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Kinetic features and industrial prospects of the selective oxidative cracking of light alkanes

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The results of kinetic investigations of selective oxidative cracking of light alkanes are analyzed and integrated. This process attracts researchers' attention owing to possible opportunities for designing new industrial processes based on light hydrocarbon feed. Particular attention is paid to ethane for which comprehensive and adequate models of oxidative conversion suitable for detailed analysis of the process kinetics have already been developed. The prospects for the practical application of methane homologues present in natural and associated gases in the selective oxidative cracking are discussed. The bibliography includes 85 references.

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I. Introduction

Efficient use of natural gaseous hydrocarbons is a primary challenge for science and engineering. First of all, this is caused by the fact that particularly gaseous hydrocarbons of various types account for the greater part of Earth Crust hydrocarbons (energy and petrochemical resources of the mankind).[1] The steady decline of the available resources of liquid hydrocarbons (oil), which are undoubtedly more convenient for the use and processing, neccessitates transition of the world economy to the gas raw materials. It is already obvious that the current century will be a gas century and, hence, a gas-based chemistry century. Owing to the noticeable decrease in the natural gas price over the last several years,[2] it is advantageous to use natural gas not only as a fuel but also as a chemical raw material. This accounts for the recent activity towards the construction of new gas-based chemical plants, especially in the USA and in Middle East countries, which have plentiful resources of cheap natural gas.

However, various sorts of natural and associated gases are highly diverse mixtures with variable compositions consisting mainly of $C_1 - C_6$ (or heavier) alkanes, which markedly differ, first of all, in the reactivity and also in

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physical properties.[3] Commercial separation of such mixtures into components requires sophisticated and expensive equipment and high energy expenditure; therefore, such separation is economically feasible only in the case of processing of large gas amounts (above 10^9 m^3 per year). The chemical processing of natural gases with high contents of heavy alkanes is an exceptionally complicated task, first of all, because of the large difference (several orders of magnitudes) between the component reactivities. The use of these gases as fuels in the modern gas turbine units and gas piston engines without pretreatment is almost impossible.[4, 5]

Furthermore, large hydrocarbon gas resources are concentrated particularly in remotely located, marginal and low-productivity sources. Among them are most of non-conventional sources of hydrocarbon gases (associated and shale gas, tight gas, coal-bed methane and so on). As the large conventional gas fields are depleted and the non-conventional sources are explored, the proportion of the latter in the world production will grow. The modern gas-based chemical processes, which are cost effective only for very large production capacity (more than a hundred thousand tonnes of the final product per year),[6] are inapplicable for solving this problem. The application of non-conventional resources as gas-based chemical raw materials and power-generating fuels requires novel technologies. The selective oxidative cracking (oxycracking) of methane homologues present in the above-mentioned mixtures may become a promising trend in the development of gas-based chemical processes and processes of natural gas pretreatment for power engineering.

Oxidative conversion is one of the most obvious and power-efficient processes for hydrocarbon gas processing, requiring a minimum quantity of additional energy. Oxidative conversion can be considered as a basic initial stage of natural gas processing to various chemical products. It is the oxidative conversion of natural gas that produces synthesis gas — one of the few products that can be obtained from methane, the major natural gas component, in a thermodynamically equilibrium reaction. Synthesis gas is used for large-scale synthesis of natural gas-based products such as hydrogen, ammonia, methanol and synthetic liquid hydrocarbons needed for chemical industry.

The key benefit of the oxidative conversion of light hydrocarbons is that it uses natural gas by itself (a cheap and readily available energy source) as a source of energy needed for the chemical conversion of its components. Furthermore, the energy evolved upon partial oxidation of the gas is input in the most efficient way, that is, directly into the bulk of the gas being converted without the need for complex and expensive heat exchange equipment. In many cases, even endothermic reactions can be fully conducted in an autothermal mode without resorting to external energy supply. In the case of heavier alkanes, heat evolution from their partial oxidation enables thermal or oxidative cracking with cleavage of weaker C – C bonds; furthermore, C – H bonds in their molecules are also considerably weaker than those in methane, which markedly facilitates the conversion, including oxidative dehydrogenation.

A review on gas-phase pyrolysis of light alkanes published several years ago [7] demonstrates the large potential of this topic for the design of new processes for hydrocarbon gas processing. However, it was noted that these processes had not been adequately explored and that more detailed investigation was needed into the oxidation kinetics of single alkanes and complex alkane mixtures corresponding to the real natural and associated gases. Over the last several years, a large body of research into the gas-phase cracking of light alkanes has been performed at the Institute of Problems of Chemical Physics, Russian Academy of Sciences (IPCP RAS) and Semenov Institute of Chemical Physics, Russian Academy of Sciences (ICP RAS); this substantially extended the views on the kinetics and the possible applications of these processes. This dictates the pertinence of the present review, which reflects the research progress along this line.

II. Multiphase nature of the oxidative cracking of light alkanes

A key feature of light alkane oxycracking which largely determines the process behaviour is that the process is, most often, multiphase. Even when the oxidative conversions of natural gas and its fractions are implemented as catalytic processes, a specific nature of these processes is related to the high energy of C – C and C – H bond cleavage in the light alkane molecules. The oxidative conversion of natural gas even in the presence of catalysts requires rather high temperatures at which not only catalytic reactions occur at a noticeable rate but also the gas-phase reactions involving less stable intermediates formed upon catalytic activation and further oxidation of alkanes. This became obvious in the studies of the mechanism of oxidative coupling of methane in which the heterogeneous initiation and the subsequent homogeneous transformations of methyl radicals form a common reaction mechanism.[8]

Meanwhile, even when these processes are conducted without catalysts, then the reactor surface usually plays a large role in the active site generation and decay, especially in laboratory experiments, because of very high activation energy of the gas-phase radical initiation. Therefore, almost in all cases, multiphase processes involving intense competition between heterogeneous and parallel gas-phase reactions take place.[9]

In view of the multiphase nature of the oxidative conversion of light hydrocarbons, the ratio of the reactor free volume to the catalyst volume is among the important parameters determining the relative contributions of homogeneous and heterogeneous reactions (and, hence, affecting directly the product distribution). In the absence of a catalyst, the ratio of homogeneous and heterogeneous reactions depends, to a large extent, on the reactor surface (S) to volume (V) ratio. In laboratory reactors with moderate diameters characterized by high S/V ratios and made of a relatively inert material such as quartz, the surface effect on the gas-phase process is very significant. Additional surface can not only retard the radical chain gas-phase reaction, thus promoting heterogeneous chain termination in a branched-chain reaction, but also induce certain changes in the chemistry of reactions involved, thus possibly affecting the composition of the products.[7]

The gas-phase process involving reactions of the alkyl radicals formed upon activation with dioxygen and oxygenated radicals ($HO_2^{\bullet}$, $HO^{\bullet}$, $O^{\bullet\bullet}$) gives rise to oxygenated compounds, which are subsequently oxidized to give mainly CO. Conversely, complete oxidation reactions on the catalyst surface markedly increase the yield of CO_2 and, hence, decrease the [CO] : [CO_2] ratio. As a consequence, the degree of conversion of oxygen is higher in the presence of a

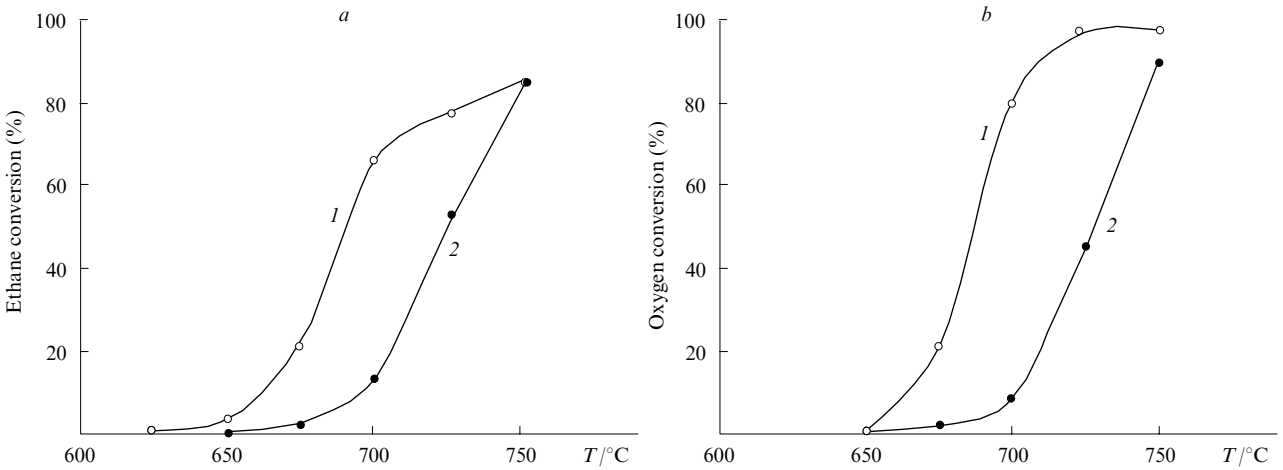


Figure 1. Temperature dependences of the conversions of ethane (*a*) and oxygen (*b*) diluted with nitrogen in the oxidative cracking of ethane in quartz reactors with inner diameter of 14 (*1*) and 8 mm (*2*).[12]
Experimental conditions: $[C_2H_6]_0 = 5\%$, $[O_2]_0 = 2.5\%$ (see †), reaction time $t_r = 1$ s.

catalyst than in an empty (without a catalyst) reactor, where a purely gas-phase reaction takes place, under the same conditions. For example, it was reported[10] that at an oxygen to ethane ratio much lower than the stoichiometric value, the complete oxygen conversion in the oxidative dehydrogenation of ethane in the presence of a mixed alkaline earth and rare earth metal oxide was already attained at 600 °C, although the ethane conversion was moderate. Meanwhile, the rates of gas-phase reactions increase much faster with increasing temperature due to higher activation energy. Indeed, in the same experiments in the absence of a catalyst at 750 °C and ethane conversion of 60%, the conversion of oxygen was only 80%, *i.e.*, at a higher temperature, the conversions of both reactants approached each other. Numerous studies have shown[7] that below 600 °C, ethane oxidative cracking proceeds at a noticeable rate only in the presence of a catalyst or on a reactor surface. Thus, the temperature is a key factor determining the relative contributions of homogeneous and heterogeneous reactions to the oxidative conversion of light alkanes.

Magomedov *et al.*[11,12] studied the effect of temperature on the roles of homogeneous and heterogeneous processes in the oxidative cracking of ethane proceeding at atmospheric pressure in a flow setup containing cylindrical quartz reactors with inner diameters of 14 mm ($S/V = 5.4$ cm^{-1}) and 8 mm ($S/V = 13.3$ cm^{-1}). The length of the heated isothermal high-temperature zone was 200 mm. To maintain the isothermal conditions in the reactors and suppress secondary processes involving the oxidative cracking products, mixtures were, most often, diluted with an inert gas, the ethane concentration being 5% and the oxygen concentration being varied over wide limits. The temperature dependences of ethane and oxygen conversions are presented in Fig. 1.

According to the obtained results, for the same t_r value, the reaction starts at higher temperature in the reactor with a smaller diameter than in the reactor with a larger diameter, *i.e.*, the reaction slows down. Presumably, the inhibition of oxidation with increase in the relative contribution of reactions on the surface is associated with decreasing concentration of the hydroperoxyl radicals $HO_2^{\bullet}$ (resulting from reactions of ethane and ethyl radicals with oxygen), which are destroyed in chain termination reactions on the reactor surface.[13] Temperature rise leads to an increase in the number of $HO_2^{\bullet}$ radicals in the system; this is accompanied by radical recombination followed by decomposition of H_2O_2 to give highly reactive hydroxyl radicals $HO^{\bullet}$, which accelerate the reaction.[13] However, at 750 °C, when the contribution of thermal pyrolysis becomes significant, ethane conversions in the reactors with different S/V ratios are nearly equal. The selectivity to major carbon-containing products in reactors with different diameters is nearly the same, indicating that the influence of quartz reactor walls on the product formation is minor.

Magomedov *et al.*[12] carried out an experiment that clearly demonstrated the patterns of catalytic and gas-phase reactions of ethane oxycracking. A small bed of IPM-02 industrial catalyst, containing 0.2 mass % of platinum supported on a mixure of γ-Al_2O_3 and synthetic mordenite, was placed on a quartz grid located at the entrance of the reactor. The usual contact time between the reactants and the catalyst was ~0.06 s, while the residence time of the reactants in the hot area behind the catalyst bed was 0.8 – 0.9 s (600 – 750 °C). The process was conducted at temperatures from 200 to 750 °C, ethane concentration of 5% and the $[C_2H_6]_0 : [O_2]_0$ ratio of 2 in a nitrogen-diluted mixture.

Since the gas-phase oxycracking of ethane follows a radical chain mechanism, which is rate-limited by chain initiation, the authors assumed that this may promote lowering of the reaction temperature and/or decrease in the reaction time as a result of heterogeneous activation of ethane followed by migration of reactive products to the gas phase. It turned out that heating of the reactor with the catalyst to only 200 °C entailed a noticeable warming up of the catalyst bed (~40 °C) compared with the reactor walls. For a reactor temperature of 300 °C, almost complete conversion of oxygen (~95%) was observed. Simultaneously, conversion of ethane was only ~11%, which approx-

† The concentrations of reactants and products in the oxycracking are in mol.% in all cases.

imately corresponded to the stoichiometry of its complete oxidation at this initial concentration of oxygen (Fig. 2). Further heating of the reactor markedly increased the conversion of ethane only when the temperature was > 650 °C, which corresponds to the onset of the gas-phase reaction (Fig. 2 *b*).

Ethane oxypyrolysis observed in the presence of a catalyst at temperatures of <400 °C gave CO_2 and H_2O as the only products (Fig. 3). The partial oxidation products — CO and H_2 — appeared only at >400 °C. The subsequent increase in the selectivity to CO and H_2 was accompanied by a decrease in the selectivity to CO_2 and H_2O; this can be interpreted as resulting from increasing contributions of endothermic catalytic reactions such as steam and carbon dioxide reforming of ethane, which are promoted by temperature rise. A substantial increase in the selectivity to ethylene and simultaneous decrease in the selectivity to carbon oxides CO_x took place only at temperatures of >650 °C.

Thus, the oxidation, which starts at low temperature, is considerably accelerated in the presence of a Pt-containing catalyst. However, this acceleration is accompanied by predominantly deep oxidation of a minor portion of ethane on the catalyst surface to CO_x and H_2O and almost complete oxygen consumption. The subsequent noticeable increase in the ethane conversion and ethylene formation occurs only at temperatures of >650 °C where oxygen-free gas-phase pyrolysis of ethane, accompanied by a fast decrease in the CO_x and H_2O selectivity and increase in the ethylene selectivity, proceeds at a noticeable rate in the free space of the reactor behind the catalyst bed. The lack of oxygen in the reactor behind the catalyst bed results in markedly lower ethane conversion compared with that in the gas-phase oxidative pyrolysis without a catalyst (see Fig. 2).

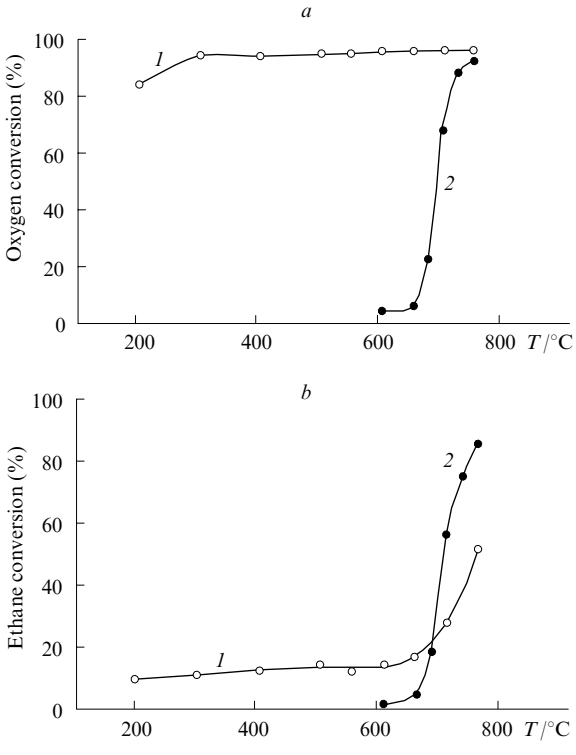


Figure 2. Temperature dependences of the conversions of oxygen (*a*) and ethane (*b*) in the presence (*1*) and in the absence (*2*) of the IPM-02 catalyst at the entrance of the reactor.[12]
Experimental conditions: $[C_2H_6]_0 = 5\%$, $[C_2H_6]_0 : [O_2]_0 = 2$, nitrogen-diluted mixture, contact time with the catalyst 0.06 s, residence time in the free hot section of the reactor 0.8 – 0.9 s.

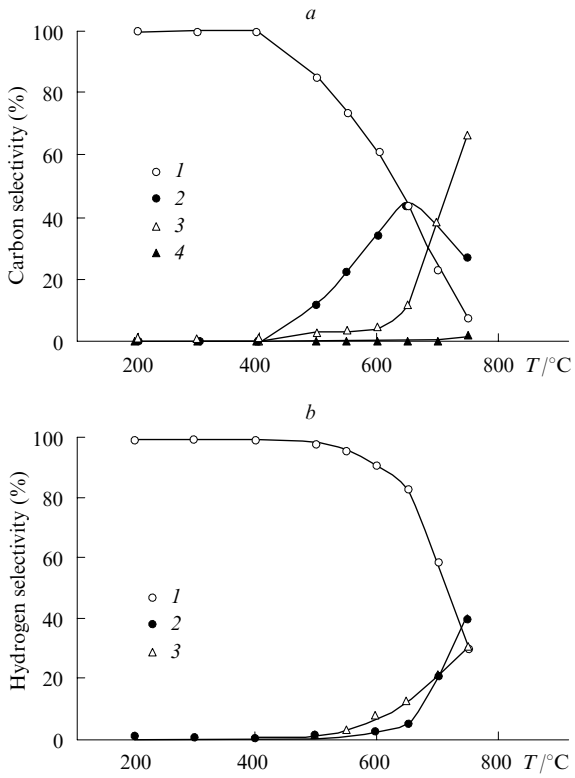


Figure 3. Temperature dependences of carbon (*a*) and hydrogen (*b*) selectivities to products of ethane oxypyrolysis in the presence of the IPM-02 catalyst.[12]
(*a*) (*1*) CO_2, (*2*) CO, (*3*) C_2H_4, (*4*) CH_4;
(*b*) (*1*) H_2O, (*2*) sum of C_xH_y hydrocarbons, (*3*) H_2.
For experimental conditions, see Fig. 2.

