20–100 atm, 650–750 K) to its oxidative condensation to ethane and ethene (1–5 atm, 900–1200 K), as well as flame propagation at not very high temperatures and cool-flame phenomena during the oxidation of methane. This model was used for the kinetic analysis of the oxidation of ethane and methane–ethane mixtures at high pressures. Preliminary results indicate that, when mixtures are used, the total selectivity of the formation of alcohols (methanol and ethanol) increases substantially and reaches a maximum when the ethane concentration in methane is 30%–40%, that it is possible to retain high selectivities for high degrees of conversion of the hydrocarbon (more than 8%), and that at $P > 20$ atm the selectivity depends only slightly on pressure.

VI. Analysis of the results of kinetic modelling of the high-pressure oxidation of methane

The present-day level of experimental studies on the DMTM process is deficient in systematic combined investigations carried out within the framework of a unified programme and there are significant discrepancies between the results which are difficult to explain. Therefore theoretical analysis of the process is of particular importance. Such analysis should certainly be based on models, which describe adequately the most reliable experimental data, but, unfortunately, experimental details which would allow a direct comparison of these data with the results of kinetic analysis are not always known. In this section, we present the results of the kinetic modelling of the DMTM process based on the model developed by Vedeneev et al.[34] (Table 7) or its modification.[64]

1. Modelling of the product yields and the process time

The kinetic modelling of the consumption of oxygen and product (methanol, formaldehyde, and carbon oxides) accumulation[34] was performed for the experimental conditions adopted in two previous studies[4,25] (Figs 14 and 15). The model reflects correctly

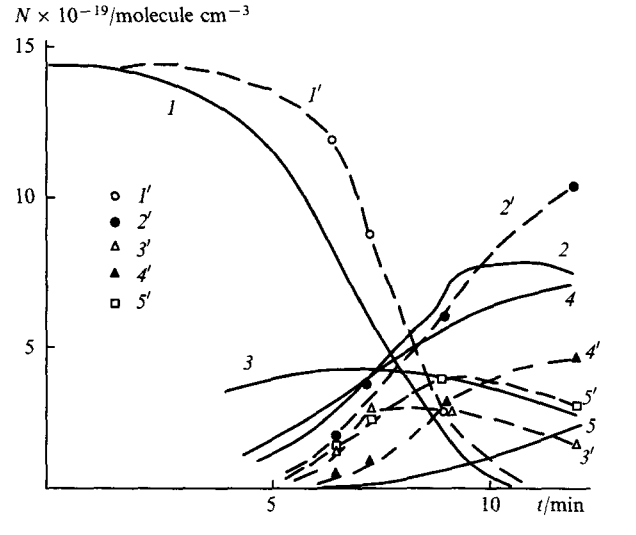


Figure 14. Kinetic curves for the consumption of oxygen (*1*, *1′*) and the accumulation of methanol (*2*, *2′*), formaldehyde (*3*, *3′*), CO (*4*, *4′*), and CO_2 (*5*, *5′*) during the oxidation of methane at $T = 614$ K, $P = 100$ atm, and for $[CH_4]:[O_2] = 8.1:1.0$. Dashed lines correspond to experimental data[4] and the continuous lines to calculations.[34]

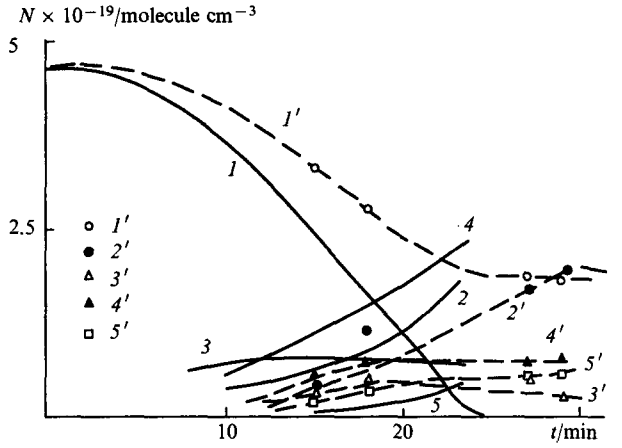


Figure 15. Kinetic curves for the oxidation of methane at $T = 585$ K, $P = 367$ atm, and for $[CH_4]:[O_2] = 9:1$. The designations are the same as in Fig. 14. Dashed lines correspond to experimental data,[25] and continuous lines to calculations.[34]

the main features of the process: the occurrence of self-acceleration, the duration of induction periods and of the whole process, the characteristic features of the product accumulation, and their dependences on temperature, pressure, and composition of the mixture. The fact that the appreciable concentrations of hydrogen peroxide (comparable to those of methanol) predicted by the model[34] were not detected in the high-pressure experiments[4,22] may be explained by its rapid decomposition on metallic surfaces.

On the basis of an extended version of the model under consideration,[34] the delay period of the self-ignition of methane under the conditions reported by Melvin[22] has been calculated.[37] The resulting self-ignition delay periods exceed the experimental values by a factor of only ~1.5, which must be regarded as a very close agreement. In the same study,[37] the experimentally observed[22] increase in the delay of self-ignition with increase in the oxygen concentration in the mixture[22] (see Fig. 12) was theoretically interpreted for the first time. It was shown that during the self-ignition delay period, oxygen inhibits the process, because the reaction of the alkoxyl radicals with molecular oxygen is virtually a chain termination reaction, since the reactive chain-propagating $CH_3O^{\cdot}$ radical is converted via this reaction into the less reactive $HO_2^{\cdot}$ radical, which is destroyed rapidly.

Figs 16–18 present the main results of the modelling of the DMTM process[64] based on the extended version of the model developed by Vedeneev et al.[34] The variation of temperature within rather wide limits, for the optimal pressure and mixture composition and virtually complete oxygen conversion $\{[O_2]/[O_2]_0 < 5\%\}$, does not influence substantially the yields of the products (Fig. 16). The selectivity of the formation and the yield of methanol pass through a weak maximum in the region of 480 °C. Conversely, the selectivity of the formation of formaldehyde increases monotonically over the whole temperature range, its increase accelerating with rise in temperature. A redistribution of the reaction paths favouring the formation of formaldehyde, ethane, and ethene[49,50] is known to occur exactly in the temperature range above 500 °C.[49,50] Since at $P > 30$ atm and $T < 500$ °C, the target products, that is, methanol and formaldehyde, virtually do not decompose in the reactor after the complete conversion of oxygen,[40] the temperature range 420–480 °C may be considered optimal. The significant decrease in temperature (by up to 100 °C) known from the literature and due to the promoting action of higher hydrocarbons (on passing to natural gas) or to the use of catalysts does not lead to a substantial change in the proportions of the products.

An increase in the temperature is naturally accompanied by a sharp decrease in the reaction time t_r (here t_r is the time required for 95% oxygen conversion). According to an estimate, the

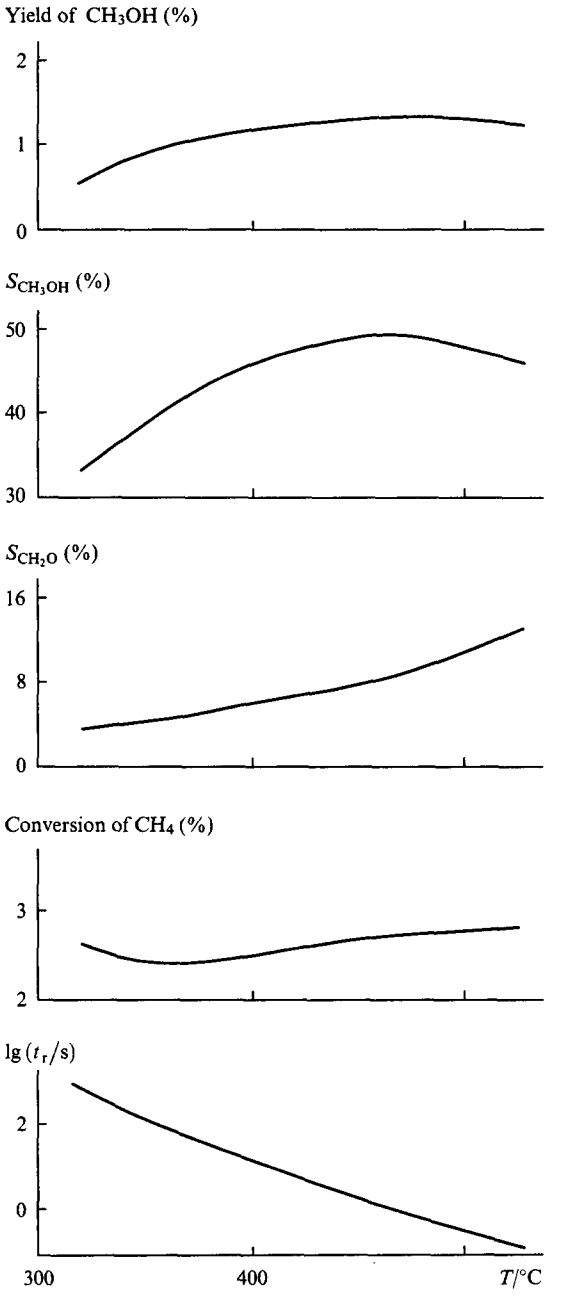


Figure 16. Calculated temperature dependences of some parameters of the DMTM process at $P = 100$ atm and $[O_2] = 3\%$.[64]

effective activation energy $E_{eff} \approx 167$ kJ mol^{-1}. This is in good agreement with the experimental value found from the temperature dependence of the self-ignition delays (from 163 to 188 kJ mol^{-1}).[22]

