Oxidative conversion of hexane as a model of selective conversion of heavy components of hydrocarbon gases

V. S. Arutyunov, M. Ya. Bykhovskii, M. Yu. Sinev, and V. N. Korchak*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (495) 651 2191. E-mail: arutyunov@center.chph.ras.ru

The possibility of selective oxidative conversion of a hexane admixture in large methane excess was shown. Hexane was chosen as a typical representative of heavy components of natural and casing-head gases. The conversion produces lighter hydrocarbons and oxygen-containing compounds with higher octane numbers. This suggests selective oxidative conversion of heavy hydrocarbon fractions as a method of preparation of natural and casing-head oil gases for the use in gas reciprocating power engines.

Key words: oxidative conversion, oxidative cracking, hexane, casing-head oil gases.

Flaring of the casing-head gas in inadmissibly large amounts is one of the most acute problems of the domestic gas-and-oil producing industry. According to some estimates, up to 50—60 billions m^3, *i.e.*, ~10% of domestic natural gas production are flared in gas flares[1]. The most feasible method for utilization of the casing-head gas is the use in the production of thermal and electric power to satisfy local demands of oil- and gas-fields and adjacent districts. However, crude natural and especially casing-head gases are unsuitable for the direct use in many types of modern power plants, especially those based on gas reciprocating power engines, because the latter contain heavy fractions of hydrocarbons C_{6+} with low octane numbers (Table 1). The presence of even insignificant (more than 1—2 vol.%) concentration of hydrocarbons C_{6+} in a gas mixture results in the knocking in the engine and does not allow it to achieve its nominal efficiency. In addition, soot formation and deterioration of parts of the engine increase, and the operation resource of the engine decreases.

Table 1. Octane numbers of normal alkanes

Hydrocarbon	Motor method	Research method
Methane	110.0	107.5
Ethane	108.0	107.1
Propane	100.0	105.7
n-Butane	91.0	93.6
n-Pentane	61.7	61.7
n-Hexane	26.0	24.8
n-Heptane	0.0	0.0
n-Octane	−17.0*	−19.0*
Naphtha	41.0—56.0	43.0—58.0

* Calculation (see Ref. 2).

Mild selective oxidative conversion of heavy components of the mixture to lighter and higher-octane-number compounds can be one of the efficient methods for the solution of this problem. Similar thermooxidative cracking of liquid hydrocarbons has been proposed[3] as early as in 1930s to enhance the octane number of motor fuels. Last time, interest in such processes has increased due to the need to use hydrocarbon raw materials in oil processing and petrochemistry more efficiently. The possibility of oxidative activation of thermocracking of heavy hydrocarbons (tar) has recently[4] been shown: the introduction of only 1% oxygen accelerates twofold the extraction of light fractions.

Oxidative conversion (oxypyrolysis, oxycracking) of alkanes C_{3+} has recently attracted much attention as a potential method for the production of lower olefins (see, *e.g.*, Refs 5—10). This process occurs efficiently in the presence of catalysts similar to those of oxidative coupling of methane (OCM), which proceeds through the formation and consecutive transformation of free radicals.[11] This allows one to describe oxycracking processes in terms of approaches and heterogeneous—homogeneous kinetic schemes of the same type as those developed[12] for the description of the OCM process. However, under certain conditions, hydrocarbon conversion during oxycracking occurs rather efficiently in the absence of a catalyst,[7] and even higher conversion than that in the catalytic reactor is achieved.[6]

The purpose of this work is to study the possibility of using oxycracking for the selective conversion of heavy fractions C_{6+} in natural and casing-head gases to lighter and high-octane-number products. Hexane was used as a model hydrocarbon.