Similar observations were made in another study:[14] switching to fast reaction (ignition) of an argon-diluted mixture of ethane with air ($[C_2H_6] : [O_2] = 2$) in the presence of a monolithic catalyst containing 1 mass % of Pt on heating above 200 °C resulted in a sharp increase in the oxygen conversion to 90% for ethane conversion of $<20\%$. Further heating of the reactor up to 650 °C was accompanied by a slow increase in the ethane and oxygen conversions; then complete oxygen conversion was reached and a sharp increase in the ethane conversion took place. Carbon oxides, hydrogen and water were the major reaction products at a low conversion of ethane. The carbon dioxide and water selectivities decreased with increasing temperature, while the formation of carbon monoxide and hydrogen increased up to a temperature of 650 °C, at which the selectivities to these products were maximum. Above 650 °C, the selectivity to ethylene started to increase. In an empty reactor (without a catalyst), a gas-phase transformation of ethane and oxygen started at >550 °C, while a sharp increase in the reactant conversion occurred at about

> 650 °C, which is consistent with the above-described results.[12]

Similar results were obtained for oxidative dehydrogenation of ethane in a nitrogen-diluted mixture with the ratio $[C_2H_6]:[O_2] = 1$ carried out in an annular reactor in the presence of the commercial 5 mass % $Pt/\gamma\text{-}Al_2O_3$ catalyst.[15]

Lange *et al.*[16] proposed a two-step mechanism for the oxidative cracking of ethane in the presence of a Pt catalyst. The process was carried out in an autothermal mode at 950 – 1100 °C and 2.5 bar, most often, using platinum catalysts prepared by impregnation of various oxides (Al_2O_3, TiO_2, ZrO_2, CeO_2, *etc.*) and containing 0.05 mass % to 5 mass % of Pt, platinum grids or catalysts based on monolithic structures containing 5 mass % of Pt. The residence time in the catalyst zone was 5 to 15 ms and that in the space behind the catalyst bed was 150 – 500 ms. It was concluded that the first step comprised catalytic oxidation of a part of ethane accompanied by heat evolution and the second step was the gas-phase thermal cracking of the remaining ethane to give ethylene. The role of the catalyst is limited to initiation of exothermic oxidation reactions and influence on the amount of heat evolved, which depended on the selectivity ratio between complete (to CO_2 and H_2O) and partial (to CO and H_2) oxidations. It is likely that the catalyst does not have any significant effect on the subsequent cracking, which proceeds in the gas phase after a sufficiently high temperature has been reached.

Analogous patterns for homogeneous and heterogeneous processes were also observed in the oxycracking of heavier alkanes. A study of the oxidative conversion of hexane in the absence of a catalyst and in the presence of typical catalysts of oxidative coupling of methane (OCM) and carbon dioxide reforming of methane (CDM)[17] demonstrated that in the presence of catalysts, the reaction proceeded at a markedly lower temperature than without catalysts (Fig. 4). However, as the temperature was raised, hexane conversion without catalysts sharply increased; at 700 °C, it was slightly different from the conversion in the catalytic process and at 730 °C, it was substantially higher than that in the presence of catalysts.

The retardation of the gas-phase process with increasing S/V ratio of the reactor was also observed[18] in a study of the oxidative dehydrogenation of n-butane. At a constant temperature, in a reactor with the hot area being filled by crushed quartz, the reaction rate decreased by more than an order of magnitude, although the residence time decreased only twofold. At 580 °C and t_r = 1.8 s, the butane conversion in the presence of crushed quartz was 2.5%, whereas in the empty reactor it reached 62% under the same conditions. The authors reasonably assumed that at a high S/V ratio, the contribution of homogeneous reactions decreased as a result of branched-chain termination upon radical interaction with the reactor surface.

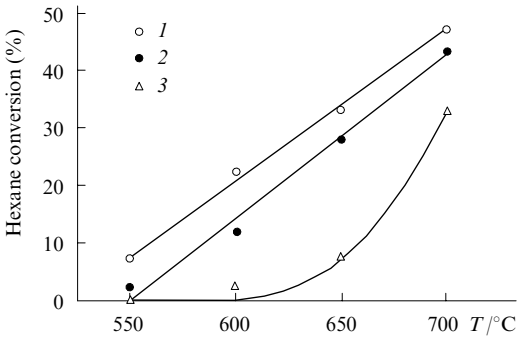


Figure 4. Temperature dependences of hexane conversion with nitrogen diluent in the presence of catalysts for OCM (*1*) ($[N_2]_0:[O_2]_0 = 96.0:4.0$) and CDM (*2*) ($[N_2]_0:[O_2]_0 = 96.7:3.3$) and in the absence of catalysts (*3*) ($[N_2]_0:[O_2]_0 = 96.6:3.4$).[17] Reactor diameter 3 mm, gas flow rate 7 ml min^{-1}.

In another study,[19] the partial oxidation of n-hexane (7.8% in air) in a reactor completely filled with silicon carbide particles started at 400 °C, whereas its conversion in an empty reactor was already ~45% at this temperature. The replacement of a steel reactor by a glass reactor resulted in a lower hexane conversion and a considerable increase in the selectivity to hexenes owing to a decrease in the selectivity to carbon oxides.

Thus, while considering gas-phase partial oxidation processes, one should take into account not only the reactor surface area to volume ratio, but also the catalytic activity of the material of the reactor walls and any other additional surface. The results obtained in the works cited[12 – 19] may be considered as evidence supporting the view of a two-step mechanism of oxidative cracking of light alkanes in the presence of highly active Pt-containing catalysts.[7]

III. Oxidative cracking of ethane

Ethane oxycracking has now been apparently studied more comprehensively and thoroughly than the oxycracking of other alkanes. The reason is not only the practical importance of this process and fast buildup of facilities for ethane pyrolysis (especially in the USA). The investigation of the oxycracking of ethane as a representative of light alkanes is of particular interest also owing to the fact that rather complete and adequate models for the mechanism of its oxidative conversion have already been developed and, hence, it is possible to analyze the process kinetics. For the oxycracking of heavier hydrocarbons, this research is still to be done.[8] Detailed experimental investigation and kinetic modelling of the oxidative cracking of ethane at atmospheric pressure have been carried out.[11, 12]

III.1. Effect of temperature

Analysis of the temperature dependence of the oxygen and ethane conversions during oxycracking demonstrated that above 625 °C at similar concentrations of the reactants in the mixture, there is a quantitative correlation between the conversions of both reactants, which is typical of gas-phase processes. The correlation holds up to a temperature where complete conversion of oxygen is attained. At higher temperature, the increase in the ethane conversion with increasing temperature slows down. Apparently, in this stage, the increase in the ethane conversion is a consequence of the increasing contribution of thermal cracking and dehydrogenation. The large contribution of these reactions (characterized by high activation energies) at high temperatures suppresses the accelerating effect of oxygen on the conversion of ethane.

Attention is attracted by the quite narrow (< 50 °C) temperature range in which the system shifts from a slightly noticeable reaction to almost complete conversion of oxygen (Fig. 5 *a*) accompanied by high ethane conversion (see Fig. 5 *b*). This critical switching to fast reaction taking

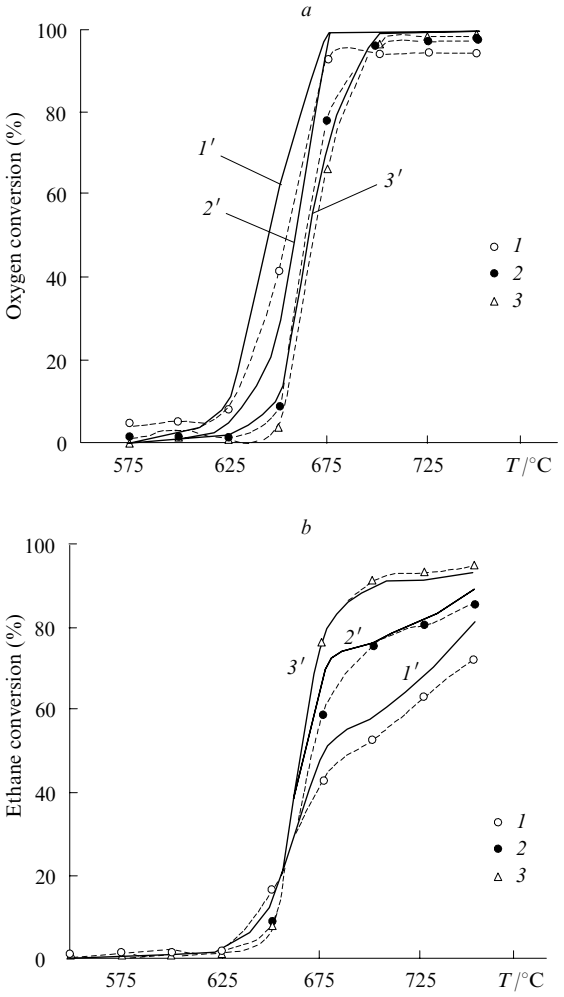


Figure 5. Temperature dependences of oxygen (*a*) and ethane (*b*) conversions.[11]
The dashed lines and dots correspond to experimental results and solid lines are the results of kinetic modelling. $[O_2]_0$ = 1 (*1*, *1′*), 2.5 (*2*, *2′*), 5% (*3*, *3′*); $[C_2H_6]_0$ = 5%, t_r = 2 s, P = 1 atm.

place in a narrow temperature range is inherent in branched-chain reactions. The transition of the system to the branched-chain state is also indicated by the very high (>100 kcal mol^{-1}) apparent activation energy determined by formal processing of the results in this temperature range.

When the initial oxygen concentrations $[O_2]_0$ were 2.5% and 5%, the amount of oxygen was much lower than that required for complete oxidation of ethane, and oxygen was consumed almost completely (see Fig. 5 *a*). However, in the case of $[O_2]_0$ = 1%, a residual oxygen concentration at about ~0.05% was always retained. An approximately equal incomplete consumption of oxygen was also observed in experiments dealing with partial oxidation of methane.[3,9]

Experiments reported by Magomedov *et al.*[11] were accompanied by kinetic modelling using a detailed model for partial oxidation of C_1-C_2 hydrocarbons specially developed for the temperature range of 600 – 1200 K, pressure range of 1 – 100 atm and a broad range of $[O_2]_0 : [C_2H_6]_0$ ratios. According to the principles of modelling, which have been described in detail,[8] all the numerical values for kinetic parameters were taken from independent literature sources, mainly from the NIST chemical kinetics database.[20] The kinetic parameters were not varied during the modelling. The draft model reported by Arutyunov *et al.*[21] was supplemented by several reactions. The hydrogen peroxide-involving reactions and hydrogen peroxide formation and decomposition were represented in terms of the so-called Lindemann mechanism,[22] that is, explicitly assuming the formation of excited species, evolving both towards deactivation and towards decomposition of the activated complex. All this improved the agreement between the experimental data and modelling results. The modified model, including the added reactions, comprised 490 elementary steps. The calculations were carried out for isothermal conditions using the KINTECUS V450 program ‡ designed for modelling the kinetics of oxidation, combustion and other reactions.

The kinetic model not only qualitatively described the critical nature of switching of the reaction to the ignition region under these conditions but also provided a quite satisfactory quantitative agreement with experimental results. In view of the accepted principle of independent modelling,[8] it can be stated that the theoretical views are quite consistent with the observed process kinetics. However, the fact that the theoretical conversion of oxygen reached 100% at any initial concentration, whereas the value found in experiments was somewhat lower in all cases is an example of discrepancy between the experimental and modelling results that has not yet been interpreted (Fig. 6 *a*). Furthermore, according to the kinetic modelling results, the increase in the initial concentration of oxygen leads to increasing the temperature (see Fig. 5 *a*) and time needed to reach the 100% conversion of oxygen (see Fig. 6 *a*). In experiments, as the oxygen concentration increased from 2.5% to 5%, its conversion somewhat increased and the time it took to reach its quasi-steady-state value decreased. An increase in the oxygen concentration in the mixture entails not only an increase in the maximum conversion of ethane at a specified temperature but also a shortening of the time needed to reach this value (see Fig. 6 *b*).

A virtually complete consumption of oxygen was accompanied by only a partial conversion of ethane, which decreased with decreasing initial concentration of oxygen (decrease in the $[O_2]_0 : [C_2H_6]_0$ ratio). As the initial concentration of oxygen increased, its consumption per converted ethane molecule monotonically increased. Correspondingly, the degree of conversion of ethane achieved at the temperature of maximum oxygen conversion increased more slowly than the initial oxygen concentration (Fig. 7). This pattern of dependence of ethane conversion on the initial concentration of oxygen is apparently caused by increasing consumption of oxygen for the oxidation of the products formed. Vigorous gas-phase oxidation of ethylene and air mixtures (in 3 to 10 ratio) at atmospheric pressure has been observed.[23] This process occurred in approximately the same temperature range (starting from 550 °C) as that in the study of Magomedov *et al.*[12] and resulted in the formation of mainly the same products (CO, CH_4, CO_2), as was adequately described by a gas-phase model. The gas-

‡ See http://www.kintecus.com

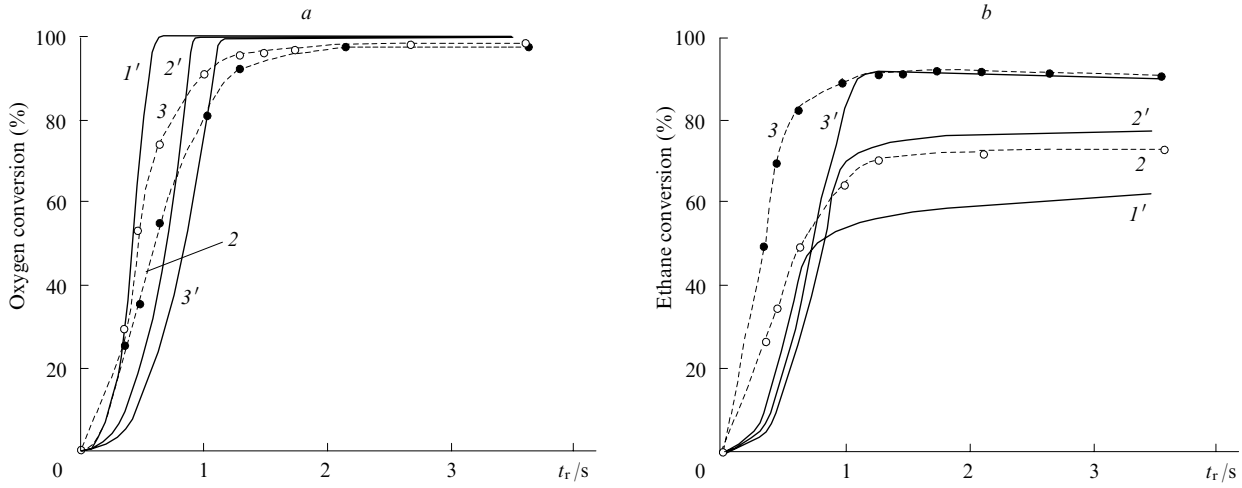


Figure 6. Conversions of oxygen (*a*) and ethane (*b*) *vs.* residence time of the reaction mixture in the reactor ($[C_2H_6]_0$ = 5%, T = 700 °C).[11] The dots and dashed lines correspond to experimental results and solid lines are modelling data. $[O_2]_0$ (%): (*1′*) 1; (*2*, *2′*) 2.5; (*3*, *3′*) 5.

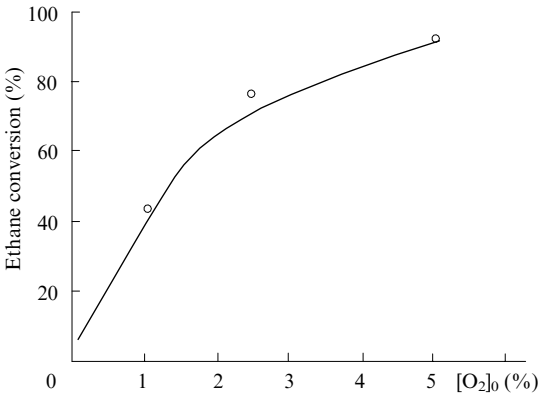


Figure 7. Ethane conversion attained at the temperature of complete conversion of oxygen *vs.* initial oxygen concentration.[11] $[C_2H_6]_0$ = 5%, t_r = 2 s. The dots correspond to experimental results and the solid line is modelling.

phase oxidation of ethylene in a mixture ($[C_2H_4]_0 : [O_2]_0 = 1 : 1$) highly diluted with helium was reported[13] to start at temperatures of >670 °C and to afford mainly water and carbon monoxide, the carbon monoxide selectivity being ~90%.

When the temperature increased beyond the temperature of complete oxygen consumption, the conversion of ethane slowly increased, but still remained lower than the oxygen conversion even at an equimolar ratio of oxygen and ethane. This is in good agreement with the published data,[7,11] according to which ethane oxycracking differs considerably from the oxycracking of heavier alkanes [in the latter case, the conversion of oxygen is, as a rule, somewhat lower than (or equal to) the conversion of the hydrocarbon]. The ratio of the consumed ethane and oxygen attained at a temperature of complete oxygen consumption monotonically decreased with increasing oxygen concentration. The decrease in this ratio from ~2 for $[O_2]_0 : [C_2H_6]_0 = 0.2$, which formally corresponds to the overall reaction

$$C_2H_6 + 0.5\,O_2 \longrightarrow C_2H_4 + H_2O \quad (1)$$

to ~1 for $[O_2]_0 : [C_2H_6]_0 = 1$ may be attributable to increasing contribution of the overall reactions

$$C_2H_6 + O_2 \longrightarrow 2\,CO + 3\,H_2 \quad (2)$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \quad (3)$$

$$C_2H_4 + O_2 \longrightarrow 2\,CO + 2\,H_2 \quad (4)$$

The kinetic model adequately describes the experimental dependence of ethane conversion on the initial concentration of oxygen (see Fig. 7).

Analysis of the curves shown in Fig. 5 indicates that for $[C_2H_6]_0$ = 5% and $[O_2]_0$ < 2.5%, the temperatures of the onset of the reaction and the attainment of complete consumption of oxygen increase as the initial oxygen concentration increases. Formally, this can be attributed to inhibition of the radical oxidation of ethane by oxygen. A similar trend was observed in a study,[13] in which the gas-phase dehydrogenation of ethane carried out under similar conditions without oxygen started at a 40 °C lower temperature than that with oxygen, *i.e.*, oxygen inhibited the reaction. However, as the temperature increased in the presence of oxygen, the ethane conversion markedly increased to reach 75% at 700 °C, whereas in the absence of oxygen, the conversion reached only 44%. Similar oxygen inhibition of a branched-chain process was also noted in the partial oxidation of methane at high pressure.[3,9]

The effect of temperature on the composition of ethane oxidation products is illustrated by Fig. 8. At low temperature, ethylene and water were the primary products of oxycracking; they appeared simultaneously with the onset of reactant transformation. All other products were formed at higher temperature and (except hydrogen) in markedly lower amounts.

The results of modelling attest to the formation of hydrogen peroxide apart from water. Hydrogen peroxide was not detected in experiments, but, according to modelling data, it was mainly formed at low temperatures. Its maximum calculated concentration was 0.44% at 675 °C; at higher temperatures, it rapidly decomposed, and this was accompanied by a sharp increase in the ethane conversion

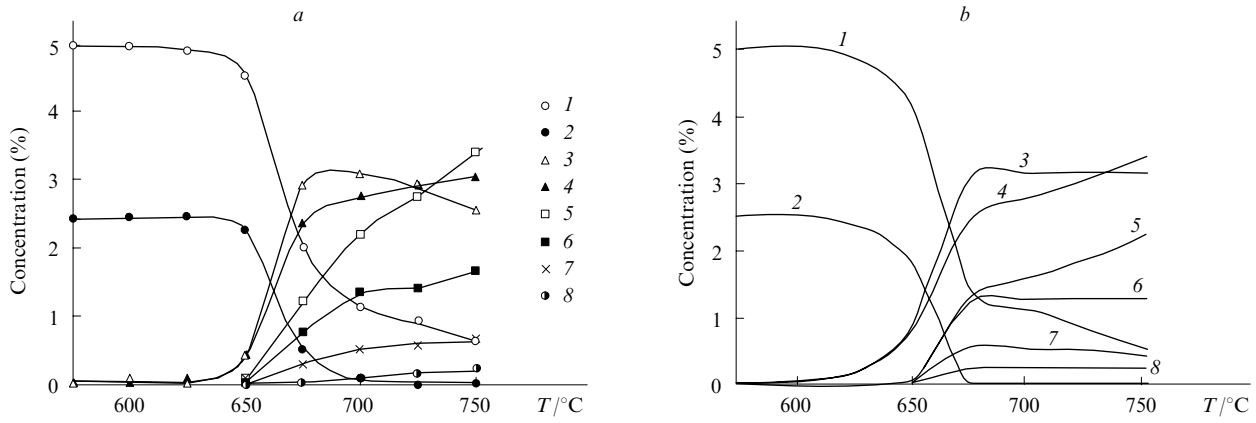


Figure 8. Experimental (*a*) and calculated (*b*) temperature dependences of the concentrations of reactants and products of ethane oxidation.[11]
$[C_2H_6]_0$ = 5%, $[O_2]_0$ = 2.5%, t_r = 2 s. (*1*) C_2H_6, (*2*) O_2, (*3*) H_2O ($H_2O + H_2O_2$ in Fig. *b*), (*4*) C_2H_4, (*5*) H_2, (*6*) CO, (*7*) CH_4, (*8*) CO_2.

rate. This is in good agreement with the view that during alkane oxidation in the region of >500 °C, hydrogen peroxide decomposition becomes one of the major chain-branching reactions.[24] Magomedov *et al.*[11] compared the experimental results with the theoretical sum of hydrogen peroxide and water concentrations. It is also noteworthy that the products of ethane oxidative cracking differ fundamentally from the products of ethane partial oxidation at high pressure: the latter mainly contain oxygenates,[25, 26] which are not observed at higher temperatures inherent in oxycracking.