An increase in the oxygen concentration results primarily in an increase in the degree of conversion of methane (Fig. 17) and in heating of the mixture. The calculations were carried out for two extreme process regimes, namely isothermal and adiabatic regimes. Although significant difficulties are associated with the practical realisation of an isothermal regime at high pressures, these calculations are of undoubted interest, since they demonstrate the possibility, in principle, of improving a number of characteristics of the process, primarily, the yield of methanol, relative to the process conducted under nonisothermal conditions. At $[O_2] \leqslant 3\%$, when the real temperature rise does not exceed 120 °C, virtually identical results are achieved in both regimes. Allowance for nonisothermal conditions affects only the

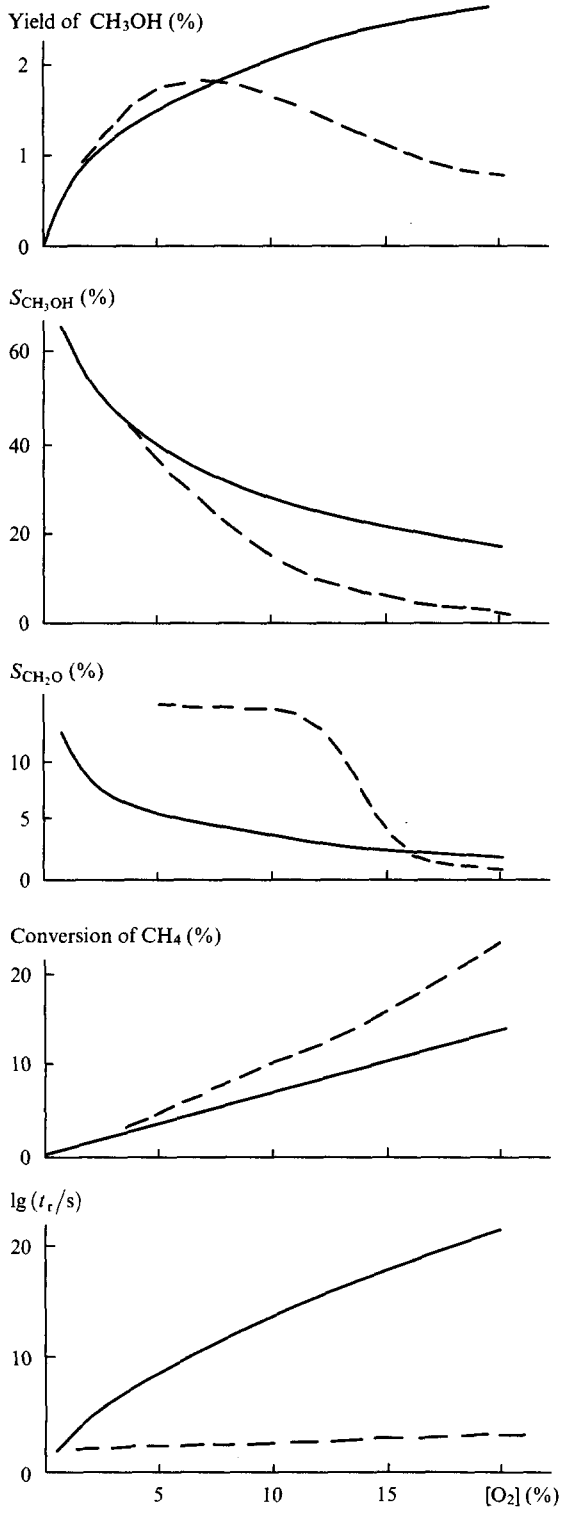


Figure 17. Calculated dependences of some parameters of the DMTM process on the initial oxygen concentration (P = 100 atm, T = 420 °C). Continuous lines correspond to the isothermal regime and dashed lines to the adiabatic regime.[64]

selectivity of the formation of formaldehyde and the reaction time (Fig. 17). Both versions of the calculation confirm the experimentally observed sharp decrease in the selectivity of the formation of methanol with increase in the oxygen concentration. At the same time, the isothermal calculation indicates that the yield of methanol grows slowly and monotonically as the oxygen concentration increases. The adiabatic calculation gives a qualitatively different picture. In this case, the selectivity of the formation of methanol drops so sharply that at [O_2] > 5% its yield also decreases. Thus, the use of mixtures with a higher concentration of oxygen to increase the yield of methanol is not expedient unless the problem of heat removal has been fully solved.

It is noteworthy that, according to the calculations, one of the initial reactants, namely oxygen, is virtually an inhibitor, since an increase in its concentration leads to a decrease in the rate of reaction (an increase in its duration). Even a substantial increase in the temperature of the gas mixture by its adiabatic heating does not balance entirely the inhibitory effect of oxygen.

The calculated pressure dependences of the yields of the main products are in good agreement with the experimental results

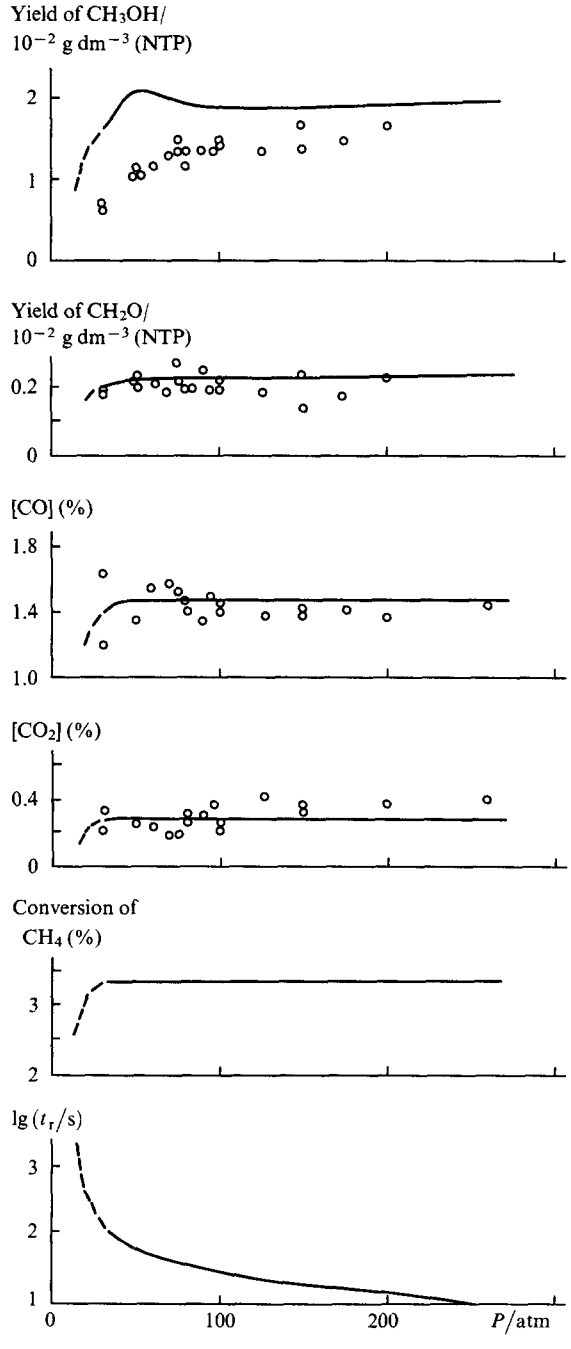


Figure 18. Calculated and experimental pressure dependences of some parameters of the DMTM process {T = 420 °C, [O_2] = 3%}. Continuous lines correspond to calculations[64] and circles correspond to experimental data.[62]

obtained in a pilot plant [62] (Fig. 18). According to the authors, the lower (by ~20%) yield of methanol is caused to a large extent by the imperfect separation unit, which does not exclude up to 10%–20% of the methanol formed being carried away with the gas phase.

Since the version of the model [34] used by Arutyunov et al.[64] (Table 7) is meant for describing processes occurring at pressures not less than 30 atm, the calculations carried out for pressures of 20 atm and especially 10 atm yield only qualitative results. Nevertheless, they reflect correctly the tendency towards a sharp decrease in the conversion of methane and in the product yields at pressures below 30 atm (see the dashed lines in Fig. 18). The sharp increase in the reaction time implies that, in this pressure region, there is a critical transition from the fast branched-chain reaction to a much slower chain-radical process.[57]

Together with the experimental results, Fig. 1 presents a calculated plot of the selectivity of the formation of methanol in the DMTM against the degree of conversion of methane.[64] It is clearly seen that the vast majority of the experimental points lie near the theoretical plot.