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Experimental

The process was carried out under atmospheric pressure in quartz reactors 3 and 6 mm in diameter. The lengths of the heated reactor zone was 100 mm. The reactor was heated with an electric resistance furnace. The temperature was controlled with a Miniterm 300 regulator. The starting mixture of gases (nitrogen or methane with different oxygen contents) was saturated with hexane to the concentration 6 vol.% in a bubblier at 0 °C and was fed to the heated reactor. The gas mixture consumption was varied from 7 to 66 mL min^{-1} (under normal conditions), which corresponded to the change in its residence time in the reactor 6 mm in diameter for 7.1—0.75 s. The fraction 0.2—0.5 mm in size was used in experiments with catalysts. The catalyst load was 50 mg, and the reactor volume filled with the catalyst was 0.15 mL.

Hexane and hydrocarbons obtained by oxycracking were analyzed on a Kristall-2000 chromatograph using a capillary column with the ZB-1 phase and a flame-ionization detector. Oxygen, nitrogen, methane, and carbon oxide were separated on a column with molecular sieves 13X, whereas CO_2, ethylene, and ethane were separated on a column packed with Porapak Q. In both cases, a heat conductivity detector was used. According to the chromatographic analysis data, the minimum initial concentration of oxygen determined by its admixture in the nitrogen used in our experiments was 0.1—0.15%.

Hexane conversion was studied in an empty reactor and in the presence of typical catalysts used in the three processes.

1. Oxidative coupling of methane (OCM) (catalyst Nd(10%)/MgO). In this reaction occurring at 700—900 °C the most efficient are oxide catalysts capable of C—H bond cleaving under oxidative atmosphere to form surface OH groups and free radicals. Since the energy value and the number of C—H bonds in hexane and methane molecules differ substantially, it can be assumed that hexane molecules are predominantly activated on the catalyst of this type. In addition, free radical formation should initiate the gas-phase process in which conversion of hexane should dominate.

2. Carbon dioxide methane conversion (CMC) (catalyst NiO(6%)/α-Al_2O_3). As a rule, such catalysts are also active in the production of syngas from methane and oxygen at temperatures close to 800 °C. It can be expected that in the presence of this catalyst hexane would react at lower temperatures than methane.

3. Oxidative dehydrogenation of lower alkanes (C_2—C_4) (catalyst V(14.7%)+Sb(2.7%)+Cr(3.0%)/Al_2O_3). Catalysts of this process are able to activate alkane molecules containing C—C bonds and to manifest rather low activity in methane conversions. Therefore, the predominant conversion of hexane in the presence of high methane concentrations can be expected.

The procedure of preparation of these catalysts and the results of studies of their physicochemical properties and catalytic activity have been published earlier.[13—15]

Results and Discussion

The data presented in Table 2 and Fig. 1 show that in the presence of the catalysts Nd/MgO and NiO/Al_2O_3 the conversion of hexane increases noticeably with an increase in the temperature and oxygen concentration.

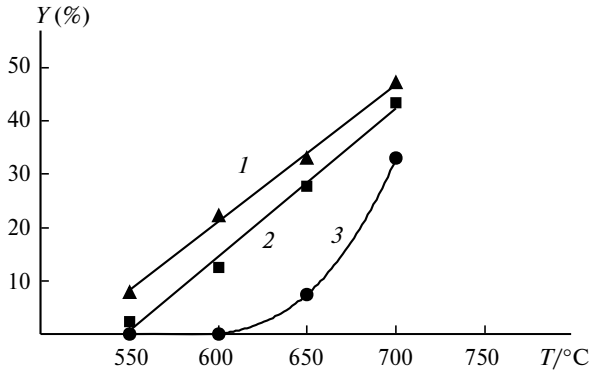

Fig. 1. Conversion of hexane (*Y*) in nitrogen *vs* temperature in the presence of the OCM (N_2/O_2 = 96.0/4.0) (*1*) and CMC (N_2/O_2 = 96.7/3.3) (*2*) catalysts and in the empty reactor (*3*) (N_2/O_2 = 96.6/3.4); reactor diameter 3 mm, discharge of mixture 7 mL min^{-1}.