A comparison of theoretical and experimental results demonstrated [11] that the kinetic model describes quite adequately not only the temperature dependences and qualitative composition of the products but also the product yields. An exception is the hydrogen concentration, which is underestimated approximately by half and somewhat underestimated CO and CH_4 concentrations. The cause for these discrepancies has not yet been elucidated.

The increase in the $[H_2]:[CO]$ ratio with temperature rise is apparently caused by increasing contribution of the thermal C–H bond cleavage in the ethyl radical, the rate of which in the temperature range of interest far exceeds the rate of hydrogen atom elimination by oxygen.[13] The ethylene concentration continues to increase, together with the hydrogen concentration, after the complete consumption of oxygen (see Fig. 8 *b*), apparently, as a result of thermal dehydrogenation of ethane at high temperature according to reaction (3). An important product of ethane oxidation is methane, which is formed at temperatures of >650 °C where C–C bond cleavage in ethane and oxidative cracking of ethylene start to proceed at noticeable rates.[13]

The temperature dependences of the selectivities to ethane oxidation products (Fig. 9) correspond to the tem-

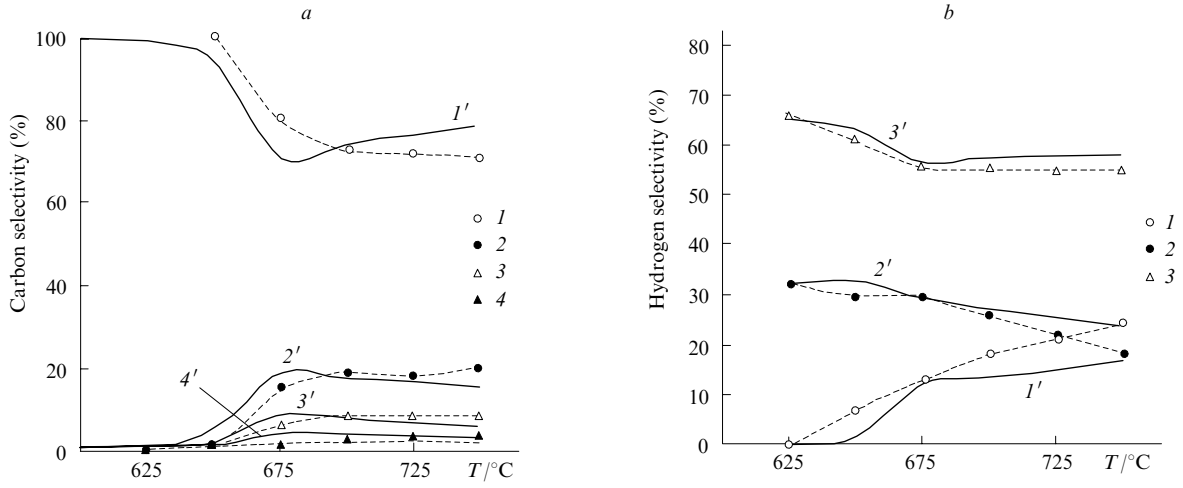


Figure 9. Temperature dependences of the carbon (*a*) and hydrogen (*b*) selectivities to ethane oxidation products.[11]
$[C_2H_6]_0$ = 5%, $[O_2]_0$ = 2.5%, t_r = 2 s. The dots and dashed lines correspond to experimental results and solid lines are modelling data.
(*a*) (*1*, *1′*) C_2H_4; (*2*, *2′*) CO; (*3*, *3′*) CH_4; (*4*, *4′*) CO_2;
(*b*) (*1*, *1′*) H_2; (*2*, *2′*) H_2O; (*3*, *3′*) C_xH_y.

perature dependences of their concentrations considered above. At temperatures of < 650 °C and, correspondingly, at low reactant conversions, ethylene and water are virtually the only oxycracking products (modelling implies the formation of a sum of water and hydrogen peroxide instead of just water). With increasing the temperature to 700 °C where oxygen is completely consumed, both the calculated and experimental carbon selectivities to ethylene decreased from 100% to ~70%. On further temperature rise, these values decreased insignificantly. In the 600 – 750 °C temperature range, the selectivities to CO and CH_4 reached 18% – 20% and 7% – 8%, respectively, and as the temperature was further increased, these values remained almost invariable (see Fig. 9 *a*). Meanwhile, over the whole temperature range of interest, the selectivity to H_2O decreased almost linearly in parallel with the increase to the selectivity to H_2 (see Fig. 9 *b*). This may be caused by an increase in the rate of ethane thermal dehydrogenation with respect to the rate of its oxidative dehydrogenation and by redistribution of oxygen towards carbon oxide formation reactions.

Thus, whereas at low temperature and, hence, low ethane conversion, the oxidative dehydrogenation of ethane is the major process, at high temperature, the contributions of parallel thermal cracking and dehydrogenation as well as ethane and ethylene deep oxidation markedly increase.

III.2. Effect of the residence time of reactants in the reactor

Magomedov *et al.*[11] also considered the effect of the residence time of reactants in the reactor on the composition of the products. Until oxygen is completely consumed, the concentrations of all reaction products monotonically increase with time (Fig. 10). Ethylene and water are the primary products of ethane conversion, their concentrations being nearly equal until oxygen is completely consumed, in conformity with overall reaction (1). At 700 °C and short reaction times, a considerable amount of hydrogen is formed as a result of a high rate of thermal dehydrogenation. The other products are formed after some time delay, probably, upon secondary ethylene oxidation reactions. As a consequence, the increase in the ethylene concentration starts to lag behind the increase in the water concentration; this is confirmed by kinetic modelling, which describes the experimental results quite adequately (see Fig. 10 *b*). However, because of a higher theoretical rate of oxidation, the time required for complete consumption of oxygen according to the model is approximately twice shorter than the experimental value. In addition, the model predicts fast complete consumption of oxygen, whereas in the experiment, this process is extended and a residual concentration of oxygen mentioned above is retained.

After complete consumption of oxygen, the process virtually stopped; the concentrations of the products changed insignificantly during the observation time, despite rather large amount of remaining ethane. This attests to a low rate of ethane pyrolysis in the absence of oxygen in the given temperature range. Only a minor increase in the hydrogen and ethylene concentrations with the concomitant decrease in the ethane concentration was observed.

The invariability of water vapour concentration after exhaustion of oxygen is indicative of the absence of a noticeable role of the gas-phase steam reforming of ethane under the experimental conditions.[11] This is in line with the results of Schadel *et al.*,[27] who found that below 900 °C where active gas-phase pyrolysis of ethane and higher alkanes takes place, the conversion of water vapour without a catalyst is very low — not more than 5%.

III.3. Effect of the initial oxygen concentration

The initial concentration of oxygen ($[O_2]_0 : [C_2H_6]_0$ ratio) is an important parameter influencing not only the rate of ethane oxycracking, but also the distribution of products. All other conditions (ethane concentration, reaction time and temperature) being the same, increasing the initial oxygen concentration results in higher selectivity to oxygenated products (CO and water) and in monotonically decreasing selectivities to ethylene and to the sum of hydrocarbons and hydrogen (Fig. 11).

Although the selectivity to ethylene decreased with increasing ethane conversion, the yield of ethylene at ethane conversions of $< 50\%$ almost did not depend on the oxygen concentration for the experimentally studied[11] $[O_2]_0 : [C_2H_6]_0$ ratios (Fig. 12). As shown by the kinetic modelling, for ethane conversions below 40%, the selectivity to ethylene even increased as the oxygen concentration increased from 1% to 2.5%; this may be attributed to higher dehydrogenation rate in the presence of O_2.

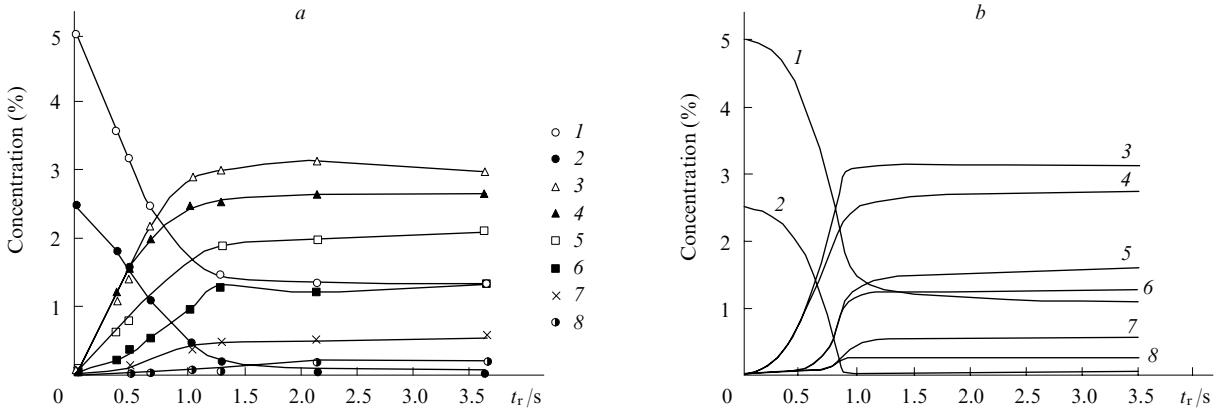


Figure 10. Experimental (*a*) and calculated (*b*) concentrations of reactants and products of ethane oxidation *vs.* residence time of the reaction mixture in the reactor.[11]
$[C_2H_6]_0 = 5\%$, $[O_2]_0 = 2.5\%$, $T = 700$ °C. (*1*) C_2H_6, (*2*) O_2, (*3*) H_2O ($H_2O + H_2O_2$ in Fig. *b*), (*4*) C_2H_4, (*5*) H_2, (*6*) CO, (*7*) CH_4, (*8*) CO_2.

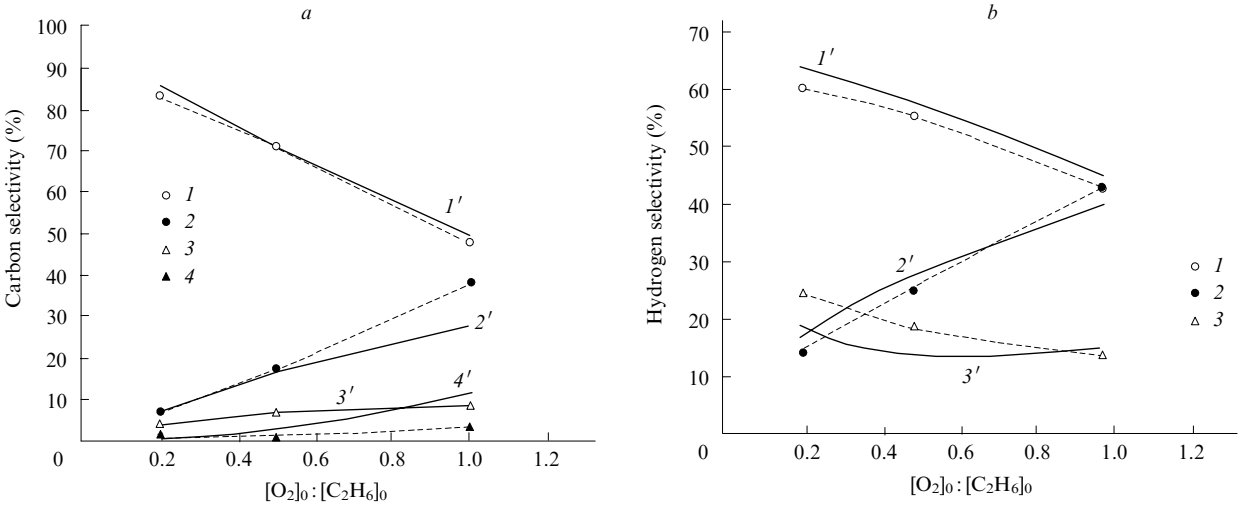


Figure 11. Concentration dependences of the carbon (*a*) and hydrogen (*b*) selectivities to ethane oxycracking products.[11] $[C_2H_6]_0$ = 5%, T = 700 °C, t_r = 2 s. The dots and dashed lines correspond to experimental results and solid lines are modelling data. (*a*) (*1*, *1′*) C_2H_4; (*2*, *2′*) CO; (*3*, *3′*) CH_4; (*4*, *4′*) CO_2; (*b*) (*1*, *1′*) C_xH_y; (*2*, *2′*) H_2O; (*3*, *3′*) H_2.

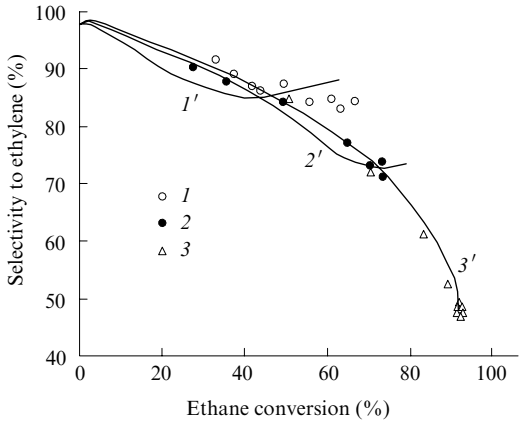


Figure 12. Selectivity to ethylene *vs.* conversion of ethane.[11] $[C_2H_6]_0$ = 5%, T = 700°C, t_r = 0.3–3.9 s. The dots correspond to experimental results and solid lines are modelling data. $[O_2]_0$ (%): (*1*, *1′*) 1; (*2*, *2′*) 2.5; (*3*, *3′*) 5.

In order to estimate the effect of secondary reactions on the oxidative conversion of ethane, experiments were carried out [11] with different initial concentrations of ethane but the constant ratio $[O_2]_0 : [C_2H_6]_0 = 0.5$. It was found that the increase in the ethane concentration from 2% to 10% leads to a ~75 °C decrease in both the temperature of the beginning of the fast reaction (ignition) and the temperature at which complete oxygen consumption is attained. This is quite consistent with the views on the effect of hydrocarbon concentration on the ignition temperature. The modelling confirmed the experimental results on a qualitative level; however, the effect of the ethane concentration on the temperature at which the reaction starts was less pronounced according to calculations than according to experimental results. It is noteworthy that the initial concentration of ethane barely affected the distribution of products.

Similar results were obtained by Machli *et al.*[28] for reaction time of 2.4 s, the initial concentration of ethane in helium $[C_2H_6]_0$ = 6% and $[O_2]_0 : [C_2H_6]_0$ ratio being varied from 0.2 to 1. In this work, the oxidative dehydrogenation of ethane was studied at a somewhat lower temperature and in a narrower temperature range (575–650 °C) than it was reported by Magomedov *et al.*;[11] furthermore, the reactor was partly loaded with pieces of quartz. However, the results were generally quite comparable. A noticeable conversion, similar for both reactants, started above 575 °C; in the case of $[O_2]_0 : [C_2H_6]_0 = 1$ and the highest experimental temperature of 650 °C, the ethane and oxygen conversions reached 80% and 90%, respectively. Magomedov *et al.*[11] observed this value of ethane conversion at a ~25 °C higher temperature. The authors attributed this discrepancy to small differences in the experimental conditions. Ethylene and carbon oxides (mainly CO) were the major carbon-containing products;[28] at 650 °C, their yields were 56% and 20%. respectively. This is in good agreement with the ethylene yield reported by Magomedov *et al.*[11] for a similar ethane conversion and the same initial ratio between the reactants.

III.4. Effect of the diluent gas

An important factor affecting the oxycracking of ethane is the composition of the gas atmosphere in which the process takes place. The temperature dependences of the oxygen conversion during the oxidative cracking of ethane in various diluents are shown in Fig. 13. When nitrogen is replaced by helium, which has higher thermal conductivity, the reaction starts at a higher temperature. Nitrogen has a higher molar heat capacity and is more efficient than helium as a third body in radical recombination. Owing to this, the concentration limits of ignition of methane–air mixtures close to the stoichiometric composition narrow down to a larger extent in nitrogen than in helium.[29] However, in the partial oxidation of ethane under nearly isothermal conditions, helium is more efficient than nitrogen for retarding the initiation of the branched-chain reaction. Presumably, this is caused by higher thermal conductivity of helium,

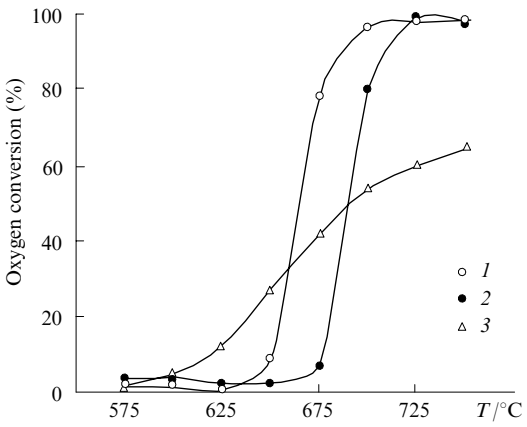


Figure 13. Temperature dependences of oxygen conversion in N_2 (*1*), He (*2*) and CH_4 (*3*).[12]
$[C_2H_6]_0 \approx 5\%$, $[O_2]_0 = 2.5\%$, $t_r = 2$ s.

which provides for faster heat withdrawal and decrease in the gas temperature, although Magomedov *et al.*[12] carried out the process under isothermal conditions in a heated and properly insulated reactor of a relatively small diameter.

Of particular interest is ethane oxidation in a large excess of methane, which corresponds to a real composition of natural and associated gases. Methane has a much higher heat capacity than nitrogen or helium. A study of the ignition of C_1-C_5 alkanes in shock pipes demonstrated the following:[30] the delay of methane ignition is almost an order of magnitude greater than that of C_2-C_5 alkane ignition, which is due to the low reactivity of methane in comparison even with ethane. When the reaction times are about a second, a noticeable methane pyrolysis starts only above 1000 °C.[31,32] However, when the radical chain reaction of ethane occurs in parallel, methane is no longer an inert gas and, hence, its effect on the process is more difficult to interpret.

In the presence of methane, the pattern of temperature dependence of the oxygen conversion crucially changes (see Fig. 13). Below 650 °C with methane dilution, the conversion of oxygen increases; formally this can be interpreted as promoting of ethane oxidation by methane. This may presumably be a consequence of the formation of methylperoxyl radicals, which ensure high efficiency of chain branching during the low-temperature oxidation of methane.[3,9,26] Above 650 °C, the conversion of oxygen becomes lower than those in nitrogen or helium. This can be attributable to either higher efficiency of methane as the third body in the recombination of radicals or involvement of methane into the radical process as a reactant that reduces the rate of chain branching and concentration of highly reactive radicals.