2. The role of pressure in the critical transitions between the steady-state regimes in the oxidation of methane

As shown in the previous section, the high-pressure oxidation of methane generally occurs by a branched-chain mechanism. In the present section, we consider the results of a theoretical study of the influence of pressure on the regime in which the reaction proceeds.[57]

The calculations were carried out for a mixture with the composition $CH_4 : O_2 = 9 : 1$ in the temperature range 600–750 K and the pressure range 1–100 atm. Fig. 19 shows the calculated pressure dependence of the reaction time (the time required for 95% oxygen conversion). It is clearly seen that there exists a narrow pressure range (the critical pressure P_{cr}) in which the process rate changes by several orders of magnitude. This can be caused only by a change in the reaction mechanism. The critical pressure is temperature dependent: it decreases from 6.2 atm at 600 K to 1.4 atm at 750 K (Fig. 20).

A change in the reaction mechanism should be manifested primarily by a change in the reaction kinetics. At pressures below P_{cr}, the shape of the kinetic curves is typical for nonbranched-chain reactions (more precisely, for reactions with weakly degenerate branching) (Fig. 21*a*). At pressures above P_{cr}, the self-acceleration of the reaction becomes much more clear-cut and the initial rate increases by a factor of approximately 10^3 (Fig. 21*b*).

The appearance of the critical phenomena discovered by calculations may be explained by analysing the initial stage of

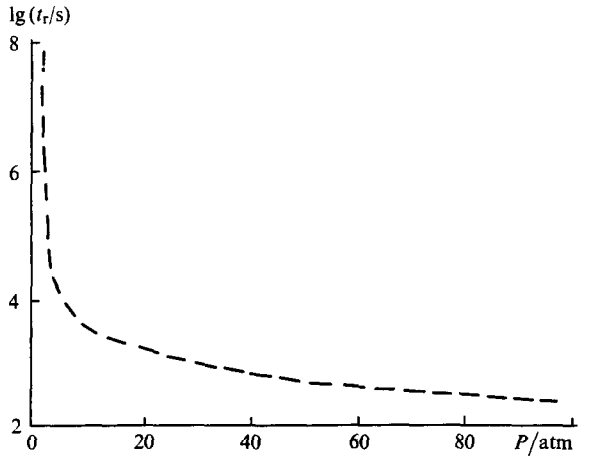


Figure 19. Pressure dependence of the reaction time at $T = 650$ K.[57]

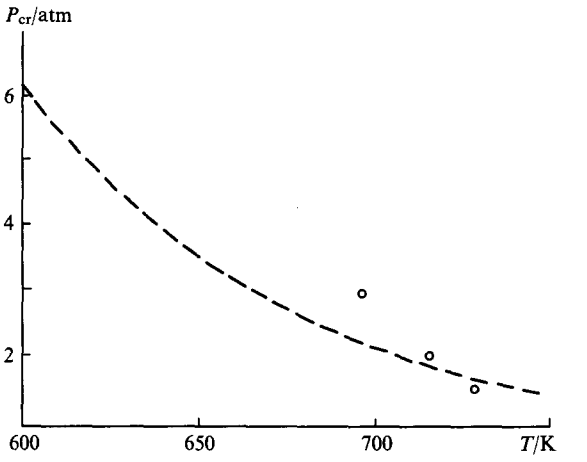


Figure 20. Temperature dependence of the critical pressure.[57] The circles represent experimental [119] temperatures of the onset of the reaction at $P = 1.5$, 2, and 3 atm.

the process [33] (Section V, 3b), where a steady-state branched-chain reaction occurs and the increase in the concentration of radicals is limited by the quadratic recombination of active centres.

In the one-centre approximation, one can easily obtain the expression

$$d[CH_3OO^{\cdot}]/dt = 2k_1[CH_4]_0[O_2]_0 + \varphi[CH_3OO^{\cdot}] - 2k_7[CH_3OO^{\cdot}]^2,$$

which implies that the character of the process is determined by the branching factor

$$\varphi = 2k_{17}[CH_4]_0 - k_{57},$$

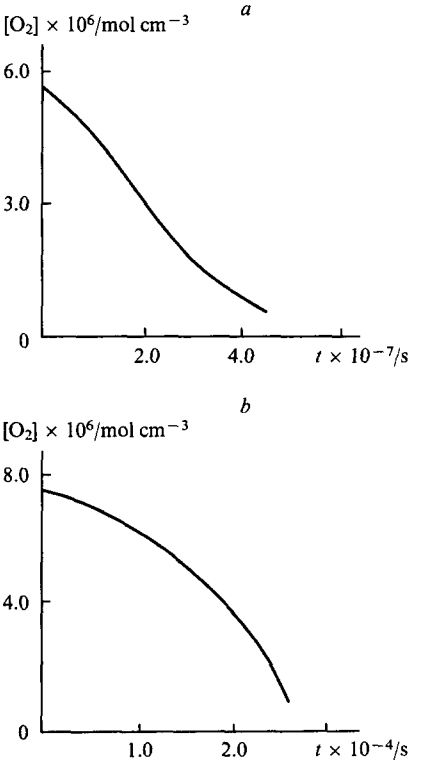


Figure 21. Kinetics of the consumption of oxygen at $T = 650$ K:[57] (*a*) $P = 3$ atm; (*b*) $P = 4$ atm.

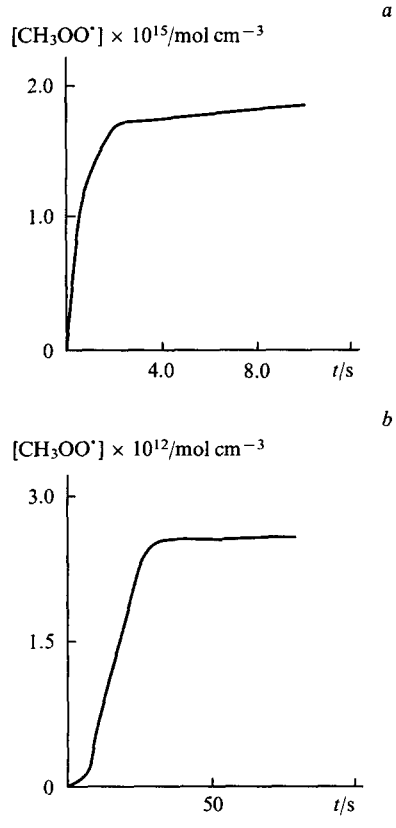


Figure 22. Kinetics of the accumulation of the methylperoxyl radicals at $T = 650$ K:[57] (*a*) $P = 3$ atm; (*b*) $P = 4$ atm.

(the numbers of the reactions and of the corresponding constants are given in Table 7).

At low pressures, $\varphi < 0$ and the concentration of the chain-propagating radicals is governed by the ratio of the rates of their generation and heterogeneous destruction. As the pressure increases, there is a transition to the region in which $\varphi > 0$, and the concentration of the propagating $CH_3OO^{\bullet}$ radicals is determined by the ratio of the rate of branching to the rate of their quadratic destruction. Since the rate of branching is several orders of magnitude higher than the rate of generation, the concentrations of the $CH_3OO^{\bullet}$ radicals at $\varphi > 0$ and $\varphi < 0$ differ from each other by approximately the same factor (Fig. 22). Figure 22 illustrates the calculations carried out using the full process scheme; however, the one-centre approximation for the initial stage of the DMTM gives the critical pressures $P_{cr}(600\,K) = 6$ atm and $P_{cr}(700\,K) = 2$ atm, which are in good agreement with the values found by calculations based on the full model.[57]

The calculated critical pressures correspond to the experimental plot of the temperature of the onset of reaction in the pressure range of 1.5–3 atm[119] (Fig. 20), despite the fact that the precise value of the critical pressure may depend on certain parameters that are difficult to take into account, for example, the reactor design. From the calculations performed, it is clear that the experimental conditions influence very strongly the initial stage and, consequently, the whole oxidation process. For example, whereas at $T = 650$ K and $P = 3$ atm the presence of a catalyst or a change in the reactor design has a substantial influence on the process, when the pressure is increased to 4 atm (this leads to an increase in the quasi-steady-state concentration of radicals by a factor of $10^3 - 10^4$) this influence can disappear almost entirely.

The results presented by Vedeneev et al.[57] account for the fact that the introduction of catalysts, or homogeneous promoters, or other initiation methods (Section III) does not influence appreciably the DMTM process, carried out at sufficiently high pressures. In fact, at $\varphi > 0$, an additional generation of radicals, even in much larger quantities than in the thermal process, cannot compete with their generation in the branched-chain reaction itself. Apparently, the fact that the use of catalysts becomes unnecessary when the oxidation of methane to formaldehyde is carried out at $P > 3$ atm in the temperature range 873–923 K can be explained in a similar way.[44]

3. Theoretical study of the possibility of the occurrence of cool-flame phenomena during the high-pressure oxidation of methane

As stated in Section V, the mechanism of the oxidation of methane is highly nonlinear, because virtually all the main chain initiation, chain propagation, chain termination, and branching reactions are nonlinear. Experimental results also indicate that, during the oxidation of methane, nonlinear phenomena can arise. These phenomena include the temperature oscillations at high pressures,[42] the appearance of cool flames,[101–103] and the existence of a region where the reaction rate has a negative temperature coefficient.[104] It is natural to assume that similar regimes may also arise in the oxidation of methane under other conditions that have not yet been studied, for example, at high pressures.