Unlike helium and nitrogen, methane is a multiatomic gas with a higher heat capacity; therefore, it is more efficient as the third body in the recombination of radicals. This may increase the square-law chain termination rate and decrease the radical reaction rate.[3] In addition, the chain-branching rate may decrease as a result of inevitable participation of methane as a reactant in the radical reaction. If the methane concentration is high, methane efficiently competes with oxygen for the hydrogen atoms formed mainly upon decomposition of $C_2H_5^{\bullet}$ radicals

$$C_2H_5^{\bullet} \longrightarrow C_2H_4 + H^{\bullet} \quad (5)$$

$$H^{\bullet} + O_2 \longrightarrow OH^{\bullet} + O^{\bullet} \quad (6)$$

$$H^{\bullet} + CH_4 \longrightarrow H_2 + CH_3^{\bullet} \quad (7)$$

Reaction (6) is the most important chain-branching reaction in the combustion of hydrocarbons at temperatures >1200 °C,[3] but in the given temperature range (575–750 °C) it also contributes to acceleration of the process together with hydrogen peroxide decomposition. According to kinetic data,[20] at 723 °C, the rate constant for reaction (7) is ~2–6 times greater than the rate constant for reaction (6). Presumably, highly reactive $OH^{\bullet}$ and $O^{\bullet}$ radicals formed upon decomposition of H_2O_2 and in reaction (6) rapidly react with methane, which is present in a much higher concentration than ethane or ethylene

$$OH^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + H_2O \quad (8)$$

This results in increasing content of methyl radicals in the system; under the given conditions at temperatures >600 °C, the major pathway for consumption of these radicals is the reaction with ethane (or ethylene) and recombination[8]

$$CH_3^{\bullet} + C_2H_6 \longrightarrow C_2H_5^{\bullet} + CH_4 \quad (9)$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6 \quad (10)$$

Thus, excess of methane promoting the formation of methyl radicals can decrease the rate of chain branching as a result of competition of $CH_3^{\bullet}$ radicals with oxygen for hydrogen atoms as well as for ethane and ethylene. The resulting decrease in the concentration of highly reactive $H^{\bullet}$, $OH^{\bullet}$ and $O^{\bullet}$ radicals should lead to a decrease in the ethane oxidation rate in the presence of methane diluent.

It is noteworthy that the temperature of switching from promoting to inhibiting action of methane (~650 °C) is nearly equal to the temperature above which the concentration of methylperoxyl radicals, providing chain branching during the low-temperature methane oxidation, becomes negligibly low.[3,26] Meanwhile, the accelerating action of methane on the oxidative cracking of ethane at low temperatures was qualitatively confirmed[12] by the results of kinetic modelling using a detailed model for oxidation of these hydrocarbons. The pronounced effect of methane on the yields of the products of ethylene oxidation (which plays a noticeable role in the ethane oxycracking) under conditions very close to the conditions of the described experiments[11,12] was reported by Pogosyan *et al.*[33] Thus, it is necessary to take into account not only physical properties (heat capacity, thermal conductivity) of the gas in which the process is conducted and its efficiency for radical recombination, but also the mutual influence of hydrocarbons, which is present during the oxidation of real gases almost in all cases.

Since the variation of the reactant concentrations with increasing temperature is less pronounced in the case of ethane oxidation in excess methane (see Fig. 13), there appears the possibility to estimate the effective activation energy (E_a) of this process. Magomedov *et al.*[12] found the value $E_a \approx 35$ kcal mol^{-1} in the approximation of first-order kinetics with respect to oxygen; this value is quite consistent with the effective activation energy for the high-temperature oxidation of C_{2+} alkanes (~30 kcal mol^{-1}).[34]

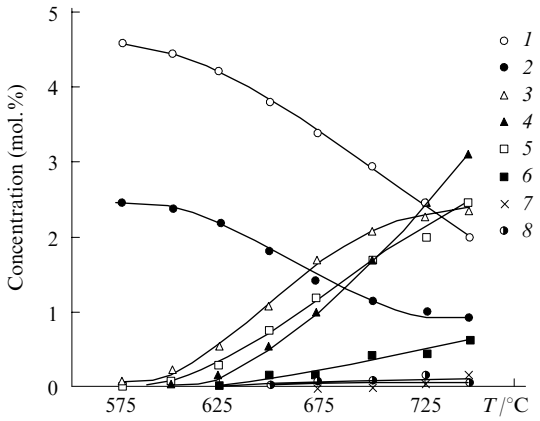


Figure 14. Temperature dependences of the concentrations of reactants and major products of ethane oxidative cracking in methane.[12]
$[C_2H_6]_0 = 4.6\%$, $[O_2]_0 = 2.5\%$, $t_r = 2$ s.
(*1*) C_2H_6, (*2*) O_2, (*3*) H_2O, (*4*) H_2, (*5*) C_2H_4, (*6*) CO, (*7*) C_3H_6, (*8*) CO_2.

The temperature dependences of the reactant and product concentrations in the oxidative cracking of ethane in excess of methane (Fig. 14) confirm the absence of sharp acceleration of the process below 750 °C. Meanwhile, the composition of products formed in the presence of methane does not differ from that observed in experiments[11] with nitrogen and helium dilution. As can be seen from Fig. 14, oxidative dehydrogenation of ethane to give mainly ethylene and water proceeds predominantly at 625 °C. Increasing the temperature increases the contribution of deep oxidation and thermal dehydrogenation, giving rise to CO and hydrogen, the concentration of which above 700 °C exceeds the concentration of ethylene. Like in the case of reactant dilution with nitrogen and helium, most probable are reactions giving methane, which are typical of cracking. However, it is difficult to determine the yield of methane when it is present in a high concentration, because it is simultaneously formed and consumed during the reaction. This is indicated by the higher content of carbon in the products than in the consumed ethane noted by Magomedov *et al.*[12] The conversion of ethane formed upon recombination of methyl radicals is also difficult to estimate, as their concentration should be much higher in excess of methane. Furthermore, with methane dilution, the yield of propylene is higher than that in inert diluents, which may be due to the reaction of methyl radicals with ethylene.

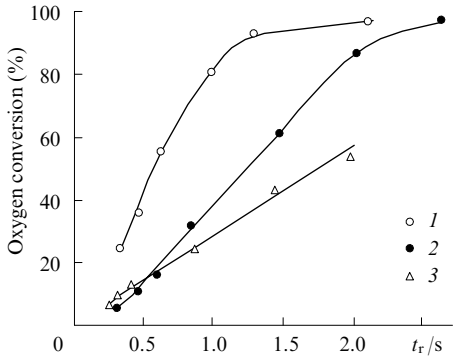


Figure 15. Conversion of oxygen in the oxidative cracking of ethane *vs.* residence time in the reactor in N_2 (*1*), He (*2*) and CH_4 (*3*).[12]
$[C_2H_6]_0 \approx 5\%$, $[O_2]_0 = 2.5\%$, $T = 700$ °C.

For ethane oxidation in excess of methane, the dependence of oxygen conversion on the residence time in the reactor (Fig. 15) differed noticeably from these dependences observed in nitrogen or helium. First of all, there was no self-ignition of the mixture. At 700 °C, the rate of oxygen conversion in methane diluent is almost invariable and is much lower than that in nitrogen or helium, indicating, most likely, that under these conditions, the reaction proceeds beyond the range of branched-chain ignition or that the branched-chain reaction is quasi-steady state.[11,12] The reactant and product concentrations throughout almost the whole process vary linearly with time and $\Delta[C_2H_6] \approx \Delta[O_2]$.[35]

IV. Selective oxidative cracking of C_3-C_5 hydrocarbons

The oxycracking of alkanes that are heavier than ethane follows generally the same patterns at atmospheric pressure than ethane oxycracking.[35] As the initial oxygen concentration grows, the conversion of all C_3-C_5 alkanes monotonically increases, as shown in Fig. 16 for n-butane.

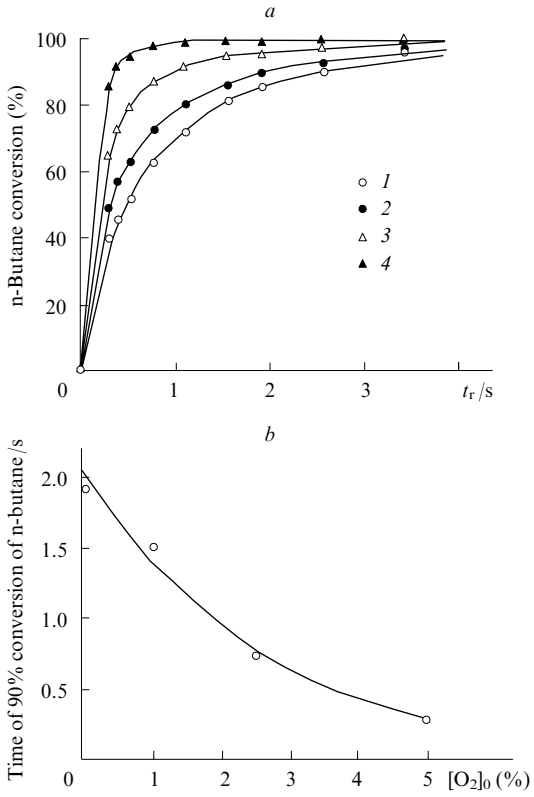


Figure 16. Conversion of n-butane *vs.* residence time in the reactor at various initial concentrations of oxygen (*a*); and time of 90% conversion of n-butane *vs.* initial concentration of oxygen (*b*).[35]
$[n\text{-}C_4H_{10}]_0 = 5\%$, the rest is N_2, $T = 750$ °C; (*a*) $[O_2]_0 = 0$ (*1*), 1 (*2*), 2.5 (*3*), 5% (*4*)

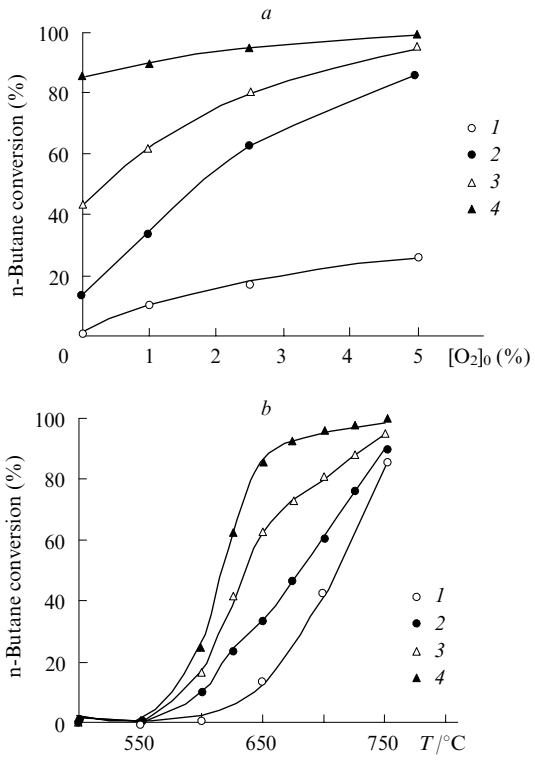


Figure 17. Conversion of n-butane *vs.* initial oxygen concentration for various process temperatures (*a*) and *vs.* temperature for various initial oxygen concentrations (*b*).[35]
$[n\text{-}C_4H_{10}]_0$ = 5%, the rest is N_2, t_r = 2 s.
(*a*) T = 600 (*1*), 650 (*2*), 700 (*3*), 750 °C (4); (*b*) $[O_2]_0$ = 0 (*1*), 1 (*2*), 2.5 (*3*), 5% (*4*).

The effect of oxygen on the conversion of light alkanes depends appreciably on the reaction temperature. The effect of oxygen concentration on the alkane conversion is especially strong in the temperature range of 600 to 700 °C. This effect is much weaker at lower temperatures where catalytic oxidation predominates and at higher temperature where the contribution of thermal cracking is noticeable. The data presented in Fig. 17 show the temperature dependence of n-butane conversion in the presence of oxygen for a constant reaction time sufficient for complete conversion of oxygen and attainment of stable concentrations of the major reaction products (see Fig. 10).

The concentration of oxygen ($[C_nH_{2n+2}]_0 : [O_2]_0$ ratio) is also high. The alkane conversion grows most efficiently at low oxygen concentrations when $[C_nH_{2n+2}]_0 : [O_2]_0 > 2$ (see Fig. 17 *b*). With increasing oxygen concentration, its relative promoting effect decreases.

Naturally, heavier alkanes give a more diverse set of oxidation products. The high-temperature oxidation of n-butane gave, apart from the C_3-C_4 alkenes, butadiene and acetylene; together with C_3H_4, these products can be considered to a certain degree as soot precursors.[36] According to experiments,[35] with increasing oxygen concentration, the yields of butadiene and, to some extent, acetylene decrease. Thus, oxygen appears to inhibit the processes that lead to heavy condensation products able to be converted to resin and soot.

At a relatively low temperature (600 °C), the increase in the oxygen concentration from 1% to 10% has a minor effect on the carbon selectivities to the major products of n-pentane oxidative cracking (except for some decrease in the formation of C_3H_6, C_2H_6 and CH_4 in favour of CO). The selectivity to ethylene (~30%) remained almost constant in this oxygen concentration range. However, at higher temperature (750 °C), it decreased linearly from ~47% to ~39% with increasing oxygen concentration, and this was accompanied by a linear increase in the selectivity to CO from ~3% to 35%. This is indicative of a higher contribution of the secondary deep oxidation of reactants and products. When the concentration of oxygen was < 5%, carbon imbalance increased, probably, due to enhanced formation of undetectable heavy products. In the oxidation of nitrogen-diluted pentane – oxygen mixtures with an oxygen concentration of > 5% ($[C_5H_{12}]_0 : [O_2]_0 \leqslant 1$), a region of negative temperature coefficient of the reaction rate was found in the 350 to 500 °C range. At lower oxygen concentrations ($[C_5H_{12}]_0 : [O_2]_0 \geqslant 1$), only switching to self-ignition was observed at ~500 °C.

The results of Arutyunov *et al.*[35] are in good agreement with those of Pogosyan *et al.*[37] describing the oxidative cracking of propane under closely similar conditions ($P \approx 1$ atm, T = 530 – 820 °C, t_r = 2 s) in a two-section flow reactor (Fig. 18). A pronounced increase in the propane conversion with increasing concentration of oxygen was noted. The reaction products were virtually identical to those observed in the former paper,[35] not only in the composition but (nearly) in the amounts, despite the high $[C_3H_8]_0 : [O_2]_0$ ratio. Although some oxygenates (methanol and acetaldehyde) were formed at low temperatures, their concentrations rapidly decreased with temperature rise (see Fig. 18).

In both studies cited above,[35, 37] a considerable temperature rise resulted in a decrease in the concentration of the propylene product, while the concentration of ethylene remained the same or even somewhat increased (see Fig. 18), *i.e.*, for a higher yield of propylene, less drastic conditions are desirable. The increase in the initial concen-

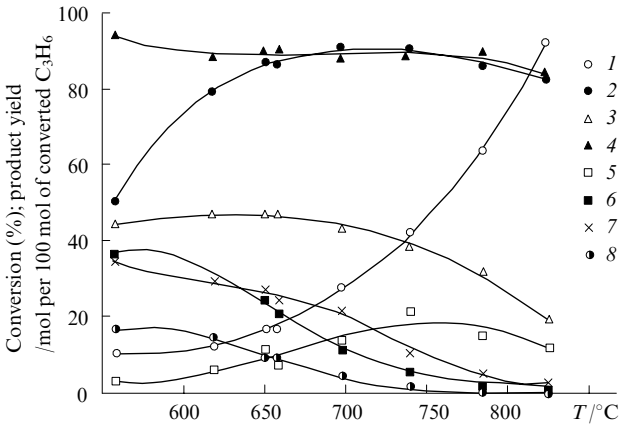


Figure 18. Temperature dependences of the conversions of propane (*1*) and oxygen (*2*) and product yields (*3* – *8*).[37]
Products: (*3*) C_3H_6, (*4*) $C_2H_4 + C_3H_6$, (*5*) CO, (*6*) CO_2, (*7*) CH_3CHO (×100), (*8*) CH_3OH (×10); P = 650 Torr; $[C_3H_8]_0 : [O_2]_0$ = 8 : 1, t_r = 2 s.

tration of oxygen over rather broad limits (but not exceeding the initial concentration of propane) affects slightly the relative yields (in relation to the converted propane) of propylene and ethylene and, hence, their ratio. Thus, a rather high relative yield of alkenes, up to almost 90 moles per 100 moles of converted propane, can be achieved at a rather high conversion of propane. However, as the initial concentration of oxygen increases, the content of carbon oxides in the products rapidly increases, which reduces the selectivity to alkenes and dictates the need for thorough optimization of this parameter.

In both publications, methane was found to markedly influence the oxidative cracking of propane and composition of the products, as shown above in consideration of ethane oxycracking; this may be caused by increasing concentration of methyl radicals resulting from participation of methane in the propane free radical oxidation and the subsequent reactions involving these radicals. The observed increase in the propane conversion in the presence of oxygen is obviously associated with appearance of a chain initiation step more favourable than the thermal C – C and C – H bond cleavage reactions involved in the pyrolysis

$$C_3H_8 \longrightarrow CH_3^{\bullet} + C_2H_5^{\bullet},\ E_a \approx 91.5 \text{ kcal mol}^{-1} \quad (11)$$

$$C_3H_8 \longrightarrow C_3H_7^{\bullet} + H^{\bullet},\ E_a \approx 97.5 \text{ kcal mol}^{-1} \quad (12)$$

that is, chain initiation *via* oxidative dehydrogenation with hydrogen atom abstraction by molecular oxygen

$$C_3H_8 + O_2 \longrightarrow C_3H_7^{\bullet} + HO_2^{\bullet},\ E_a \approx 50.9 \text{ kcal mol}^{-1} \quad (13)$$

In addition, it was shown [35] that under certain conditions in the presence of oxygen, the reaction follows a branched-chain mechanism, which sharply increases the concentration of chain carriers (reactive radicals) and, hence, the conversion of propane. The results confirmed the considerable difference between the mechanisms of homogeneous and heterogeneous oxidative cracking of alkanes.[12, 17] Note the different patterns of the temperature dependences of hydrocarbon and oxygen conversions observed in several works,[11, 12, 35] especially at low temperatures when heterogeneous processes make a significant contribution to the reactant transformations.

It was shown [35] that an increase in the number of carbon atoms in the alkane molecule leads to a monotonic decrease in the temperature of fast gas-phase conversion (self-ignition limit). In terms of the temperature of switching to fast gas-phase conversion, light alkanes can be split into three major groups: methane, ethane – butane and pentane and heavier alkanes (Fig. 19). As noted above, gas-phase conversion of methane under these conditions requires a temperature >1000 °C.[31, 32] Therefore, selective gas-phase oxidation of C_{3+} alkanes in complex gas mixtures such as natural and associated gases, without substantial oxidation of methane, is possible.[3, 5, 17]

This opportunity was implemented in a new process for treatment of natural and associated gases for the use in power engineering.[3, 5, 35]

V. Effect of pressure on the oxycracking of alkanes

Pressure is a principal parameter affecting the oxycracking, together with the temperature and reaction time. The effect of pressure has been considered in detail [38] in relation to the oxycracking of $C_2 - C_4$ alkanes in a quartz flow reactor in the pressure range of 1 – 5 atm and temperature of 300 – 750 °C. The resulting temperature dependences of the reactant conversions during the oxycracking of ethane at different pressures are shown in Fig. 20.