The main sign of the existence of cool flames in the oxidation of hydrocarbons is that a rapid increase in temperature is replaced by the retardation of the process before the reactants have undergone complete chemical conversion. The attainment of the peak conversion rate is usually accompanied by the luminescence of excited formaldehyde. Then the reaction either stops or, conversely accelerates again, up to the hot ignition of the mixture. Two or more cool-flame flashes can occur. In those cases where the appearance of cool flame is followed by the self-ignition of the mixture, the process includes at least two stages, namely, the cool-flame stage and the hot-ignition stage.[99, 100]

Basevich et al.[105] carried out mathematical modelling of the homogeneous oxidation of methane under nonisothermal conditions, with heat removal from the reactor surface, based on the kinetic scheme for the oxidation of methane to methanol suggested previously[34] (Table 7).

The calculations were first carried out for conditions under which successive cool-flame oxidation and ignition have been observed experimentally in methane–oxygen mixtures.[101] At initial temperatures $T_0 < 710$ K, the reaction does not occur for up to 700 s. In the temperature range $T_0 = 728 - 753$ K, flashes with incomplete heat evolution are observed and are followed by retardation of the reaction, which is accompanied by a temperature drop caused by the cooling of the reaction mixture by the reactor walls (Fig. 23). At $T_0 > 758$ K, ignition occurs (the arrows

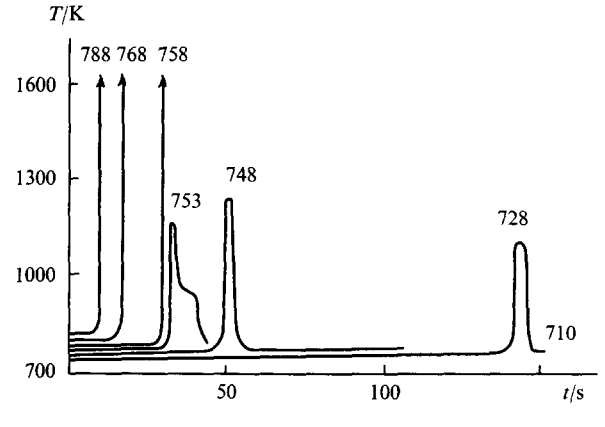


Figure 23. Calculated reaction time dependences of the reaction temperature for methane–oxygen mixtures[105] under the following experimental conditions: $[CH_4]_0 = 67\%$, $[O_2]_0 = 33\%$, $P = 0.92$ atm. The numerals denote the initial temperatures (K).

at the ends of the curves denote a further increase in the temperature). The calculations are in fairly good agreement with the experimental results.[101]

There are almost no experimental data dealing with cool-flame phenomena under the conditions of the high-pressure oxidation of methane. Therefore, a series of calculations involving gradual transition to high pressures were performed in the modelling, so that signs of the appearance of a cool flame could be detected in each stage.[105] The calculations were carried out for the pressures $P_0 = 1$, 1.8, 4.6, 9.2, 18.4, 70, and 100 atm, at the constant initial temperature $T_0 = 710$ K, and at the initial concentrations $[CH_4]_0 = 67\%$ and $[O_2]_0 = 33\%$.

In the analysis of the results of modelling, a general rule was discovered: an increase in pressure leads to the self-ignition of the mixture, the ignition being achieved after progressively shorter periods. Even intense heat transfer (within the limits of reasonable heat-transfer coefficients) from the gas to the reactor walls cannot stop ignition and cause a reverse temperature variation, although it does increase the induction periods (the times required for the development of the reaction before self-ignition). However, the increase in temperature is accompanied by explicit signs of the cool-flame stage. Fig. 24 shows a typical dependence of the temperature of the mixture on reaction time. When the time scale is expressed in seconds, there are no signs of the appearance of a cool flame, and the curve can seemingly be referred to a normal self-ignition process. However, on the microsecond time scale one can see that, after $t = 4.65$ s, the increase in the temperature to 1400 K is followed by retardation of the reaction, and the next flash occurs only ~ 10 μs later. Thus, in the present case, the duration of the first stage is 4.65 s and that of the second is ~ 10 μs. Of course, it is extremely difficult to detect these two stages experimentally. The calculated kinetic curves and the time dependences of the reaction temperature under the conditions of the self-ignition of methane–oxygen mixtures at 70 atm are presented in Fig. 25. A similar $T(t)$ plot is also obtained in the absence of heat losses. Further analysis showed that similar features are also observed at low pressures, for example, under the conditions indicated in the caption to Fig. 23 (at $T \geqslant 750$ K), when the ignition on the time scale expressed in seconds seems to be a one-stage process.

The calculations were also carried out for $P_0 = 100$ atm and the temperatures $T_0 = 683-710$ K, but for lower oxygen contents, which is typical for the direct homogeneous oxidation of methane to methanol. It turned out that, as the oxygen content decreases, the signs of a cool flame become increasingly less clear-cut and for $[O_2] \leqslant 5\%$ they disappear entirely.

The elucidation of the mechanism of the appearance of cool flames and the subsequent retardation of the reaction remains the most important problem. This is a very complex nonlinear process involving critical phenomena, which is not amenable to a simple interpretation. For example, it cannot be explained by the mere shift of the equilibrium

$$CH_3^{\cdot} + O_2 \rightleftharpoons CH_3OO^{\cdot},$$

to the left with increase in temperature, although the decomposition of the methylperoxyl radical certainly leads to a decrease in its concentration and to a change in the reaction mechanism, because in the first stage, prior to the appearance of a cool flame, branching is accomplished primarily via methyl hydroperoxide, whereas after the appearance of a cool flame, in the high-temperature region, it occurs mostly via hydrogen peroxide. Other reactions of methylperoxyl radicals are also significant in the mechanism by which a cool flame arises.

It should be emphasised that a qualitative agreement between the calculations[105] and the experimental results[101] was achieved without any adjustment of the kinetic parameters of the model, except that the pressure dependences of the rate constants for some reactions were taken into account.[34] No attempts to attain a closer agreement with the experimental values were undertaken, because the main task was to discover whether a kinetic description of phenomena of this type is possible in principle.

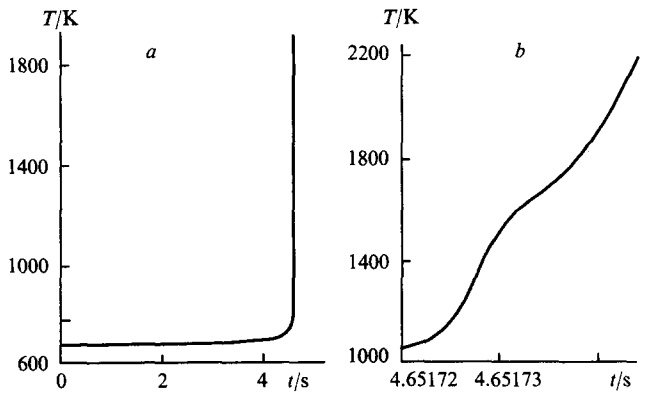


Figure 24. Calculated reaction time dependences of the reaction temperature on time scales in terms of seconds (*a*) and microseconds (*b*) for methane-oxygen mixtures at a high pressure.[105] $[CH_4]_0 = 67\%$, $[O_2]_0 = 33\%$, $P = 70$ atm, $T_0 = 710$ K.

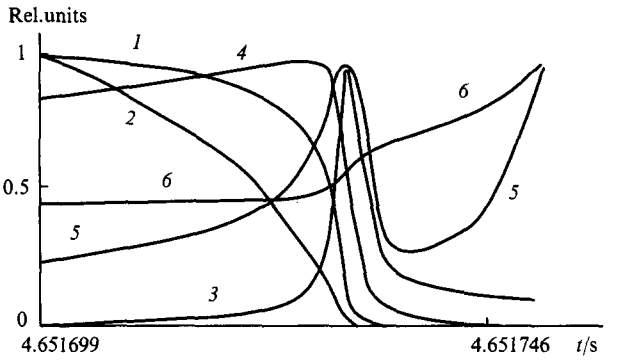


Figure 25. Calculated kinetic curves (*1*–*5*) and reaction time dependence of the reaction temperature (*6*) under the conditions of the self-ignition of methane-oxygen mixtures at a high pressure.[105] $[CH_4]_0 = 67\%$, $[O_2]_0 = 33\%$, $P = 70$ atm, $T_0 = 710$ K. The maximum concentrations corresponding to 1 on the ordinate axis (mol cm^{-3}): (*1*) $[H_2O_2] = 2.279 \times 10^{-6}$; (*2*) $[CH_3OOH] = 1.412 \times 10^{-8}$; (*3*) $[HO_2^{\cdot}] = 1.619 \times 10^{-6}$; (*4*) $[CH_3O_2^{\cdot}] = 2.156 \times 10^{-7}$; (*5*) $[H^{\cdot}] = 1.420 \times 10^{-8}$. The maximum temperature T_{max} on curve *6* is 2273 K.

4. The influence of mixing of the reactants on the product yield

In the kinetic modelling of the homogeneous oxidation of methane to methanol, the transverse and axial diffusion processes are usually neglected, for the sake of simplicity, even in the most commonly encountered case where the initial reactants, methane and an oxidant (oxygen or air), are mixed directly in the reactor. However, some workers, for example, Gesser et al.,[28] have noted that it is very important to achieve the homogeneity of the mixture in order to obtain a high yield of methanol. Therefore, the need arose to find out whether or not the influence of mixing on the main chemical reaction may be ignored and to identify the conditions under which this influence is insignificant. This problem has been analysed by Basevich et al.[120]

A very simple flow reactor was considered in which air is supplied along an axial channel and methane is supplied along an outer coaxial channel. Then the reactants are mixed and interact to afford methanol. To simplify the complex two-dimensional problem arising during the joint consideration of the transverse (along the y axis) and axial (along the x axis) diffusion, these two types of diffusion were considered independently of each other.

In addition, the process was assumed to be isothermal, which is fairly close to the actual conditions during the oxidation of methane to methanol.

In the calculations with allowance for the transverse diffusion, two further assumptions were made:

(1) the rates of entry of the reactants via both channels are identical (isokinetic flow) and coincide with the flow rate in the reactor;

(2) the concentration gradients along the x axis are small compared with those along the y axis and may be ignored.

The initial distribution of the methane and oxygen concentrations was specified as power functions taking into account the position of the initial point in the reactor. The location of the boundary between methane and oxygen corresponded to the chosen ratio of $[CH_4]$ and $[O_2]$, and the time t determined the position x of the cross-section being considered: $x = vt$, where v is the flow rate of the gas in the reactor.

The modelling was based on the mechanism suggested by Vedeneev et al.[34] (Table 7) with some refinements.[120] The problem under consideration is much more complex than the simple kinetic problem for a homogeneous mixture, since in this case one should take into account not only the chemical reaction but also the diffusion of all the components. Hence, a space coordinate is added to the time coordinate and the kinetic problem is solved simultaneously at all the points in space specified by the plotting step. Therefore, a number of additional expedients were used in the calculations in order to reduce the size of the kinetic scheme being processed and diminish the scale of the calculations.[120]

Two extreme gas flow regimes in the reactor were considered separately. These are laminar flow (Reynolds numbers $R < 2000$), which corresponds to the normal conditions in laboratory experiments, and turbulent flow ($R > 2000$), which is more typical for industrial large-scale reactors. This large difference between the conditions in the flow of the gas mixture and hence between the mixing conditions in laboratory reactors and industrial units permanently poses the question whether data obtained in laboratory studies may be legitimately transferred to industrial plants.

The calculations were carried out for the methane–air system at a pressure of 100 atm and a temperature of 683 K in a reactor 4 cm in diameter with a central channel of variable cross-section for the air supply. Typical results of the calculation carried out for a laminar flow are presented in Fig. 26, which gives an estimate of the spatial distribution of the methane, oxygen, and methanol concentrations at various times.

In the initial moment, $t = 0$, the reactants are not mixed, the concentration of the oxidant at the reactor axis $[O_2]_0 = 20.9\%$, and the concentration of methane at the periphery $[CH_4]_0 = 100\%$. For the chosen reactor size, this corresponds to the $[CH_4]:[O_2] = 33.6:1$ ratio, typical for the DMTM process. At consecutive times of 0.93, 2.40, and 3.90 s, the concentrations of the components are affected by the diffusion of oxygen to the periphery, by the diffusion of methane to the reactor axis, and by the simultaneous chemical reaction producing methanol. The distribution of the concentrations of all the other intermediate and final products was also calculated.

From Fig. 26, it can be seen that the concentrations of the reactants do not level off over the reactor cross-section in the time interval under consideration: the methane concentration on the reactor axis ($y = 0$) at the end of the process is only 58%, and that of free oxygen is 12%. The time required for the reaction in the homogeneous mixture to be completed (that is, the time required for the consumption of 99% of the oxygen $t_r = 4.45$ s) is insufficient for the complete mixing of the reactants, i.e. $t_r < t_{mix}$, where t_{mix} is the mixing time. This accounts for the low degree of conversion η, which proved to be only 0.32%. The selectivity with respect to methanol, $S_{CH_3OH} = 47.6\%$, is also lower than that in the homogeneous mixture, in which $S_{CH_3OH} = 50.2\%$ (Table 8). In addition, during the oxidation of methane with slow molecular mixing along the whole length of the reactor, large volumes of the mixture with an oxygen content more than 5%, capable of self-ignition, are formed (Fig. 26), which makes the process less stable.

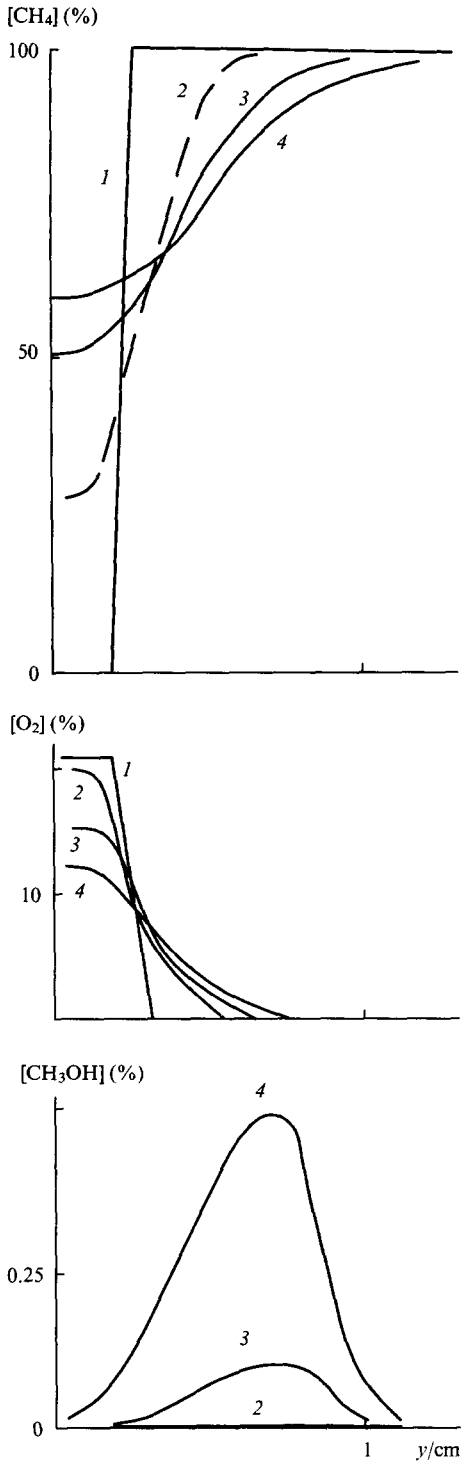


Figure 26. Concentration profiles for some components of the methane oxidation reaction in the transverse cross-section of a reactor with molecular diffusion.[120] $P = 100$ atm, $T = 683$ K, $[CH_4]:[O_2] = 33.6:1$, air as the oxidant. Time (s): (*1*) 0; (*2*) 0.93; (*3*) 2.40; (*4*) 3.90.

In the case of turbulent flow, the diffusion coefficient, which is the same for all the components, was calculated from the equation[121]

$$D = \varepsilon v L,$$

Table 8. Influence of the transverse diffusion of the reactants and of the conditions in the flow of gas mixture on the degree of conversion of methane and the selectivity of the formation of methanol.[120]

Flow	t/s	$[O_2]_0$ (%)	η (%)[a]		S_{CH_3OH} (%)[a]	
			A	B	A	B
Laminar	2.27	0.52	0.86	0.19	68.2	63.0
	4.45	2.61	2.87	0.32	50.2	47.6
	6.87	4.7	5.14	2.5	39.6	33.6
Turbulent	2.27	0.52	0.86	0.89	68.2	68.7
	4.45	2.61	2.87	2.66	50.2	54.0
	6.87	4.7	5.14	5.0	39.6	41.5

[a] Supply of the reactants: A — joint, B — separate.

adopting the recommended values for the degree of turbulence $\varepsilon = 0.03$ and the scale of turbulence $L = 0.35d$ (d is the reactor diameter). The calculations for a pilot unit[31] ($d = 4.0$ cm, flow rate $v = 3$ m s^{-1}) yielded $D = 12$ cm^2 s^{-1}, which is greater than the molecular diffusion coefficients by three orders of magnitude.

The distribution of the concentrations in the case of turbulent diffusion at various times is shown in Fig. 27 under the same conditions as in Fig. 26. In this case, the mixing is very rapid and is completed in less than 0.9 s. During this time, less than 1% of the final quantity of methanol is formed. After that, the reactions proceed in the resulting homogeneous mixture. In the example shown in Fig. 27, the degree of conversion is practically the same as in a homogeneous mixture (2.66%), and the selectivity with respect to methanol $S_{CH_3OH} = 54\%$ (Table 8), i.e. the case where $t_{mix} < t_r$ is realised. Thus, for turbulent diffusion, the degree of conversion is similar to the corresponding value attained in a homogeneous mixture and the selectivity is even somewhat higher. This is natural, because the duration of the chemical reaction is much greater than the characteristic time of the turbulence (frequencies from 10 to 1000 Hz). Hence, the turbulence does not influence the course of the reaction. The results obtained are in agreement with the experimental data indicating that good characteristics of the process are achieved when the reactants are quickly mixed by jets, the velocity of which is close to the velocity of sound.[27] For rapid turbulent mixing, mixtures capable of self-ignition exist only in the initial section of the reactor (Fig. 27); in other words, the process is more stable than that involving slow molecular mixing.