At atmospheric pressure, the reaction proceeds at a noticeable rate only above 625 °C, the beginning of the reaction being accompanied by a sharp increase in the conversion of both reactants up to complete consumption of oxygen and high conversion of ethane. It was noted above in the discussion of the ethane oxycracking that transition from the barely observable reaction to nearly complete consumption of oxygen in a small (<50 °C) temperature range is typical of branched-chain oxidation reactions. At temperatures above the temperature of complete consumption of oxygen, ethane conversion continues to increase at any pressure, including atmospheric but the rate of its increase with temperature sharply slows down (see Fig. 5). The increase in the conversion is interpreted as being due to growing contributions of ethane oxygen-free thermal cracking and dehydrogenation,[11] which have higher activation energy; this accounts for attenuation of the accelerating effect of oxygen on the ethane conversion with temperature.

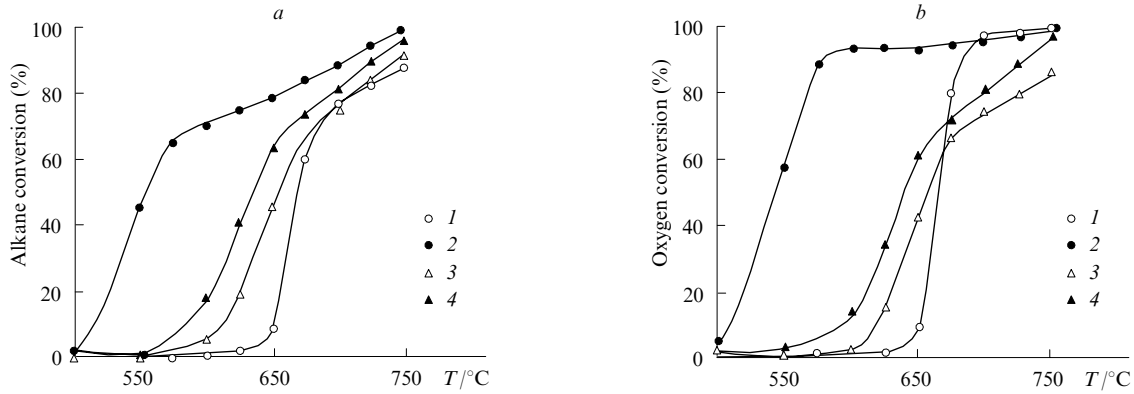


Figure 19. Temperature dependences of the oxidative conversion of $C_2 - C_5$ alkanes (*a*) and oxygen (*b*).[35] $[C_nH_{2n+2}]_0 = 5\%$, $[O_2]_0 = 2.5\%$, the rest is N_2, $t_r = 2$ s; (*1*) C_2H_6, (*2*) n-C_5H_{12}, (*3*) C_3H_8, (*4*) n-C_4H_{10}.

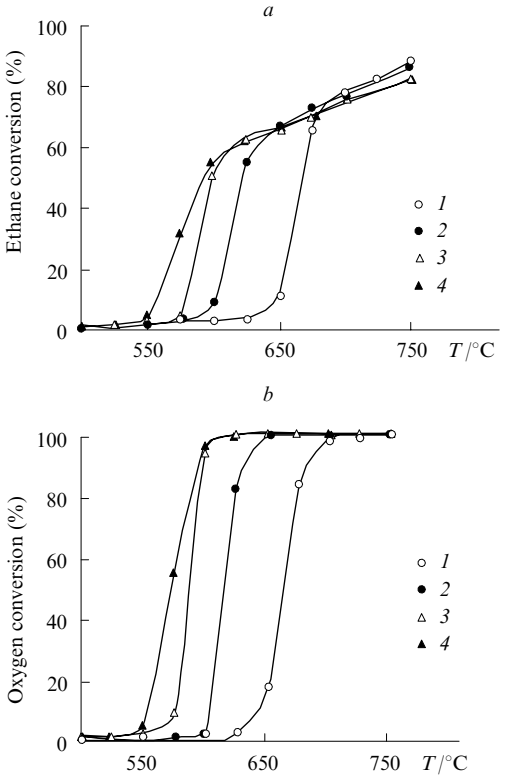


Figure 20. Temperature dependences of the conversion of ethane (*a*) and oxygen (*b*) at a pressure of 1 (*1*), 2 (*2*), 3 (*3*) and 4 atm (*4*).[38] $[C_2H_6]_0 = 4.5\%$, $[O_2]_0 = 2.5\%$, the rest is N_2, $t_r = 2$ s.

Pressure rise leads to a noticeable decrease in the temperature at which the fast reaction starts and, hence, in the temperature at which the reactants are completely consumed (see Fig. 20). As the pressure increases from 1 to 2 atm, the temperature of the onset of reaction decreases by 50 °C. However, on going from 3 to 4 atm, this temperature decreases by less than 20 °C (Fig. 21). On further 10-fold pressure rise (up to 50 atm), the temperature of partial oxidation of ethane decreases by only 100 °C.[39] It is noteworthy that virtually complete consumption of oxygen is accompanied by only partial conversion of ethane, which

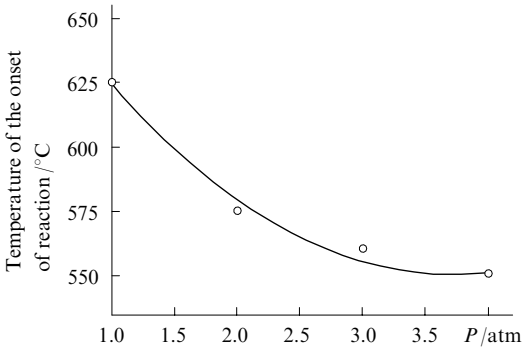


Figure 21. Temperature of the onset of ethane oxycracking *vs.* initial pressure in the reactor.[38]
$[C_2H_6]_0 = 4.5\%$, $[O_2]_0 = 2.5\%$, $t_r = 2$ s.

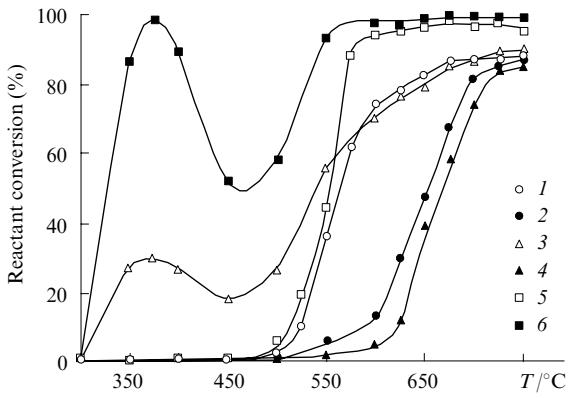


Figure 22. Temperature dependences of the conversion of n-butane (*1*–*3*) and oxygen (*4*–*6*) at a pressure of 1 (*2*, *4*), 3 (*1*, *5*) and 5 atm (*3*, *6*) (according to Ref. 38).
$[C_4H_{10}]_0 = 4.5\%$, $[O_2]_0 = 2.5\%$, $t_r = 2$ s.

decreases with increasing initial pressure in the system (see Fig. 20).

It was noted above that ethane and methane markedly differ in the chemical properties from higher alkanes containing CH_2 groups with weak C–C and C–H bonds. The presence of these groups in C_{3+} alkane molecules and radicals accounts for the difference between the mechanisms of oxidative cracking of ethane and heavier hydrocarbons.

The temperature dependences of the conversion of reactants in n-butane oxidative cracking at pressures of 1 and 3 atm are shown in Fig. 22. As in the ethane oxycracking, the pressure increase results in a decrease in the process temperature by 100 °C. However, as opposed to the oxidation of ethane, which soon arrives at a virtually complete oxygen consumption in the given temperature range and at atmospheric pressure, in the oxidation of butane above 675 °C, when thermal pyrolysis already occurs at a noticeable rate,[40] the increase in the oxygen and n-butane conversions slows down. This can be attributed to a decrease in the contribution of oxygen consumption channels and, hence, retardation of the oxygen conversion. In the oxidative cracking of C_{3+} alkanes at atmospheric pressure, the hydrocarbon conversion in the temperature range of 500–700 °C is higher than the conversion of oxygen. This is attributable to a contribution of thermal cracking processes — the major reactions giving alkenes and alkanes with fewer carbon atoms. Meanwhile, oxygen is predominantly consumed in the partial and complete oxidation to give mainly water, CO and CO_2. However, as the pressure increases to 3 atm, the limiting conversion of oxygen considerably increases, while the limiting conversion of butane barely changes (see Fig. 22).

Of particular interest is the region of negative temperature coefficient of the rate of butane oxycracking at a pressure of 5 atm found by Nikitin *et al.*[38] It was noted [41] that the temperature at which the reaction switches from low-temperature kinetics to a 'high-temperature' mechanism increases with pressure rise. According to kinetic analysis,[38] a pressure increase at temperatures >550 °C results in higher contribution of pathways involving the $HO_2^{\cdot}$ peroxyl radical. At atmospheric pressure, the butyl radical undergoes thermal decomposition according to the reaction

$$C_4H_9^{\bullet} \longrightarrow C_4H_8 + H^{\bullet} \quad (14)$$

to give a hydrogen atom, which in turn reacts with oxygen thus generating the $HO^{\bullet}$ and $O^{\bullet\bullet}$ radicals

$$H^{\bullet} + O_2 \longrightarrow HO^{\bullet} + O^{\bullet\bullet} \quad (15)$$

This reaction is the major pathway of chain branching in this temperature range at atmospheric pressure.

The increase in the pressure to 5 atm leads to higher contribution of the reaction of butyl radicals with oxygen to give peroxyl radicals

$$C_4H_9^{\bullet} + O_2 \longrightarrow C_4H_8 + HO_2^{\bullet} \quad (16)$$

The increase in the concentration of the latter radicals gives rise to hydrogen peroxide

$$C_4H_{10} + HO_2^{\bullet} \longrightarrow C_4H_9^{\bullet} + H_2O_2 \quad (17)$$

which decomposes

$$H_2O_2 + M \longrightarrow 2\,HO^{\bullet} + M \quad (18)$$

(M is some molecule) to provide an additional chain-branching pathway.

The results reported in two publications [13, 38] are consistent. Of special note is good agreement between the results of kinetic analysis of the conversions of reactants during the oxycracking of butane in the region of negative temperature coefficient of the reaction rate at elevated pressure carried out by Nikitin *et al.*[38] and experimental results. Thus, an increase in the pressure makes it possible to conduct the oxycracking of heavy components of associated petroleum gas under milder temperature conditions to attain virtually complete conversion of oxygen. However, operation in the pressure range >5 atm is inexpedient, because this no longer leads to a significant change in the process temperature, but requires more complex and heavy equipment.

The conversions of reactants as functions of the reaction time during the oxidative cracking of propane at 1 and 2 atm are shown in Fig. 23. At atmospheric pressure, the conversions increase nearly linearly with reaction time up to the limiting conversion of propane and then virtually do not change, although the residual concentration of propane is still rather high. This may be indicative of a low rate of oxygen-free thermal pyrolysis of propane under these conditions. When the pressure is increased to only 2 atm, the time required to reach the limiting conversion of reactants is reduced from 4 to 1.5 s.

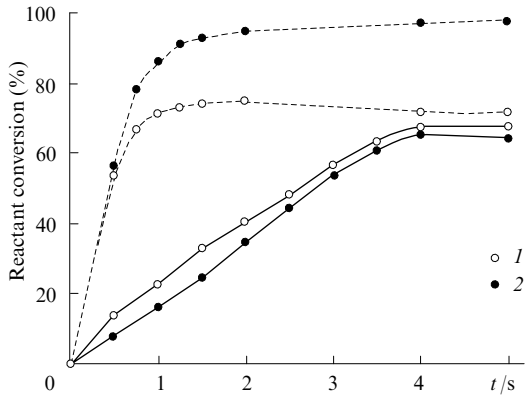


Figure 23. Time dependences of the conversion of propane (*1*) and oxygen (*2*) at $P = 1$ (solid lines) and 2 atm (dashed lines) in the oxidative cracking of propane.[38]
$[C_3H_8]_0 = 4.5\%$, $[O_2]_0 = 2.5\%$, $T = 650$ °C.

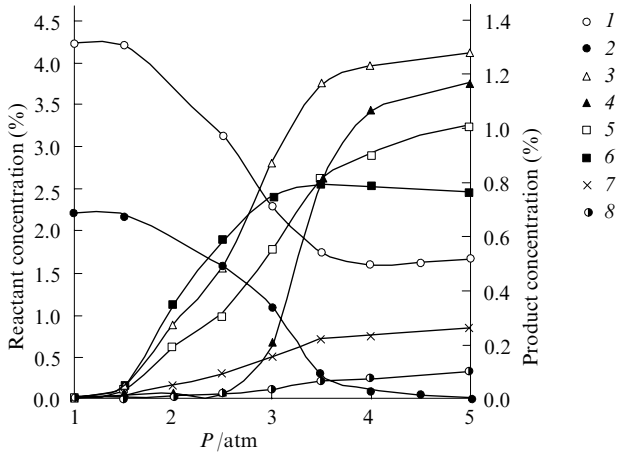


Figure 24. Concentrations of reactants (*1*, *2*) and products (*3*–*8*) of the oxidative cracking of propane *vs.* pressure.[38]
(*1*) C_3H_8, (*2*) O_2, (*3*) C_2H_4, (*4*) CO, (*5*) CH_4, (*6*) C_3H_6, (*7*) H_2, (*8*) CO_2.
$[C_3H_8]_0 = 4.3\%$, $[O_2]_0 = 2.3\%$, $T = 575$ °C, $t_r = 2$ s.

The major products formed in the oxidative cracking of C_2–C_4 alkanes are alkenes (ethylene, propylene and butylenes) and oxygenates resulting from partial and complete oxidation — water, CO and CO_2.

The concentrations of reactants and products as functions of pressure in the oxycracking of propane are presented in Fig. 24. It can be seen that at atmospheric pressure, the reaction virtually does not proceed, while at 2 atm the reaction rate becomes much higher and the concentrations of reactants decrease. The content of oxygen under these conditions is below the stoichiometric amount and, after oxygen has been completely consumed at 3.5 atm, further pressure rise does not change the concentrations of propane or conversion products. These experimental results provide the conclusion that the oxycracking rate increases with increasing pressure under these conditions, whereas thermal reactions are slightly pressure-dependent. In the region of high propane conversions, the selectivities to the major products (ethylene, propylene, methane, CO and water) virtually do not change with pressure (Fig. 25), *i.e.*, despite the fact that pressure rise promotes higher conversion of alkanes, it affects only slightly the carbon and oxygen distribution between the major products.

Note that the partial oxidation of light n-alkanes in methane is of special interest, as it corresponds to the oxidation of real associated gases. The temperature dependences of the conversion of reactants during propane oxycracking in nitrogen and methane at pressures of 1 and 3 atm are presented in Fig. 26. It was shown [12, 35, 42] that under these conditions, methane noticeably inhibits the oxidation reactions but slightly affects thermal cracking. However, in the oxycracking of light alkanes at pressures >3 atm, methane no longer inhibits the oxidation at high temperatures.

Thus, the cited results [38] provide the conclusion that 2–4 atm is the most favourable pressure range for the

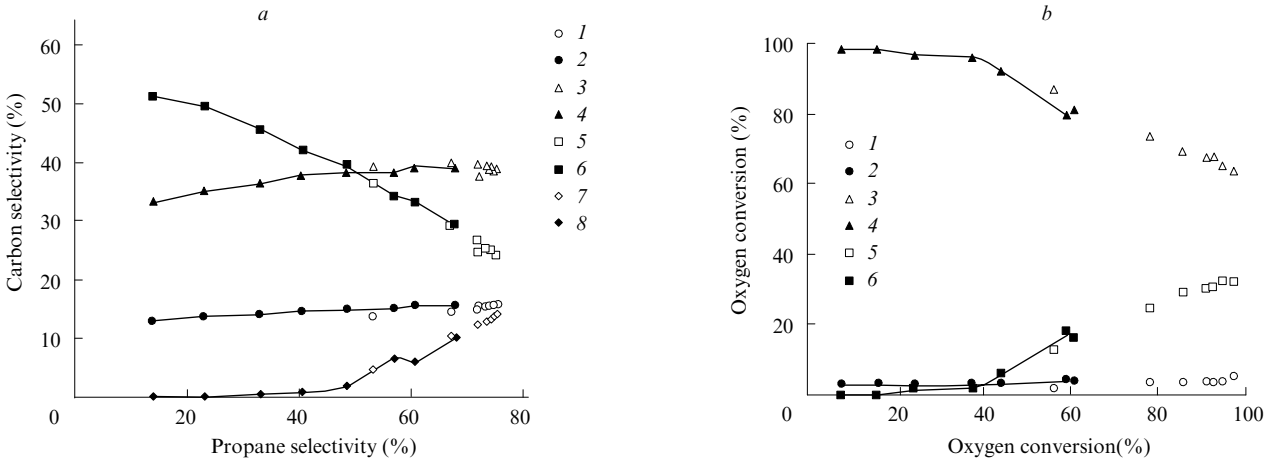


Figure 25. Selectivities to carbon-containing products (*a*) and oxygenates (*b*) *vs.* conversion of reactants at $P = 1$ (dark dots) and 2 atm (light dots).[38]
(*a*) (*1*, *2*) CH_4; (*3*, *4*) C_2H_4; (*5*, *6*) C_3H_6; (*7*, *8*) CO; (*b*) (*1*, *2*) CO_2; (*3*, *4*) H_2O; (*5*, *6*) CO; $T = 500 - 700$ °C, $[C_3H_8]_0 = 4.5\%$, $[O_2]_0 = 2.5\%$, $t_r = 0.5 - 4$ s.

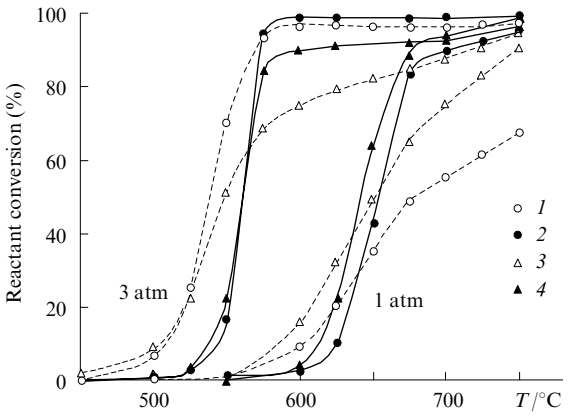


Figure 26. Temperature dependences of reactant conversion in the oxidative cracking of propane diluted with nitrogen (solid lines) and methane (dashed lines) at $P = 1$ and 3 atm.[38]
In methane: (*1*) O_2, (*3*) C_3H_8; in nitrogen: (*2*) O_2, (*4*) C_3H_8; $[C_3H_8]_0 = 5.0\%$, $[C_3H_8]_0 : [O_2]_0 = 1 : 1$, $t_r = 2$ s.

selective oxycracking of $C_2 - C_4$ light alkanes; this is virtually coincides with the pressure of associated gas coming from the first separation stage.