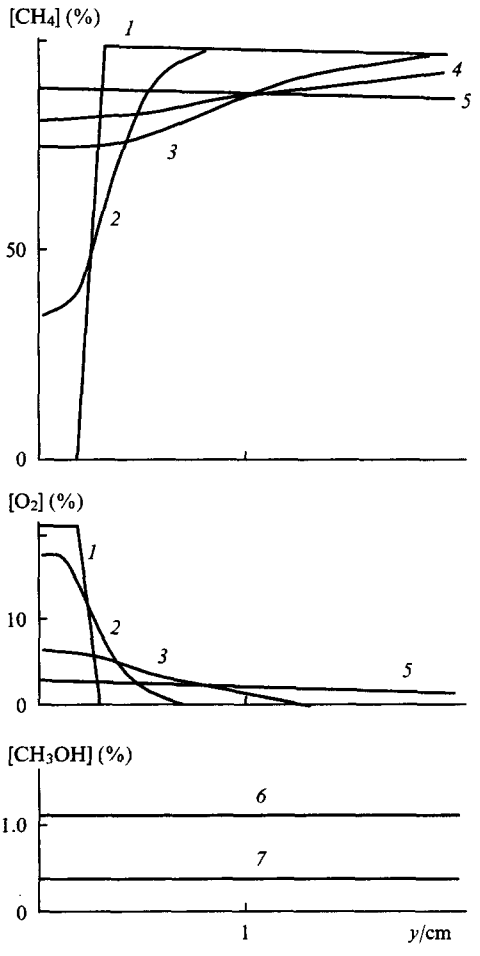


Figure 27. Concentration profiles for some components of the oxidation of methane in the transverse cross-section of a reactor with turbulent diffusion.[120] $P = 100$ atm, $T = 683$ K, $[CH_4]:[O_2] = 33.6:1$, air as the oxidant. Time (s): (*1*) 0; (*2*) 0.0015; (*3*) 0.014; (*4*) 0.029; (*5*) 0.9; (*6*) 6.3; (*7*) 90.

Calculations[120] have shown that, for molecular diffusion coefficients, axial diffusion has no influence on the DMTM process. When the diffusion coefficients correspond to a turbulent regime, the observed influence of axial diffusion is slight: the concentration profiles shift somewhat along the axis to the left, that is, to the entry to the reactor, and the yields of all the main products virtually do not change.

Thus, the following conclusions can be drawn:

(a) kinetic modelling with no allowance for diffusion under the conditions of rapid mixing provides a qualitatively correct description of the chemical process and evaluation of the product yields;

(b) when methane and oxygen are supplied separately, their rapid mixing ensuring that the $t_{mix} \ll t_r$ relation holds is a necessary condition for a high degree of conversion of methane and high selectivity of the formation of methanol;

(c) in the case of slow mixing, the process is less stable.

5. Modelling of circulation regimes in the oxidation of methane

To make the DMTM process suitable for the industrial production of methanol, one should increase the degree of conversion of natural gas, while maintaining the high selectivity of the formation of methanol. In reality, this can be achieved by conducting the process according to a circulation scheme. In this process, reactive gas-phase products (carbon monoxide and hydrogen and also nitrogen, in the case where oxidation is carried out with air) can accumulate in the circulating gases. This naturally influences the characteristics of the DMTM technological process. To elucidate the possibility of improving the characteristics of the process by using a circulation scheme, the corresponding theoretical analysis has been carried out with the aid of a special kinetic programme.[122] The kinetic model developed by Vedeneev et al.[34] supplemented by reactions that take more precise account of the interaction between the products formed, was used in the calculations.

The methane oxidation process with product recirculation includes three stages.

1. Methane and an oxidising agent (air or oxygen) enter the reactor, where methane is oxidised.

2. The gases leaving the reactor are cooled and the liquid phase containing the target product (methanol) is separated. As this takes place, all the unstable intermediates decompose.

3. The gaseous products are partly discarded, and the rest is mixed with fresh methane (which makes up for the lost liquid phase and for the discarded part of the gas phase) compressed to the operating pressure, heated, and injected into the reactor once again, together with the oxidising agent.

The calculations were carried out for conditions close to the optimal conditions for a flow-type process: a temperature of

713 K, a pressure of 100 atm, a reaction time corresponding to the consumption of oxygen (several seconds), and a constant oxygen concentration at the reactor inlet of 2.2%.

The relative quantity of the gas being recycled λ has the greatest influence on the course of the process involving circulation ($\lambda = 0$ means that all the gas is discarded, which corresponds to a flow regime; $\lambda = 1$ means that no gas is discarded, and stable gaseous products are accumulated in the circulating gas, while the methane concentration at the reactor inlet continuously decreases). If oxygen is used as the oxidant, even a considerable number of cycles N carried out at $\lambda = 1$ influences only slightly the initial methane concentration $[CH_4]_0$ (Fig. 28). Accordingly, the quantity of methanol formed in each cycle decreases equally slowly. The total amount of the methanol collected continuously increases, so that at $N = 30$ its overall yield $\Sigma[CH_3OH]$ reaches ~30%. The only component that is also accumulated continuously in the circulating gas is carbon dioxide (Fig. 29); its concentration reaches 17%. The other gaseous products (carbon monoxide, hydrogen, and ethane) are accumulated much more slowly, because they are consumed during the reaction. The concentrations of these compounds after 30 cycles are 2.4, 1.2, and 0.17%, respectively.

The selectivity of the formation of methanol in the first pass under these conditions is 57.2%. As the number of cycles increases, S_{CH_3OH} decreases somewhat, but for $N = 30$ it is still fairly high and amounts to 50%, so that on average $S_{CH_3OH} = 52\%$. The results obtained for $0 < \lambda < 1$ are intermediate between those observed in the flow and closed-loop (without discard) regimes.

Thus, when the circulation scheme is used, the degree of conversion in one pass virtually does not decrease, the selectivity decreases only slightly, but, in return, the overall quantities of methane being converted and methanol formed increase sharply. At $\lambda < 1$, after a fairly large number of cycles have been carried out, the system approaches a steady state in which the concentrations of the reaction products at the end of each step remain virtually constant. This corresponds to the realisation of the circulation scheme in the steady-state regime. The higher the rate of accumulation of the nonconsumable inert gases (carbon dioxide and nitrogen), the larger the proportion of the gas, which needs to be discarded (that is, the smaller the value of λ) and the smaller the number of cycles required for a steady-state to be achieved. However, the degree of conversion of the initial

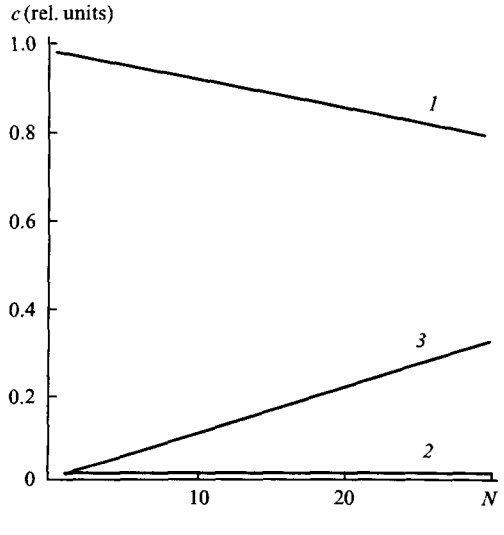


Figure 28. Dependences of the initial methane concentration (*1*), the final current methanol concentration (*2*), and the overall yield of methanol (*3*) on the number of cycles (N) at $P = 100$ atm, $T_0 = 713$ K, $[O_2]_0 = 2.2\%$, $[CH_4]_0 = 97.8\%$.[122]

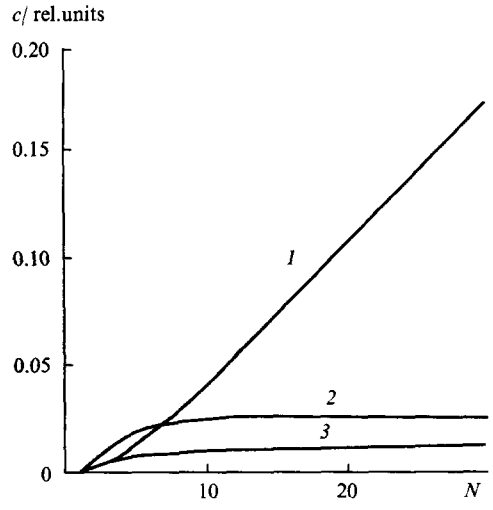


Figure 29. Dependences of the final concentrations of CO_2 (*1*), CO (*2*), and H_2 (*3*) on the number of cycles (N) at $P = 100$ atm, $T_0 = 713$ K, $[O_2]_0 = 2.2\%$, $[CH_4]_0 = 97.8\%$.[122]

methane diminishes correspondingly. The selectivity at steady-state depends on the ratio between the steady-state concentrations of methane and oxygen, which is determined by the value of λ, chosen from the standpoint of attaining the optimal yields of the products.

The DMTM circulation scheme has also been modelled for the case where air is used as the oxidising agent.[122] The λ parameter was varied within limits ensuring a steady-state proportion of nitrogen in the working medium (up to 60%).