VI. Application of the selective oxidative cracking of methane homologues present in natural and associated gases in power engineering

In this and subsequent Sections, we consider the prospects for practical applications of the selective oxidative cracking of C_{3+} alkanes, heavy components of natural and associated gases. One such application is associated with pretreatment of these gases for the use as a power-generating fuel. The problem is that crude natural and, especially, associated petroleum gases are inapplicable for the direct use in modern electric power plants, in particular, based on gas piston engines, because they contain low-octane C_{3+} hydrocarbons. High contents of C_{3+} hydrocarbons in the gas mixture brings about engine knock (detonation) and prevents the engine from attaining the rated power; furthermore, soot deposition takes place and wear of engine parts is accelerated; hence, the engine service life decreases. It was shown[43] that the presence of even 1% of $C_3 - C_5$ alkanes substantially shortens the methane ignition delay (Fig. 27). This is directly indicative of the corresponding decline of the antiknock properties of this gas mixture.

Fast decrease in the ignition delay with increasing pentane content in methane is indicated by the fact that as little as 0.5% of pentane contained in methane leads to a two- to three-fold reduction of the ignition delay of a stoichiometric methane – air mixture, and addition of 10% of pentane to methane results in ignitability virtually equal to that of pentane. As the number of carbon atoms in the added alkane molecule increases, the effect of this alkane on the methane ignition delay is enhanced; this leads to a monotonic decrease in the self-ignition delay (Fig. 28). However, C_{5+} alkanes have rather similar effects on the self-ignition delay of methane. Therefore, the influence of these higher alkanes on the self-ignition delay may be considered by taking their total concentration and the delay approximately equal to that induced by pentane. The more so, because in real gases, the concentrations of alkanes decrease very rapidly with increasing number of carbon atoms in the molecules.

The ignition delay, which follows a non-linear dependence on the concentration of heavier alkanes, decreases mainly in their concentration range of 0.5% to 1% (see Fig. 27). Thus, this concentration can be taken as a rough estimate for the admissible content of heavy components in a gas fuel for gas piston engines at which their effect on the antiknock properties of the fuel is low and does not lead to significant loss of the generated power. At higher pressures inherent in gas piston engines, the relative decrease in the ignition delay caused by the presence of alkanes does not differ much from the values determined at atmospheric pressure. Thus, according to experimental data,[43] a sufficiently high octane (methane) number of a natural gas

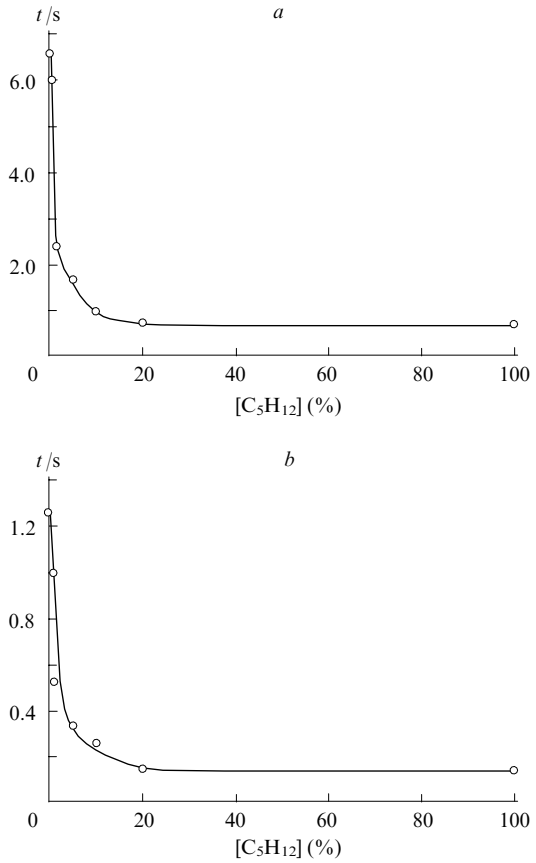


Figure 27. Ignition delay for a methane–pentane–air mixture (t) *vs.* pentane concentration at $P_0 = 1$ atm, a stoichiometric ratio between the fuel and the oxidant and $T = 890$ (*a*), 990 K (*b*).[43]

engine fuel can be achieved when the total content of the C_{5+} hydrocarbons is not more than 0.5%.

Certain requirements are imposed on the fuel gas quality to ensure normal operation of the equipment and performance characteristics claimed by manufacturers of gas piston engines. These requirements may differ somewhat depending on the type and design of the engine; most typical of them are listed below:[44]

— methane content of $>70\%$;
— lower heating value of 30–36 MJ m^{-3};
— gas density of 0.7–1.2 kg m^{-3}.

A highly important characteristics of gas fuel is the methane index (MN),[45] which characterizes the antiknock properties in terms of the scale in which MN = 100 is taken for methane and MN = 0 is taken for hydrogen. The methane number is calculated using various software (available on the Internet);§ it is related to the motor octane number (MON) by the empirical expression

$$MN = 1.624\,MON - 119.1 \quad (19)$$

Crude wet natural and associated gases usually have high calorific values (the lower heating value Q_H exceeds 40 MJ m^{-3}) and low methane number, usually <52. However, the manufacturers of gas piston engines demand, most often, smaller calorific values and greater MN. Indeed, Cummins Westport specialists believe that steady operation of engines can be achieved with gas mixtures with methane numbers >65 (see§). The component composition of natural gases depends appreciably not only on the location and climatic conditions of the production area but also on the season of production, gas treatment and transportation methods and some other conditions, in particular, the gas composition is constantly changing as the deposit is being depleted. The separation of heavy components from natural gas by known compression, cryogenic and adsorption methods requires expensive equipment and high energy expenditure, which do not pay off with the use of small power units, mainly used for power supply of most remotely located oil-and-gas production enterprises.

In the case of small gas volumes, the known gas treatment processes based on additional chemical processing of the heavy components of hydrocarbon gases also have low cost efficiency. For example, for the production of syngas from gas mixtures containing C_{3+} hydrocarbons, Haldor Topsoe (Denmark) uses mild catalytic pre-reforming involving steam conversion of C_{3+} hydrocarbons to CH_4, CO and hydrogen at 450–550 °C.[46] A similar process was considered by Zyryanova *et al.*[47] However, the substantial rise in the cost and in the complexity of equipment upon introduction of the additional steam pre-reforming stage and the additional energy expenditure for this highly power-consuming operation preclude extensive use of this process in the field. Therefore, many producing enterprises have to deliver expensive liquid fuel, while simultaneously flaring huge amounts of associated petroleum gas. New, more facile and flexible processes for associated petroleum gas pretreatment that would enable utilization of the gas directly in the field are thus required.

A promising way for solving this issue is selective homogeneous oxidation of heavy components of associated petroleum gas. The possibility of selective gas-phase oxidation of C_{3+} alkanes in complex gas mixtures such as natural and associated gases without significant oxidation of methane was implemented in a new technology for pretreating crude natural and associated gases for the use in power engineering.[3, 5, 35, 48, 49]

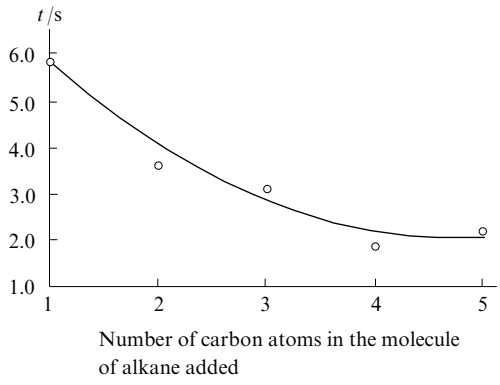


Figure 28. Self-ignition delay *vs.* number of carbon atoms in the molecule of alkane added.[43]
Alkane concentration 5%, stoichiometric ratio between the fuel and the oxidant, $P_0 = 1$ atm, $T = 890$ K.

§ See *Natural Gas as Fuel. Fuel Quality Calculator*. http://www.cumminswestport.com/fuel-quality-calculator.

Table 1. Changes in the fuel characteristics upon oxycracking of hydrocarbon gas mixtures at 750 °C and reaction time of ~2 s.[51]

Oxygen in the feed (see [a])	Feed gas						Effluent gas						
	CH_4	C_3H_8	C_4H_{10}	C_5H_{12}	MN	Q_H /MJ m^{-3}	CH_4	CO	C_2H_4	C_{3+}	N_2	MN	Q_H /MJ m^{-3}
	(vol. %)						(vol. %)						
Methane + butane mixture, oxidant — oxygen													
27	95.1	–	4.9	–	64.1	40.2	89.7	1.4	3.7	1.8	–	79.7	36.9
10	95.3	–	4.7	–	64.9	40.0	91.1	0.6	3.3	2.1	–	79.1	37.4
Methane + pentane mixture, oxidant — 60% O_2 + 40% N_2													
56	94.1	–	–	5.9	60.5	42.5	81.3	4.0	5.2	1.7	3.2	75.7	35.4
Methane + pentane mixture, oxidant — air													
67	94.1	–	–	5.9	60.5	42.5	66.9	2.1	4.5	2.5	19.0	74.8	30.4
Methane + propane + pentane mixture, oxidant — 60% O_2 + 40% N_2													
96	88.0	6.0	–	6.0	52.9	46.0	72.6	6.6	7.4	2.9	4.8	66.6	35.2
Methane + ethane (6%) *+ propane + butane mixture, oxidant — oxygen*													
162	82.0	8.0	4.0	–	54.3	45.7	71.2	9.4	7.6	1.7	0.7	69.6	34.2

[a] Litres of oxygen per hour per 1000 litres of the feed gas.

The oxidative cracking gives compounds with both high (methane and CO, $MN_{CO} = 73$) and low (ethylene, $MN_{C_2H_4} = 16$) methane index and hydrogen. The CO to ethylene concentration ratio in the resulting gas mixture can be controlled by varying the ratio between oxygen and hydrocarbon gas.[50] Study of the composition and fuel characteristics of gas mixtures resulting from the oxidative cracking of hydrocarbon gases of various compositions demonstrated [51] that even minor amounts of oxygen added decrease substantially the content of C_{3+} hydrocarbons (Table 1), and the fuel characteristics of the resulting gas mixture approach the requirements for a gas piston engine fuel.

It is noteworthy that oxycracking gases contain alkenes; therefore, additional investigations are required to elucidate their effect on the performance of power units and environmental aspects of the use of this type of fuel. The problem can also be solved by using an additional process to remove alkenes from oxycracking gases, for example, absorption with an appropriate solvent or carbonylation or oligomerization reactions involving alkenes.[52 – 55]

The possibility of practical implementation of fuel gas pretreatment based on selective oxycracking of heavy components of associated gas was confirmed by pilot tests,[3, 35, 56] which demonstrated that the process can involve up to 90% of the C_{5+} fraction and up to 80% of the $C_3 - C_4$ fraction (Fig. 29 *a*).

As a result of this oxidative conversion, heavy components of associated gas are converted to lighter products (mainly H_2, C_2H_4, CH_4 and CO and minor amounts of C_2H_6 and C_3H_6), which makes the obtained gas suitable as a gas piston engine fuel. Apart from the ease of industrial implementation, other benefits of this method are that the initial calorific value of the gas can be used almost completely, no additional products requiring disposal are formed, and there is no need to use catalysts or other expendable materials. According to our estimates, the application of such process in oil fields could reduce the

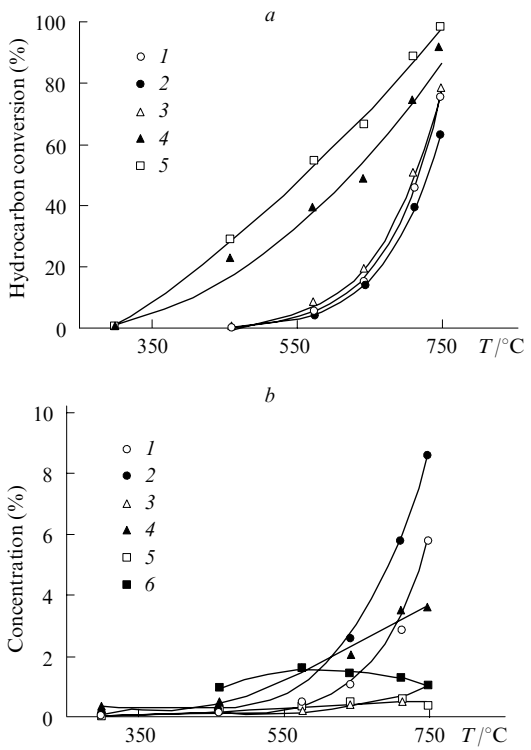


Figure 29. Results of pilot experiments on the oxidative cracking of a typical associated gas with the composition (%): CH_4, 81.0; C_2H_6, 1.22; C_3H_8, 17.0; C_4H_{10}, 2.81; C_5H_{12}, 1.50; n-C_6H_{14}, 1.83.[56] (*a*) Conversion of C_2H_6 (*1*), C_3H_8 (*2*), n-C_4H_{10} (*3*), n-C_5H_{12} (*4*), n-C_6H_{14} (*5*); (*b*) concentrations of the major products (%): (*1*) H_2, (*2*) C_2H_4, (*3*) C_3H_6, (*4*) CH_4, (*5*) C_2H_6, (*6*) CO.15% of air added, $t_r \approx 1$ s.

volume of burned associated gas by 20% – 30%, let alone the cut of the expenses for liquid fuel delivery.

VII. Preparation of gas mixtures with a controlled ethylene to carbon monoxide ratio

The formation of gas mixtures containing basic products such as ethylene and CO upon the selective oxycracking of light alkanes opens up the opportunity to prepare a variety of compounds based on these products. However, practical implementation of these processes requires detailed understanding of the kinetics of the oxidative cracking of light alkanes, investigation of the routes for increasing the product yields and optimization of the ethylene to CO ratio depending on the composition of the compounds to be synthesized.

The possibility to prepare both synthesis gas and unsaturated hydrocarbons for the subsequent carbonylation or hydroformylation by the oxycracking of light alkanes was mentioned by Lange *et al.*[16] It was shown that in the oxycracking of ethane and isobutane on a Pt/Al_2O_3 catalyst conducted autothermally, the yield of unsaturated hydrocarbons can reach 40% – 50% while the yield of CO varies in the 15% – 40% range. In turn, this corresponds to the $[C_2H_4]:[CO]$ molar ratio from 1 : 1 to 1 : 2 in the case of ethane and the $[C_2H_4 + C_3H_6]:[CO]$ molar ratio from 1 : 1 to 1 : 3 in the case of isobutane. It was emphasized that the process can give a substantial amount of CO or synthesis gas.

A systematic research into the production of gas mixtures with a controlled ethylene to carbon monoxide ratio by gas-phase oxidative cracking of light alkanes has been undertaken by Magomedov *et al.*[50] The experiments were carried out at atmospheric pressure in a unit described in detail earlier,[11] comprising a 350 mm long flow quartz reactor with an inner diameter of 14 mm, at temperatures from 500 to 750 °C and residence times of the reactants in the isothermal section of the reactor of 0.3 to 5.3 s. The hydrocarbon concentration in the mixture was 5% and the oxygen concentration was varied from 0% to 10%. Nitrogen or methane were used as diluents. Since mixtures of hydrocarbons and oxygen were highly diluted, the experimental conditions can be considered to be close to isothermal. The effects of the key process parameters — temperature, contact time and initial concentrations of alkane and oxygen — on the ethylene to carbon monoxide ratio were studied.

VII.1. Temperature effect

The effect of temperature on the concentration of reactants and major products will be considered in relation to the oxidative cracking of propane (Fig. 30). During the thermal cracking of propane, the iso-$C_3H_7^{\bullet}$ radical, which has C – H bonds only in the β-position to the carbon atom with the free valence, decomposes to give mainly propylene

$$\text{iso-}C_3H_7^{\bullet} \longrightarrow C_3H_6 + H^{\bullet} \qquad (20)$$

while the n-$C_3H_7^{\bullet}$ radical mainly decomposes with C – C bond cleavage to give ethylene and the methyl radical[36, 57, 58]

$$\text{n-}C_3H_7^{\bullet} \longrightarrow C_2H_4 + CH_3^{\bullet} \qquad (21)$$

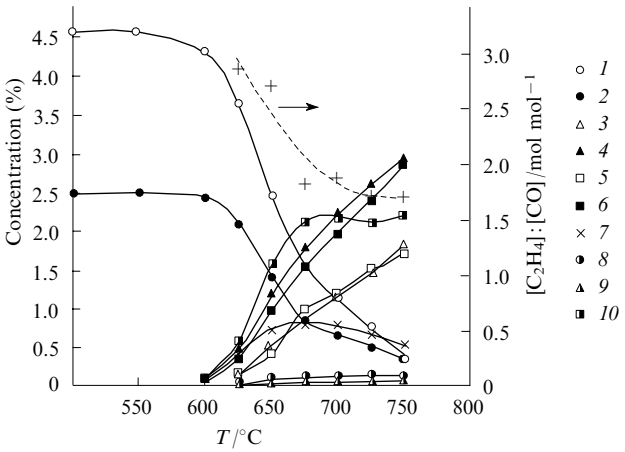


Figure 30. Temperature dependences of the concentrations of reactants and products and $[C_2H_4]:[CO]$ ratio in the gas-phase oxidative cracking of propane.[50]
(*1*) C_3H_8, (*2* O_2, (*3*) H_2, (*4*) C_2H_4, (*5*) CO, (*6*) CH_4, (*7*) C_3H_6, (*8*) C_2H_6, (*9*) CO_2, (*10*) H_2O.
$[C_3H_8]_0 = 4.6\%$, $[O_2]_0 = 2.5\%$, $t_r = 2$ s.

However, in the presence of oxygen, iso-$C_3H_7^{\bullet}$ reacts rapidly with an oxygen molecule to give propylene and hydroperoxyl radical[58]

$$\text{iso-}C_3H_7^{\bullet} + O_2 \longrightarrow C_3H_6 + HO_2^{\bullet} \qquad (22)$$

The $HO_2^{\bullet}$ radical reacts with a propane molecule to form hydrogen peroxide, which decomposes to give hydroxyl radicals — the principal radicals providing chain propagation and formation of water upon the reaction with a propane molecule.[58]

When the conversions of propane and oxygen are low, ethylene, methane, propylene and water are formed in similar amounts (see Fig. 30). This suggests that the rates of formation of n-propyl and isopropyl radicals from propane are roughly equal, like the rates of C – C and C – H bond cleavage in these radicals to give ethylene, propylene and $CH_3^{\bullet}$ and $HO^{\bullet}$ radicals — precursors of methane and water, respectively. A similar ratio of these products was observed in a study of oxidative conversion of propane at very low partial pressures of oxygen in the mixture.[58]

At temperatures above 625 °C the process soon accelerates, probably, as a result of increasing rate of hydrogen peroxide decomposition, a key chain-branching reaction in the oxidation of alkanes in the given temperature range;[11, 13, 24, 58] acceleration is accompanied by fast consumption of propane and oxygen (see Fig. 30). As the temperature and the reactant conversion increase, the contribution of deep oxidation reactions to give carbon monoxide increases. Unlike ethylene and methane, the concentrations of which, like the CO concentration, almost linearly increase with temperature, the propylene concentration and, hence, the yield pass through a maximum at ~675 °C. This is indicative of secondary reactions in which propylene is consumed (most of all, oxidation) and the possible increase in the contribution of unimolecular decomposition of propane molecules with C – C bond cleavage above 675 °C where its thermal pyrolysis starts to proceed at a noticeable rate.[59]

It is noteworthy that in the temperature range in question and at the chosen residence time, carbon monoxide and hydrogen are formed in similar amounts (see Fig. 30); this formally corresponds to the stoichiometry of the overall alkene oxidation reaction

$$C_nH_{2n} + (n/2)\,O_2 \longrightarrow n\,CO + n\,H_2 \qquad (23)$$

However, actually, CO is also formed in the reaction of oxygen with methyl radicals [58] resulting from cracking of C_{3+} alkyl radicals [see reaction (21)] and hydrogen arises upon unimolecular cleavage of C – H bonds. These reactions make greater contributions at higher temperature, because they have higher activation energies than the bimolecular reactions involving oxygen [E_a of 3 and $\sim$37 kcal mol^{-1} were reported [20] for reactions (22) and (20), respectively].

A similar effect of temperature on the distribution of products of gas-phase oxidative dehydrogenation of propane was observed by other researchers,[28, 59] who assumed that at higher temperature, propylene undergoes secondary reactions and thus decomposes to smaller and more stable molecules. Kondratenko and Sinev [60] attributed the increase in the ethylene to propylene ratio in the oxidative dehydrogenation of propane with temperature rise to higher reactivity of propylene in the subsequent oxidation reactions. Since propylene contains a weakly bound hydrogen atom in the CH_3 group, its complete oxidation proceeds much faster than the oxidation of ethylene. For example, in the 550 – 650 °C range, the rate constant for hydrogen atom abstraction from a propylene molecule by oxygen is $\sim$300 – 700 times higher than that from ethylene molecule.[60] Although the concentration of ethylene increases with temperature, a faster increase in the CO content as a result of secondary reactions leads to a lower $[C_2H_4]:[CO]$ ratio in the products (see Fig. 30).

The decrease in the propylene concentration with temperature rise is matched by fast decrease in the selectivity to propylene (Fig. 31), mainly as a result of increasing selectivity to more stable ethylene and also methane and carbon monoxide. As noted above, this is attributable to higher contributions of cracking and deep oxidation reactions.

Thus, with increasing temperature, the concentration ratio of ethylene to carbon monoxide decreases (see Fig. 30), but the fraction of converted carbon simultaneously increases (see Fig. 31), which should be borne in mind for optimization of conditions for the subsequent catalytic syntheses based on these compounds. In view of the moderate selectivity to and low yields of C_{4+} alkenes, which are relatively unstable in the temperature range of interest, one can predict, at a qualitative level, that this pattern of temperature effect on the distribution of products and the $[C_2H_4]:[CO]$ ratio would be retained on going from propane to heavier alkanes.

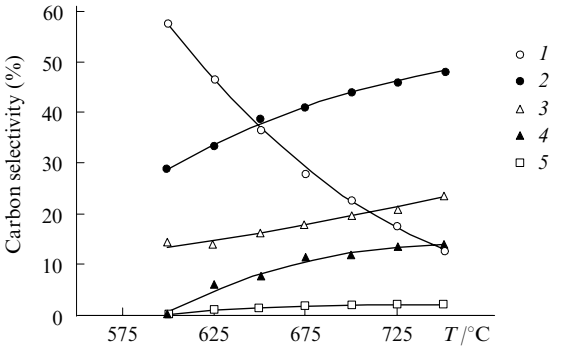


Figure 31. Temperature dependences of the selectivities to major products of the oxidative cracking of propane.[50]
(*1*) C_3H_6, (*2*) C_2H_4, (*3*) CH_4, (*4*) CO, (*5*) C_2H_5; $[C_3H_8]_0$ = 4.6%, $[O_2]_0$ = 2.5%, t_r = 2 s.

VII.2. Effect of the residence time of reactants in the reactor

Since branched-chain gas-phase oxidation reactions have an induction period, the residence time of reactants in the reactor is an important parameter affecting the conversion of reactants and distribution of products. The effect of the residence time on the concentration of products and $[C_2H_4]:[CO]$ ratio in the propane oxycracking at 700 °C is illustrated in Fig. 32. It can be seen from the curves that at short residence times (< 0.5 s) and low yields of CO (< 1%), the amount of consumed propane is $\sim$3 times as great as that of consumed oxygen, whereas according to the stoichiometry of oxidative dehydrogenation, this ratio is equal to two. This may be indicative of a considerable contribution of unimolecular decomposition reactions, as is also evidenced by the distribution of products. At relatively short times and low oxygen conversions, the major products are those resulting from cracking (methane, ethylene) and dehydrogenation (propylene, water and hydrogen), the products being formed in similar amounts, which is also the case for low temperature (see Fig. 30). The formation of hydrogen in the same quantity as propylene even at short residence times confirms the considerable contribution of thermal dehydrogenation at this temperature. Carbon monoxide is formed after a slight time delay, most likely, as a result of secondary oxidative conversion of primary products, mainly propylene, the concentration of which goes through a feebly marked maximum with increase in the residence time and then becomes markedly lower than the

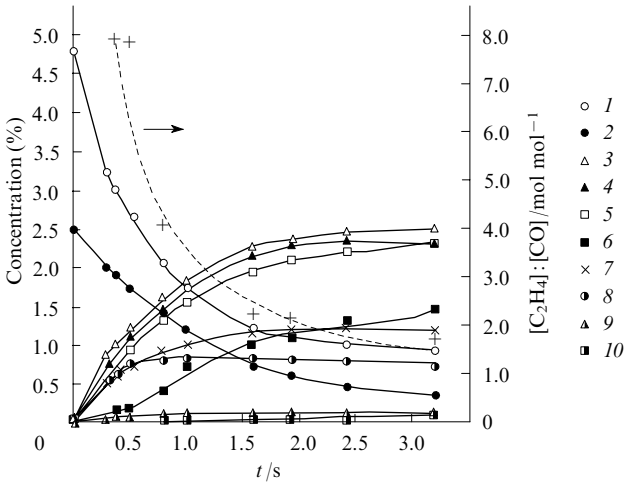


Figure 32. Concentrations of the reactants and products and $[C_2H_4]:[CO]$ ratio *vs.* residence time in the reactor in the oxidative cracking of propane.[50]
(*1*) C_3H_8, (*2*) O_2, (*3*) C_2H_4, (*4*) H_2O, (*5*) CH_4, (*6*) CO, (*7*) H_2, (8) C_3H_6, (*9*) C_2H_6, (*10*) CO_2.
$[C_3H_8]_0$ = 4.6%, $[O_2]_0$ = 2.5%, T = 700 °C, P = 1 atm.

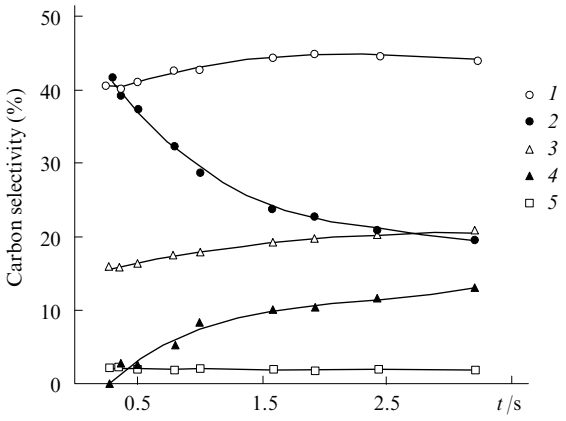


Figure 33. Selectivities to major products of the oxidative cracking of propane *vs* residence time in the reactor.[50]
(*1*) C_2H_4, (*2*) C_3H_6, (*3*) CH_4, (*4*) CO, (*5*) C_2H_6; $[C_3H_8]_0 = 4.6\%$, $[O_2]_0 = 2.5\%$, $T = 700$ °C.

ethylene and methane concentrations. The increase in the yield of CO leads to a fast decrease in the $[C_2H_4]:[CO]$ ratio in the reaction products and, hence, the reactant conversion (see Fig. 32).

As the residence time of reactants in the reactor increases, the contribution of secondary deep oxidation reactions grows, resulting in lower selectivity and formation of propylene, which is less stable and more reactive than ethylene, and in higher selectivity to CO (Fig. 33). Thus, the residence time, like temperature, determines the conversions of reactants and intermediate products and, hence, the degree of the reaction. Since the carbon distribution in the products changes, one can control the ethylene to carbon monoxide ratio in the oxidative cracking of light alkanes over a particular range by varying the residence time.

VII.3. Effect of the initial concentration of oxygen

The initial oxygen concentration (or hydrocarbon to oxygen ratio) in the starting mixture is a key parameter affecting not only the reaction rates and reactant conversions, but also the distribution of products, together with the temperature and residence time. The effect on the oxygen concentration in the feed on the concentrations of major products and the $[C_2H_4]:[CO]$ ratio in the oxidative cracking of n-butane and n-pentane at 750 °C and at invariable conversion of the hydrocarbon is illustrated in Fig. 34. At a constant and virtually complete conversion of the hydrocarbon, an increase in the oxygen concentration in the mixture (or a decrease in the alkane to oxygen ratio) results in a linear increase in the yield of CO. For oxygen concentrations below 5% ($[C_nH_{2n+2}]:[O_2] > 1$), this is accompanied by a decrease in the yield of methane and ethylene with a minor change in the yield of propylene, which starts to rapidly decrease only when the oxygen concentration is $> 5\%$ (see Fig. 34 *b*). By varying the initial alkane to oxygen ratio, one can control the $[C_2H_4]:[CO]$ ratio of the products over a broad range. For example, when the oxygen concentration in the oxidative cracking of n-pentane ($[C_5H_{12}]_0 = 5\%$) grows from 1% to 10%, the $[C_2H_4]:[CO]$ ratio diminishes from 7.4 to 0.6. It is also noteworthy that the addition of oxygen substantially increases the overall reaction rate. As the oxygen concentration increases from 0% to 5% (the n-butane to oxygen ratio decreases to 1), the residence time of reactants needed to reach 96% conversion of n-butane decreases ~8-fold, from 3.9 to 0.5 s.

Thus, whereas the temperature and (especially) the residence time of reactants can be used to control the alkene to CO ratio by varying the contributions of pathways of product formation and/or consumption with increasing conversions of reactants, the initial ratio of the alkane to oxygen is the key parameter determining the limiting $[C_2H_4]:[CO]$ ratio obtained upon a high degree of conversion.

VII.4. Distribution of products of the oxidative cracking of light alkanes

For the processing of natural and associated gases, which represent mixtures of light alkanes, it is necessary to understand how the ratio of oxidative cracking products, in particular, ethylene to CO, changes upon the change in the gas composition, *i.e.*, the contents of various alkanes in the feed. Figure 35 shows the concentrations of the major

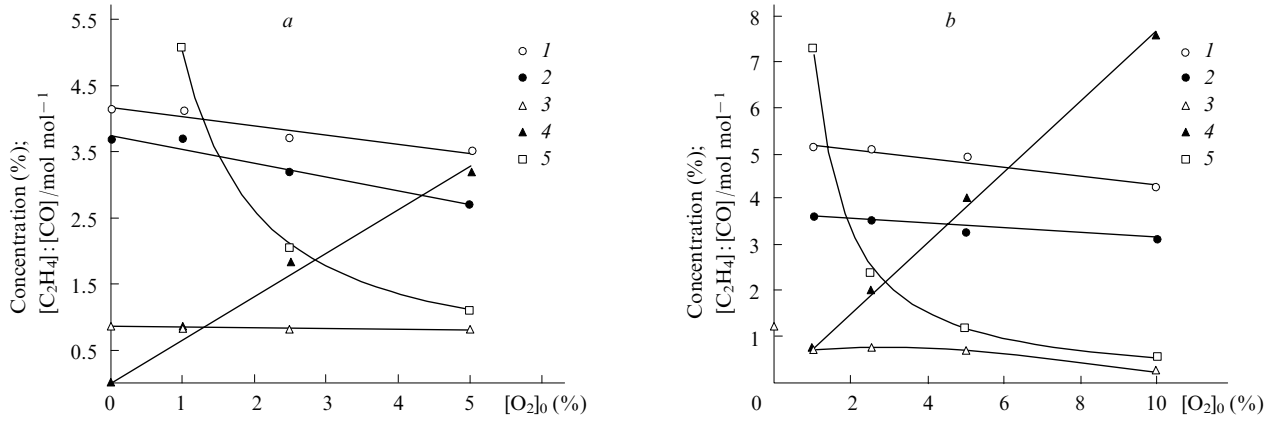


Figure 34. Concentrations of the major products (*1* – *4*) and $[C_2H_4]:[CO]$ ratio (*5*) *vs.* initial oxygen concentration in the oxidative cracking of n-butane (*a*) and n-pentane (*b*).[50]
(*1*) C_2H_4, (*2*) CH_4, (*3*) C_3H_6, (*4*) CO; $[C_nH_{2n+2}] = 5\%$, $T = 750$ °C; (*a*) n-butane conversion 96%, oxygen conversion 78% – 99%; (*b*) n-pentane conversion 99%, oxygen conversion 98% – 100%.

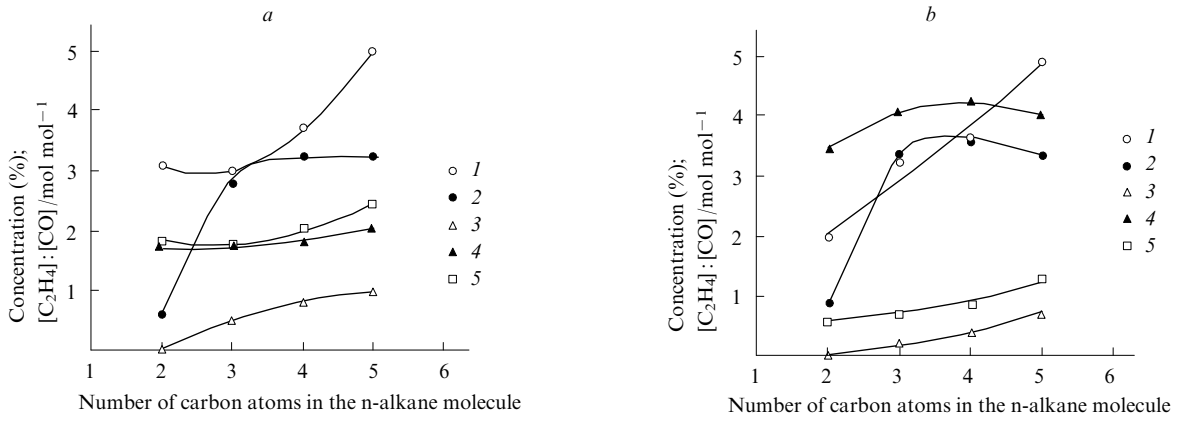


Figure 35. Concentrations of the major products of oxidative cracking (*1*–*4*) and $[C_2H_4]:[CO]$ ratio (*5*) *vs.* number of carbon atoms in the n-alkane molecule for the initial oxygen concentration of 2.5% (*a*) and 5% (*b*).[50]
(*1*) C_2H_4, (*2*) CH_4, (*3*) C_3H_6, (*4*) CO; $[C_nH_{2n+2}]_0 = 5\%$, $T = 750$ °C, $t_r = 2$ s, alkane conversion 87% – 99%, oxygen conversion 86% – 99%.

products and the $[C_2H_4]:[CO]$ ratio as functions of the number of carbon atoms in the n-alkane molecule for a temperature of 750 °C and two different initial oxygen concentrations in the mixture.

Whereas ethane oxycracking gives ethylene and carbon monoxide as the major products under the conditions of interest, the oxycracking of C_{3+} n-alkanes involves alkyl radicals in which C – C bonds in the β-position to the carbon atom with the free valence are weaker than C – H bonds, which results in a much higher proportion of C – C bond cleavage and increase in the methane concentration in the products. Furthermore, cracking of C_{3+} alkanes gives C_{3+} alkenes; in the region of practically significant conversions of reactants, the major fraction of the initial carbon among these alkenes belongs to propylene (see Fig. 35). With increasing number of carbon atoms in the hydrocarbon molecule, the concentration of ethylene in the reaction products markedly increases, while the CO concentration increases slightly; this is accompanied by an increase in the $[C_2H_4]:[CO]$ ratio. For example, for an initial oxygen concentration of 5% ($[C_nH_{2n+2}]_0:[O_2]_0 = 1$), the $[C_2H_4]:[CO]$ ratio in the products increases twofold, from 0.6 to 1.2, on going from ethane to n-pentane (see Fig. 35 *b*). Thus, with increasing content of heavier alkanes in the feed, the $[C_2H_4]:[CO]$ ratio in the oxidation products increases.

It is noteworthy that on going from ethane to heavier alkanes, the selectivity to ethylene decreases, the increase in ethylene concentration being related to the increase in the number of carbon atoms in the alkane molecule and, hence, the carbon to oxygen ratio in the feed. The nearly linear increase in the ethylene concentration in the products with increasing number of carbon atoms in the initial molecule at an equimolar ratio of the reactants (see Fig. 35 *b*) attests to roughly equal ethylene yields calculated in relation to carbon (~40%) in the oxycracking of C_2 – C_5 n-alkanes under the given conditions.

The increase in the oxygen concentration in the feed from 2.5% to 5% induces minor changes in the concentration and yield of ethylene in the case of C_{3+} hydrocarbons, whereas in the case of ethane oxycracking, the yield of ethylene decreases because of substantial decrease in the selectivity to ethylene in favour of CO. This is likely to be caused by redistribution of CO generation pahthways on going from ethane to C_{3+} n-alkanes. It was shown [13] that in the oxidative conversion of ethane, CO appears mainly as a result of secondary ethylene oxidation reactions. Meanwhile, in the oxidative cracking of heavier hydrocarbons, CO can be formed upon oxidation of both the methyl radicals,[58] the concentration of which substantially increases, and more reactive C_{3+} alkenes.[18, 28, 59, 60] A twofold increase in the initial concentration of oxygen results in an almost twofold increase in the CO concentration in the products; this is accompanied by approximately two- and threefold decrease in the $[C_2H_4]:[CO]$ ratio for C_{3+} n-alkanes and ethane, respectively.

These results indicate that apart from the reaction conditions, the structure of the hydrocarbon molecule is largely responsible for the pathways of its decomposition and the composition of the conversion products.[36, 58] The absence of secondary carbon atoms and weaker C – C bonds in the ethane molecule and the stability of the ethyl radical with only C – H bond in the β-position in the radical centre are responsible for the difference between the product distributions for ethane partial oxidation and C_{3+} n-alkane oxidation. An increase in the number of carbon atoms in the n-alkane molecule at a constant hydrocarbon to oxygen ratio induces an increase in the $[C_2H_4]:[CO]$ ratio due to higher ethylene concentration in the products.

VII.5. Effect of methane on the composition of the products of light alkane oxidative cracking

As noted above, the partial oxidation of light n-alkanes diluted with methane, which corresponds to the real composition of natural and associated gases, is of most practical value. It was shown [12] that in the temperature range >650 °C in nitrogen, a branched-chain acceleration of the reaction is observed; in methane, the oxycracking of ethane is substantially retarded as compared with that in an inert gas. The decrease in the ethane oxidation rate in excess methane is in good agreement with the study [61] in which methane involved in radical reactions was shown to reduce the chain-branching rates and concentrations of reactive radicals. A similar retardation of the oxidative cracking in the presence of methane was observed by Pogosyan *et al.*[37]

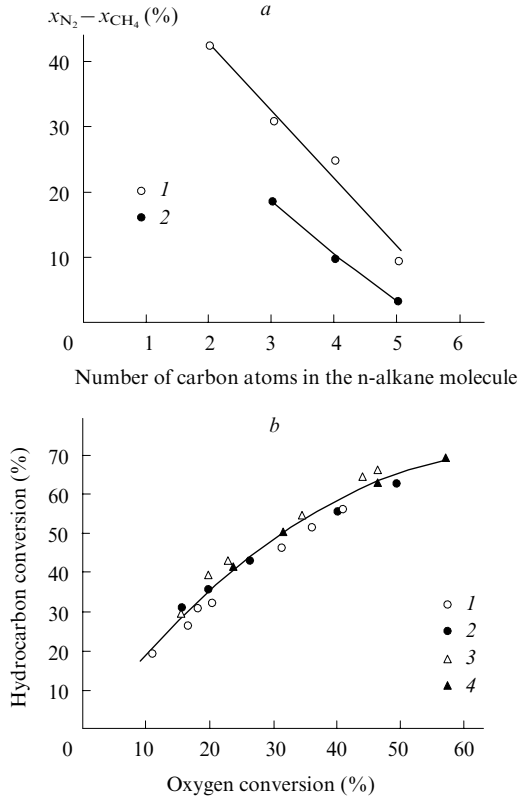


Figure 36. Difference between the conversions of oxygen (*1*) and hydrocarbons (*2*) in nitrogen and methane diluents ($x_{N2} - x_{CH4}$) *vs.* number of carbon atoms in the n-alkane molecule for $t_r = 2$ s (*a*) and hydrocarbon conversion *vs.* oxygen conversion for partial oxidation of propane and n-butane in nitrogen and methane for $t_r = 0.3-1.9$ s (*b*).[50]
$[C_nH_{2n+2}]_0 = 5\%$, $[C_nH_{2n+2}]_0 : [O_2]_0 = 2:1$, $T = 700$ °C; (*a*) (*1*) O_2, (*2*) C_xH_y; (*b*) (*1*) C_3H_8 (CH_4), (*2*) C_3H_8 (N_2), (*3*) C_4H_{10} (CH_4), (*4*) C_4H_{10} (N_2).