It may be assumed that when the circulation scheme is used, the energy expenditure is lower than in the flow regime, because in the former case the quantity of mains gas that has to be brought to the operating pressure is much smaller. However, the productivity of the reactor diminishes due to the lowering of the steady-state initial methane concentration and the decrease in the selectivity of the formation of methanol. Therefore, the optimal version of the circulation scheme should be chosen with allowance for particular technical and economic conditions including the possibility of utilising the discarded gases, for example, for heating the operating mixture, etc.

Thus, the modelling has demonstrated the possibility of implementing the circulation scheme for the oxidation of methane, in which the degree of conversion of methane increases by more than an order of magnitude with no substantial decrease in the selectivity of its formation.

VII. Technical and economic aspects of the direct oxidation of natural gas to methanol

1. Prospects for the increase in the use of methanol and other oxygenates

Methanol is among the main products of organic synthesis. The constant intense development of its production is due to the continuous extension of its applications, the main ones being the production of formaldehyde, acetic acid, solvents, ethers, and other chemicals.[81,123] In the future, methanol may form a universal basis for organic synthesis. It is finding an increasing use in the production of high-octane components of motor fuels, primarily, of methyl *tert*-butyl ether (MTBE).[124] In the overall world consumption of methanol in 1990 (19.6 million tonnes), 40% was due to the production of formaldehyde, 45% was due to other chemical products, and 14% was accounted for by fuel components.

From 1990 to 1995, the annual increase in the demand for methanol in North America should reach 6.6%, while in the

previous five years it was only 4.3%. The major part of this increase is accounted for by the production of MTBE, necessary to meet demands associated with protection of the atmosphere against the pollutants arising during the combustion of automobile fuels. The USA demand for MTBE in 1995 should be from 15 to 30 million tonnes. However, the production of oxygenates may delay the introduction of clean fuels. Without new plants for the synthesis of methanol, North America will experience a deficit in the capacity for the production of methanol estimated as 4.7 million tonnes a year already by 1995.[125]

Whereas in 1990 the producers of formaldehyde were the main users of methanol in the USA, already by 1995 from 38% to 55% of methanol will be consumed for the production of MTBE.[125] The boom in the consumption of MTBE in the USA cannot but influence the world production of MTBE and methanol, since the USA import not only MTBE but also the methanol and butane necessary for its production.[80] It is expected that in 1991–2000 the annual increase in the world consumption of methanol will be 5.6% and the increase in the consumption of MTBE will be 20%.[80] Forecasts predict that by 2001 the overall consumption of oxygenates will increase by a factor of 10 with respect to its current level[126] and the cost of their production will amount to 50 billion dollars by 2000.[127] In view of the fact that since 1995 more than 85% of the petrol used in the USA should contain oxygenates, a global deficit of oxygenates, including methanol, and a rise in their prices have been predicted.[127]

Methanol is an alternative to an oil distillate fuel. There are examples of its use in power plants as a fuel for gas turbines. Boilers can also run on methanol. The main advantage of methanol over distillate fuels is that it contains no sulfur. The possible consumers of methanol are power plants, transport, food industry, metallurgy (reducing gas), and some other industries. In certain cases, it is economically favourable to produce hydrogen from methanol.[123]

The significance of methanol as one of the most promising alternative fuels for transport has long been discussed in the literature[128–130] [see also the proceedings of the international symposia on alcohol fuels IX ISAF, Florence (Italy), 1991; X ISAF Colorado-Springs (USA), 1993]. If full advantage is taken of the beneficial motor-fuel properties, primarily the high octane numbers, of methanol, mixtures of alcohols and petrol–methanol mixtures, these fuels become quite competitive with modern petrols.[128,131] Since automobiles can run on mixtures containing about 20% of methanol or other alcohols, the use of these mixtures may become an important source of the energy for transport.[123]

The energetic efficiency of the engine specially developed to run on methanol is 30% higher than that of the analogous petrol engine.[131] Its environmental advantages are particularly attractive. However, the large-scale use of methanol is impossible without a reconstruction of both the methanol-producing and oil refining industries and, most of all, of the system of distribution of automobile fuels.

As a response to the need to improve the environmental characteristics of motor fuels, the so called 'reformulated gasoline' has been developed. This fuel contains additives such as methanol, ethanol, MTBE, ETBE, mixtures of alcohols, etc., which has made it possible to increase the oxygen content in a fuel to 3.7 %.[132] Large-capacity production of MTBE already exists in many countries and its world output in 1990 amounted to 8 million tonnes (13 million tonnes has been predicted for 1995 and 25 million tonnes for 2000).[133] However, an important place in the concept of ecologically clean fuels is occupied by the 'fuel alcohols', that is, by mixtures of alcohols used either by themselves or as high-octane additives to motor fuels.[132,134] The fuel alcohols consisting of methanol to which 20% – 30% of higher alcohols has been added make it possible to increase the octane number and to reduce the amount of harmful exhaust gases; their mixtures with petrols do not separate into layers in the presence of water and they are a real alternative to ethers.[132,134] The production of these fuels, unlike the production of MTBE and other ethers, does not require the corresponding alkenes, which are themselves valuable products and in limited supply.[132]

Methanol can be used to fuel an engine in a pure state, as an emulsion in hydrocarbons, or as one of the components in a separate fuel supply system. It can be preliminarily converted into CO and H_2 and into highly inflammable compounds (like dimethyl ether). Finally, it can be converted in the presence of catalysts (to obtain heat) or in fuel cells (to obtain electric energy). At present, one of the most feasible schemes for the operation of electric cars involves the catalytic conversion of methanol into hydrogen, which supplies the vehicle-borne fuel cells.[125]

All the promising aspects of the development of environmentally clean transport are associated in one way or another with the use of alcohols, either directly in fuel mixtures or as intermediate compounds in the synthesis of MTBE and other ethers. This raises the problem of lowering the cost of methanol, which has so far been neglected within the framework of the traditional technology for its production via synthesis gas.[83]

Natural gas is almost unreservedly considered to be the main raw material source for meeting the increasing demand for methanol, although a sharp increase in the use of natural gas for the production of methanol requires a thorough economic analysis.[135]

2. Technical and economic estimates of the technological process for the direct oxidation of natural gas to methanol

Extensive application of a new technology for the production of methanol is impossible without serious economic prerequisites. Some economic estimates of the effectiveness of this process have been reported.[67,87,136–138]

Edwards and Foster[87] have reported an economic assessment of the production of methanol by the direct catalytic partial oxidation of natural gas with an output of 2000 tonnes per day. If the selectivity of the formation of methanol is more than 77%, the direct process undoubtedly proves to be more economically viable than the traditional method. With regard to consumption of heat and hydrocarbons, the effectiveness of the direct partial oxidation of methane is also higher.[136] It has been reported[67] that methanol obtained by the direct oxidation would be 20% – 30% cheaper than the product obtained by the existing methods. Some economic aspects have been discussed by Renesme et al.[138] and Crocco.[139]

According to economic calculations, the cost of raw materials accounts for ~50% of the operating costs, however there exist vast reserves including the casing-head gas, oil refinery gases, and de-ethanisation gases, which now have no commercial value and are burned in flares, thus polluting the environment.

The use of gases containing substantial amounts of higher hydrocarbons would make it possible to decrease sharply the pressure and the temperature of the process. The degree of conversion of these gases in one pass can be as high as 20%, instead of 3%–4% obtained in the oxidation of methane; the efficiency may be increased further by using the circulation oxidation scheme. In addition, this process may yield valuable products, for example, iso-alcohols or aldehydes, in fairly high yields, and the isolation of these products would recoup a considerable part of the production costs.

The currently available technical solutions allow the selectivity of the formation of methanol in this process to be increased to 60% or more, and the process may therefore become nearly profitable.

3. Technological scheme for the direct oxidation of methane to methanol

The technological scheme for the DMTM is fairly simple, and this is one of its main advantages. The catalytic version of the process has been described in a paper cited above.[87] A basic scheme for a plant producing methanol by the direct gas-phase oxidation of natural gas with a productivity of 10 000 tonnes of methanol per

year, developed within the framework of the Russian state programme 'Environmentally Clean Power Engineering' has been reported.[55] The plant is meant to satisfy the local needs of the gas-industry for methanol and motor fuels. The project involves the development and the subsequent commercial production of self-contained modular units for the direct homogeneous conversion of natural gas into methanol and provides for the possibility of further transformation of methanol into a high-octane petrol.