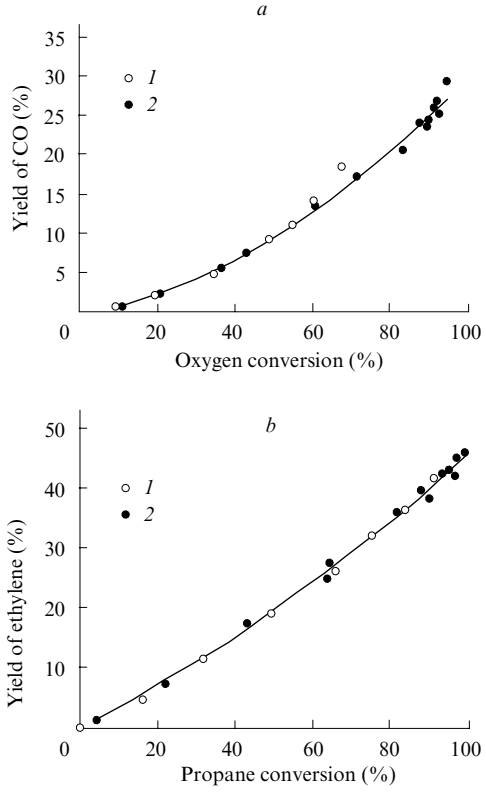


Figure 37. Yield of CO *vs.* oxygen conversion (*a*) and yield of ethylene *vs.* propane conversion (*b*) in the oxidative cracking of propane in methane (*1*) and nitrogen (*2*).[50]
$[C_3H_8]_0 = 5\%$, $[C_3H_8]_0 : [O_2]_0 = 1:1$, $T = 600-750$ °C, $t_r = 8.3-1.6$ s.

However, as the number of carbon atoms in the n-alkane molecule increases, the effect of methane on the conversion of oxygen and hydrocarbon and, hence, on the reaction rate declines. Indeed, in the ethane oxidation at 700 °C, the difference between oxygen conversions in nitrogen and methane diluents is 42%, whereas in the oxidation of n-pentane it is only 9% (Fig. 36 *a*).

Despite the fact that methane is involved in the reaction and has a considerable effect on the kinetics of partial oxidation of hydrocarbons, the ratio of n-alkane to oxygen conversions at 700 °C virtually does not change on methane dilution, as can be clearly seen in relation to propane and n-butane (see Fig. 36 *b*). This may be indicative of a moderate rate of oxidation of methyl radicals, resulting upon methane activation, in the temperature range of 650–750 °C; this is in line with the presence of the so-called window of oxidative coupling of methane, in which recombination is the major pathway of methyl radical consumption.[3] However, as shown for ethane partial oxidation, the reaction is accelerated in the presence of methane at temperatures below ~650 °C, unlike the oxidation in inert nitrogen.[12] In all probability, at these lower temperatures, methylperoxyl radicals still play a considerable role and reactions involving them determine the kinetics of low-temperature oxidation of methane.[3]

Thus, in a first approximation, the contribution of methane conversion to the target products, ethylene and CO, can be neglected under the given conditions; this is also confirmed by the identical dependences of their yields on the conversions of reactants during the propane oxidative cracking in nitrogen and methane (Fig. 37).

Since the contribution of unimolecular hydrocarbon decomposition markedly increases with temperature rise, the difference between n-alkane conversions in an inert gas and in methane rapidly declines, while the oxygen conversion at high temperature substantially decreases in the presence of methane (Fig. 38 *a*). Thus, under the conditions in question, methane markedly inhibits the oxidation but affects little the purely thermal cracking. At temperatures above ~650 °C, a constant residence time and initial alkane to oxygen ratio, this leads to greater difference between the reactant conversions and greater $[C_2H_4] : [CO]$ ratio in the products in the presence of methane as compared with the oxycracking in an inert gas (see Fig. 38 *b*). However, as shown above, this difference diminishes with pressure increase.

Investigations showed that the total yield of ethylene and CO upon the oxidative cracking of C_2-C_5 n-alkanes can exceed 70% under certain conditions. The key factors determining the ratio of ethylene to CO in the products are temperature, residence time of reactants and the initial hydrocarbon to oxygen ratio. Furthermore, whereas the residence time and temperature affect the $[C_2H_4] : [CO]$ ratio

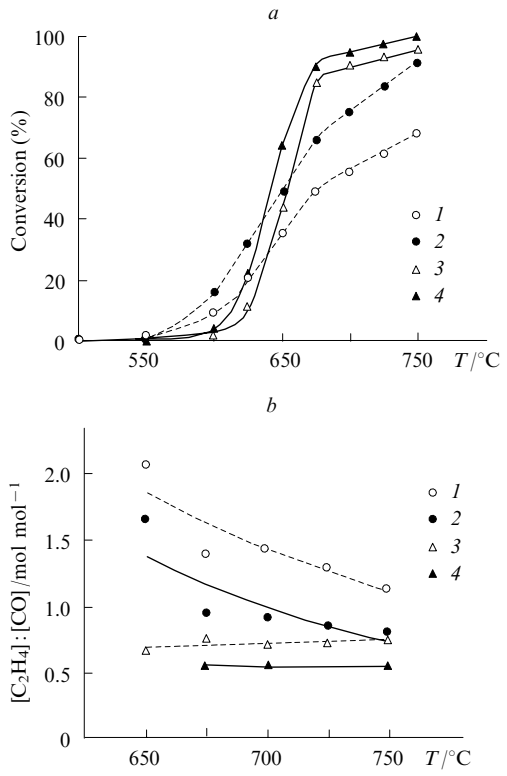


Figure 38. Temperature dependences of reactant conversions (*a*) and $[C_2H_4]:[CO]$ ratio in the products of propane oxidative cracking (*b*) in nitrogen (solid lines) and methane (dashed lines) diluents. (Figure from Ref. 50 with authors' supplements.) $[C_3H_8]_0 = 5\%$, $[C_3H_8]_0:[O_2]_0 = 1:1$, $t_r = 2$ c. (*a*) (*1*) O_2 (CH_4), (*2*) C_3H_8 (CH_4), (*3*) O_2 (N_2), (*4*) C_3H_8 (N_2); (*b*) $P = 1$ (*1*, *2*) and 3 atm (*3*, *4*).

(as the conversion of reactants increases, carbon is redistributed among the products), the initial hydrocarbon to oxygen ratio is the principal parameter determining the limiting achievable ratio of these products at high percentages of reactant conversion.

The structure of the initial hydrocarbon molecule also affects the distribution of oxidative cracking products. On going from ethane to n-pentane, the composition of major products changes; this is related, most likely, to the appearance of new pathways and redistribution of the contributions of pathways to these products. As the number of carbon atoms in the n-alkane molecule increases, while the alkane to oxygen ratio remains invariable, the ethylene concentration and, hence, the $[C_2H_4]:[CO]$ ratio in the products increase.

For the oxidative cracking of heavy components of natural gas, the effect of methane should be taken into account. Under the conditions being discussed, the contribution of reactions involving methane to the formation of target products is, most likely, relatively low. However, above ~650 °C, methane inhibits the oxidative conversion of other alkanes as compared with their oxidation in an inert gas. With all other process conditions being the same, this results in a considerable decrease in the oxygen conversion and increase in the difference between the percentages of reactant conversion and, hence, in the ethylene to carbon monoxide ratio in the products.

VIII. Prospects for the processing of the products of selective oxycracking of light alkanes

The formation of gas mixtures containing controlled ratios of ethylene and CO upon the selective oxidative cracking of light alkanes is of interest as regards the combined use of these compounds for the preparation of valuable petrochemicals. This does not require energy-consuming isolation of these compounds from reaction products. The proposed [62] concept of alternative GTL¶ processes consists in combining the homogeneous partial oxidation of hydrocarbon gases with catalytic carbonylation. These processes differ from the traditional GTL processes based on the Fischer – Tropsch synthesis [63] by the absence of the costly stage of synthesis gas production.

The first stage in the proposed alternative technologies is non-catalytic oxidative conversion of methane or hydrocarbon gas mixtures. This may be partial oxidation of the heavy components of the associated petroleum gas to give methanol and CO, or oxidative cracking to give ethylene and CO, or combination of these processes. The second stage consists of carbonylation reactions,[64, 65] providing a broad range of petrochemicals with high added value, including aldehydes, carboxylic acids, diethyl ketone, polyketones [66] or methyl propionate and methyl methacrylate.[67] The authors cited proposed carbonylation of the oxycracking products in the presence of catalysts containing Group VIII metal compounds and phosphine (arsine) ligands at temperatures of 80 – 120 °C and atmospheric pressure. Apart from carbonylation products, this process gives dry fuel gas with a high methane number deprived of heavy components.[51]

A similar approach, but based on oxidation of ethane catalyzed by mixed metal oxides at a temperature not lower than 500 °C is described in a patent.[68] It is proposed to feed the ethylene and CO mixture resulting from the oxidation to the carbonylation catalyst for the synthesis of methyl propionate, propionaldehyde or poly(oligo)ketones.

We will briefly consider the developed ethylene carbonylation processes that can use ethylene and CO mixtures without separation as the feed and give various petrochemicals. Ethylene hydroformylation (reaction with stoichiometric amounts of CO and H_2) affords propionaldehyde, which can be oxidized to propionic acid or used to prepare methacrolein *via* condensation with formaldehyde.[69] This stage is implemented as a separate process [70] or is combined with the previous stage using a biphasic catalyst.[71] In the presence of excess hydrogen, the process can also produce n-propanol; this can be done using feed mixtures containing 10% – 20% ethylene.[72] The industrial hydroformylation processes make use of several types of catalysts, of which rhodium complexes are most efficient. The $[HRh(CO)(PPh_3)_3]$-based catalyst is three orders of magnitude more active than the cobalt analogue $[HCo(CO)_4]$ and has optimal characteristics at lower pressure (7 – 5 atm *vs.* 200 – 300 atm).[73] The use of rhodium in hydroformylation became especially cost-effective after the Ruhrchemie and Rhone – Poulenc companies proposed a two-phase propylene hydroformylation to butanal not requiring the catalyst separation from the product.[74]

¶ Gas-To-Liquids refers to processes for natural gas conversion to synthetic liquid hydrocarbons.

Hydrogen for hydroformylation can be generated directly in the reaction zone from methanol using a bifunctional catalyst. The bifunctional catalyst for this process proposed in a patent [75] contains two metal/metal oxide contacts: one (CeO_2 – Pt) decomposes methanol to give CO and H_2 and the other (Pt – SiO_2) performs the hydroformylation of ethylene. The temperature proposed for the combined process was 190 °C. The excess of hydrogen with respect to CO formed upon decomposition of methanol can be balanced by CO present in the ethylene feed, and this ensures completeness of the reaction.

Platinum group metal (mainly palladium) derivatives and copper salts (a system similar to the Wacker process catalyst) can serve for the preparation of dicarboxylic acid esters from ethylene and CO in the presence of alcohols.[76] The reaction of ethylene, CO and methanol catalyzed by this system at 50 °C and 9 bar gives dimethyl succinate. Dialkyl peroxides, in particular, di-*tert*-butyl peroxide were proposed as agents preventing the catalyst from deactivation. Unfortunately, the authors did not indicate the optimal ratio of the components for the process; however, considering the reaction stoichiometry implies that it should be $[C_2H_4]:[CO]:[CH_3OH] = 1:2:2$ or higher.

E.I. DuPont De Nemours and Company (USA) patented [77] a production process for vinyl acetate (a monomer used in the paint-and-varnish and adhesive industries to manufacture quite a number of polymer bases and acting as a comonomer in the production of special brands of polyethylene) by the oxidative reaction between ethylene and acetic acid in the presence of a heterogeneous Pd catalyst. Subsequently this process formed the basis for the most popular synthesis of vinyl acetate widely used today. The initial components of this synthesis — acetic acid and ethylene — can be obtained by homogeneous partial oxidation of natural gas giving methanol and CO.

Imperial Chemical Industries PLC (USA) patented [78] a catalyst for alkoxycarbonylation of alkenes, comprising a Group VIII metal (mainly palladium) derivative and a bidentate phosphine ligand with organic sulfonic acids serving as cocatalysts. The preferred conditions for the reaction are the following: temperature of 70 – 120 °C and pressure of 5 – 50 bar. Later, the ethylene methoxycarbonylation to methyl propionate was commercialized by Lucite International as a part of the production process for methyl methacrylate, which is used as a monomer for the manufacture of acrylic plastics.[79] The subsequent development works of this company gave rise to a continuous alkoxycarbonylation process [80] using a homogeneous catalyst; the main reaction is performed in a vessel type reactor with stirring. For increasing the yields of target products, ethylene can be added to the feed up to the optimal ratios $[C_2H_4]:[CO] = (25-50):1$. Depending on the composition of the catalyst and reaction conditions, methyl propionate (up to 95%) or diethyl ketone can be formed as the major products. The process is continuous and involves recycling of the gas mixture. The gas mixture recycle is >60%.

The alternating copolymerization of alkenes with carbon monoxide carried out in the presence of palladium-containing catalysts, like those described above, gives 1,4-polyketones (γ-polyketones), which exhibit unique properties such as high crystallinity, excellent mechanical characteristics and high chemical stability.[81]

Numerous catalysts effective towards carbonylation of ethylene have been reported in the literature. However, most of them are expensive, as they contain platinum group metals. The key way for providing high selectivity of such catalysts is to use complex organic ligands; this further increases the cost and, moreover, in this case, the process can be conducted only with a solution of the catalytic complex. This is inconvenient from the engineering standpoint. A relevant task the solution of which would allow implementation of ethylene carbonylation in flow reactors is to develop highly active heterogeneous catalysts for processes of this type. An advantage of heterogeneous catalysts is their low cost, provided that they are based on cheaper transition metals.

Iodide ion-promoted Group VI metal (Cr, Mo, W) carbonyls were patented [82] as catalysts for ethylene carbon-

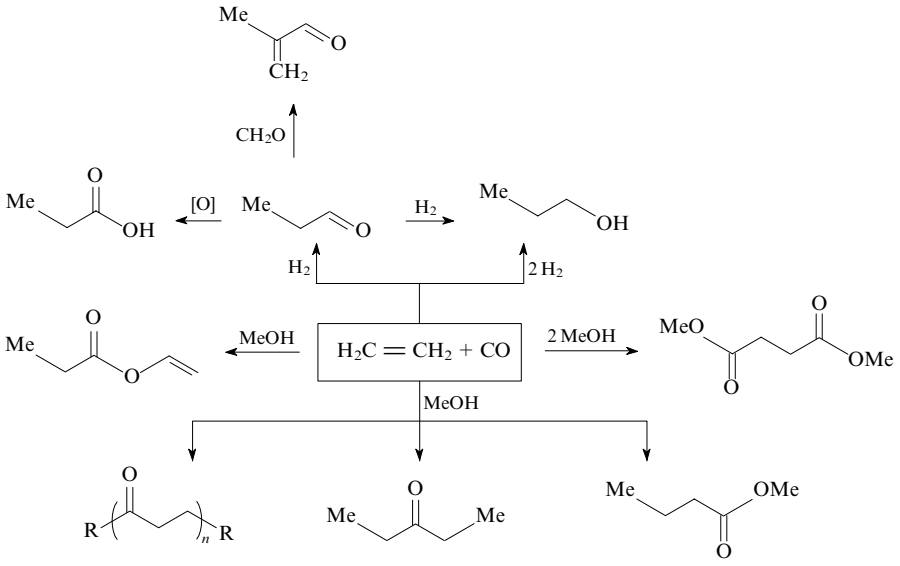


Figure 39. Possible routes for processing of ethylene and CO mixtures obtained upon the selective oxidative cracking of heavy components of natural and associated gases.

ylation to propionaldehyde or propionic acid under rather mild conditions (150 – 200 °C and 25 – 70 bar). The mechanism of this reaction has recently been studied in detail.[83] It has been shown that the products (propionic acid derivatives) can be obtained in quantitative yields, which allows one to predict the design of efficient and cheap industrial catalysts for carbonylation. It was been reported[84] that a catalyst based on molybdenum carbonyl can be successfully heterogenized. The selectivity of this catalyst to the target product remains at about 95% – 97% under relatively mild conditions (ethylene, hydrogen and CO partial pressures of 10 bar; temperature of 190 °C).

The Dow Global Technologies LLC proposed Group VIII transition metal (iron, cobalt, nickel and so on) sulfides as catalysts for alkene alkoxycarbonylation.[85] With these catalysts, the process can be conducted in the gas phase; hence, vapour – gas mixtures of ethylene, methanol and CO can be used to prepare methyl propionate. The most preferable process conditions claimed in a patent[85] include carbon monoxide to alkene molar ratios from 3 : 1 to 15 : 1, alkene to alcohol molar ratios from 0.2 : 1 to 2 : 1, temperature of 280 – 340 °C, pressure of 1.5 – 6 MPa and gas hourly space velocity of 500 – 5000 (gas litres) (catalyst litres)$^{-1}$ h^{-1}. The yield of methyl propionate in this process reaches 97%.

Thus, a large number of methods were developed for utilization of the products of selective oxycracking of heavy components of natural and associated gases for the production of valuable petrochemicals and thus for involvement of associated petroleum gas into chemical processing. The key routes for processing of ethylene and CO gas mixtures obtained in the selective oxycracking *via* catalytic carbonylation are shown in Fig. 39.

Currently, studies are in progress aimed at the development of new catalysts and engineering solutions to carry out carbonylation involving ethylene in the gas phase. This would markedly enhance the scope of potential applications of the selective oxycracking of light alkanes for the synthesis of organic compounds, including green solvents, traditional monomers and intermediates for fine organic synthesis.

* * *

The recent progress in the studies of selective oxycracking of alkanes (heavy components of natural and associated gases) opens up interesting prospects for the design of new-generation relatively simple small-scale gas treatment processes, which can provide dry natural gas with a high methane number and a variety of demanded chemicals with high added value. The construction of small-scale field units for deep processing of hydrocarbon gases *via* new type GTL processes would allow more rational utilization of natural and associated gases from remotely located and low-productivity oil fields. The development of small-scale gas-based chemistry would contribute to compliance with the conditions for Kyoto Protocol ratification by Russia. The fundamental and applied research of the kinetic patterns and industrial prospects of the selective oxidative cracking of light alkanes carried out at the IPCP RAS and ICP RAS may provide a scientific and engineering base for the design of gas-based techniques of new generation.

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