The process makes it possible to avoid the intermediate formation of the synthesis gas, which is unfavourable from the thermodynamic standpoint, and the equipment involved is relatively simple. The project is based on a kinetic analysis[33-37] and on the results of pilot tests on a unit with a production capacity of 100 tonnes of methanol per year.[31] The main parameters of the process are: pressure 5–10 MPa, temperature 380–480 °C (depending on the composition of the gas), oxygen concentration 2.8%, degree of conversion of oxygen 95%–98%, yield of crude methanol 20 kg per 1000 m^3 of the input gas or 0.63 kg per 1 kg of the converted gas.[55]

After being compressed to an operating pressure of 5–10 MPa and heated to 380–480 °C, natural gas enters a gas-phase mixer, which also serves as the reactor. Oxygen (or air) is conveyed to the same reactor at a pressure of 10 MPa. After the reaction, the mixture is cooled in a heat exchanger and then conveyed to a condenser, in which liquid products are condensed. It then goes to an apparatus for the neutralisation of acids. After that, the liquid phase is separated from the unreacted gas in a separator. The resulting liquid product is concentrated in a fractionating column. Simultaneously, the formaldehyde formed is separated as an aqueous solution (formalin). The unchanged gases are either discharged to a gas pipeline or reenter the unit inlet. If there is an additional catalytic unit for producing petrol, the crude methanol obtained is supplied directly to the inlet of this unit. The degree of conversion of natural gas in one pass is less than 3%. Since the process yields no significant amounts of incombustible side products, the natural gas may be returned to the gas pipeline or recycled.[55]

The unit is meant for the independent conversion of natural gases into crude methanol, containing more than 90% methanol, in remote gas fields where there is no developed infrastructure. It does not require a complex repair base or highly qualified personnel. The methanol produced is supposed to be consumed at site as an inhibitor of hydrate formation in the extraction and transport of natural gas and also for its direct conversion in a second unit into petrol with an octane number of 93 (3300 tonnes per year) and for other purposes. The formalin obtained as a side product also finds application in the gas fields.

In the course of the implementation of this project, a number of novel technological approaches were developed which allowed the yield of methanol to be increased by approximately 30%. The use of this technology (with the parameters already attained) in remote or relatively inaccessible oil and gas fields is at least 30% more profitable than the traditional method for the production of methanol.

As noted above, when oxygen is used as the oxidising agent, the content of incombustible impurities in the outgoing gases hardly increases and the gas can therefore be returned to the pipeline. In the case where this process is carried out just before the gas is dispensed to the consumer, the best way is to use the cheaper air as the oxidising agent.

The most significant drawback of the homogeneous partial oxidation of natural gas to methanol at high pressures is the need to maintain a low initial oxygen concentration (~3%) in order to achieve a satisfactory selectivity of the conversion of methane to methanol, and this precludes the possibility of attaining a sufficiently high degree of conversion of natural gas in a single pass through the reactor. It is therefore desirable to use a circulation scheme to increase the overall degree of conversion of natural gas.

4. The concept of small-capacity processes to meet the regional and related industrial requirements for oxygenates

At present, there are reasons for establishing a new 'sub-branch' within the structure of the gas-production industry, namely, small-capacity gas-processing chemistry, based largely on the production of methanol as the main intermediate compound. The small-capacity technological plant designed as a set of units (modular small-scale units, MSU) should be located in particular gas fields taking into account the locally available raw materials and the local needs for the hydrocarbon-based products.[140]

Estimates indicate that the operation over a period of 10–15 years of a MSU with a production capacity of ~3000 tonnes of products per year requires that the natural gas resources in the particular deposit be at least 0.3–0.5 billion m^3 and ensure a gas output of 30000 m^3 per day over the whole exploitation period. The vast majority of gas fields and newly found deposits comply with these requirements.[140]

Of the 1195 deposits of hydrocarbon gases in the C.I.S., 880 are small, their weighted average gas reserves being ~1.5 billion m^3 per deposit.[141] Connecting them to the main pipelines is unprofitable, and they also cannot be used as a source of raw materials for large-capacity chemical production. The only means of the industrial exploitation of these deposits is the processing at site of the extracted hydrocarbon raw materials by using MSU. The MSU can also be applied at condensed gas deposits, coal basins, which contain huge methane reserves, and any other hydrocarbon reserves that can be converted into the initial gaseous raw material, including biomass, the annual reproducible world resources of which are estimated as 200 billion tonnes.[140]

The undoubted simplicity of the DMTM technological scheme,[55] compared with the traditional schemes for the production of methanol or synthetic motor fuels via synthesis gas,[81] the weak dependence of the prime cost of the product on the production output, and modest demands on raw material sources are good prerequisites for the implementation of this scheme on MSU. Up to 7% of the methanol produced in our country is used to prevent the formation of gas hydrates during natural gas extraction and transportation; the expected annual demand by the gas industry for methanol in 2000 is 500 000 tonnes. The high cost of the delivery of methanol to the main gas fields, far exceeding its selling price, makes the conversion of natural gas into methanol directly in the gas fields very attractive. At the same time, these regions may be provided with motor fuels and with formaldehyde — a side product of the process.[55, 140]

Thus, the use of MSU for the direct processing of natural gas in gas fields in order to provide the corresponding regions with methanol and motor fuels proves to be intimately connected with the technological implementation of the DMTM process. The DMTM process realised as MSU may manifest its technical and economical advantages well before it finds an application in the large-capacity chemical industry.

VIII. Promising aspects of the scientific research dealing with direct oxidation of natural gas to methanol

In many countries, large investments are made in state and private research aimed at the effective use of the abundant natural gas resources.[142] The main purpose of these studies is to increase the effectiveness of the most promising processes for the production of methanol and higher hydrocarbons, which are potentially competitive with the traditional petroleum refining.

The research activity was greatly promoted by the discovery made in 1982 of catalysts ensuring high yields of ethane and ethene in the oxidative condensation of methane. In recent years, studies on the catalytic conversion of natural gas have been mostly concerned with the overcoming of kinetic barriers, which

apparently restrict the yields of C_2 hydrocarbons in the oxidative condensation of methane to ~25%.[75,118] This is sufficient to maintain interest in the scientific research but too low for the practical realisation of the process.

Regarding the direct gas-phase oxidation of methane to methanol, the challenge now is to reproduce on the pilot scale the high (up to 70% – 80%) selectivity of the process for the fairly high (more than 5%) degrees of conversion, which have been achieved in some laboratory studies.[28,38,41,43,45] These results, if obtained on the industrial scale, would permit the development of an undoubtedly profitable process.

Therefore, clear identification of the conditions or search for process regimes, which may lead, in principle, to such results, is a fundamental goal of the studies. In our opinion, this can be done by investigating periodic and cool-flame regimes in the oxidation of methane, in which the product yields may differ fundamentally from those obtained in other known regimes. The high degree of nonlinearity of the mechanism of the oxidation of methane (Section V) and the known data concerning the appearance of periodic phenomena, hysteresis, and cool flames during its oxidation (Section III, 8) make it possible to rely on the possibility of achieving in open reaction systems (among which are flow-type reactors[143]) steady-state oxidation regimes that have not yet been investigated, or those regimes which can be stabilised artificially by means of additional physical or chemical effects. This assumption is supported by the existence of several steady-state and oscillatory regimes in the oxidation of the near homologues of methane,[20] including ethane.[144] Since in such a complex system (the oxidation of hydrocarbons is apparently among the most complex systems, if biological processes are excluded[143]), a fortuitous experimental discovery of new regimes can hardly be expected, the main efforts should be concentrated on the analysis of the most realistic models (in the first place, on the stability of the regime).

The above problem is closely connected with the practically important task of analysing the stabilities of the known steady-state regimes in the case where the process is carried out in industrial-scale reactors. There are lots of reasons for the instability of a chemical process in an open system, for the appearance of non-steady-state regimes, pulsations, and oscillations, which may become dangerous. Therefore, conditions should be found in which the process would be so stable that any random fluctuation of the composition, temperature, and pressure would decay rapidly.

Yet another promising line of research is the study of the high-pressure oxidation of methane homologues, their mixtures, and the real natural gases, because the direct oxidation of gaseous hydrocarbons containing high proportions of methane homologues may provide appreciable technological and economic advantages. In our country, there are huge resources of these gases of both natural and industrial origin (ethane-containing natural gases, casing-head gases, refinery gases, de-ethanisation gases, etc.). The proportion of ethane-containing gases in the total explored gas resources is 30.5%,[145] and the amount of petroleum gas with high proportions of ethane, propane, and butane burned in flares every year reaches 12 – 15 billion m^3.[146] Since raw materials account for more than 50% of the production cost,[87] the use of gases of low value with high proportions of methane homologues can enhance sharply the economic effectiveness of the process and extend the range of its feedstock.

Evidently, the study of the influence of external parameters and gas composition on the detailed composition of the products as well as the search for various methods for its correction, including the subsequent additional catalytic treatment and partial isolation of products in order to obtain mixtures of standard composition and commercial products, will be of great importance.

The development of sufficiently predictive quantitative kinetic models of the high-pressure oxidation of methane homologues and the development of a model of the oxidation of the real natural gases based on them are also very important scientific tasks.

IX. Conclusion

Through the experimental and theoretical studies carried out for many years on the partial oxidation of methane and its homologues at high pressures, the chemical fundamentals of the direct synthesis of methanol and other oxygenates have been developed. The current level to which the technological process has been developed, its relative simplicity, its flexibility regarding production output, and its low power and capital requirements give this process in some cases real advantages over the traditional methods for the synthesis of methanol. The rapidly increasing demand of the world market for cheap methanol and other oxygenates and hence for flexible and highly-profitable methods for their production dictate the need to intensify the scientific research designed to discover the fundamental paths leading to the enhancement of the selectivity of the formation of methanol and of its yield in this process to the level of absolute profitability, to extend the range of raw materials by involving poorly utilised sources of gaseous hydrocarbons, and to develop optimal schemes for the organisation of the process.

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