Table 2. Dependences of catalytic hexane conversion (*Y*) on the temperature at different (0—4%) oxygen concentrations in the starting mixture (reactor diameter 3 mm, gas discharge 7 mL min^{-1})

T/°C	Catalyst OCM			Catalyst CMC*	
	0.0	2.3	4.0	1.2	3.3
550	0.0	1.2	7.9	0.0	2.3
600	0.0	16.2	22.2	9.6	12.5
650	14.3	22.6	33.1	22.0	27.8
700	27.6	43.1	47.2	27.1	43.5

* At the oxygen concentration 0%, $Y = 0$.

The degrees of conversion of hexane in the presence of these catalysts are close under other equivalent conditions. The presence of oxygen in nitrogen decreases the temperature of reaction onset from 650 to 550 °C. However, even at 700 °C and in the presence of 2—4% oxygen less than 50% hexane is converted. In addition, the use of mixtures with such a relatively large oxygen content results in the oxidation of a substantial portion of hexane to CO, CO_2, and water. Thus, at 700 °C and an oxygen content in the initial mixture of 4 vol.% the yield of CO_2 reaches 7.5% (selectivity 16%) and the yield of CO is 3—5% (selectivity 7—10%). In the absence of oxygen in the mixture, dark deposits were observed on the reactor walls, while they are not formed if the initial gas contains oxygen.

The catalyst of oxidative dehydrogenation was tested at 650 °C and an oxygen content in nitrogen of 3.4%, and the hexane conversion was 44%. However, strong coking of the catalyst and reactor walls was observed and, hence, all other experiments were carried out in the presence of the OCM and CMC catalysts.

The results were compared with the data obtained in the same reactor but without a catalyst (see Fig. 1). In the

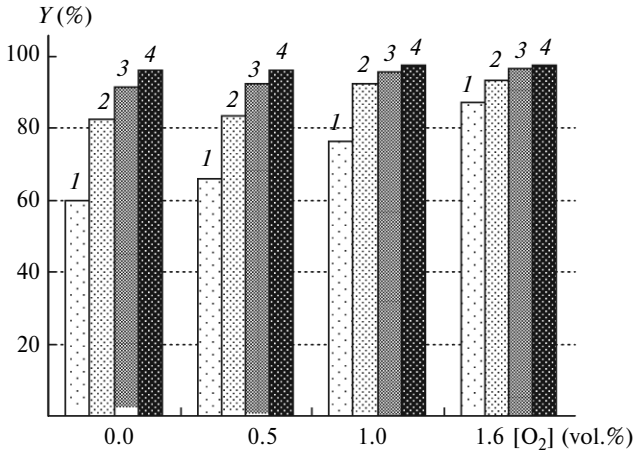

Fig. 2. Conversion of hexane (*Y*) in methane in the empty reactor 6 mm in diameter at 730 °C *vs* oxygen content at different residence times of the reactants: 0.75 (*1*), 1.66 (*2*), 3.31 (*3*), and 7.10 s (*4*).

empty reactor conversion of hexane begins to appear (see Fig. 1) at a considerably higher temperature than in the presence of the catalysts, but then its conversion increases sharply and at 700 °C it does not strongly differ from catalytic conversion. At 730 °C the hexane conversion in the empty reactor 3 mm in diameter significantly exceeds its conversion in the presence of the catalysts. An increase in the diameter of the reactor or a decrease in the gas flow rate, *i.e.*, an increase in the residence time of the mixture in the reactor, results in a nearly complete conversion (more than 95%) (Fig. 2).

It is most likely that the temperature of 730 °C is close to the optimum for this process. As can be seen from the data in Figs 2 and 3, a nearly complete hexane conversion is achieved at this temperature in both nitrogen and methane in the range of parameters studied (residence time and oxygen concentration). Although the oxygen concentration was higher in experiments with nitrogen, the effect of the oxygen concentration on the hexane conversion is already negligible in this range of C_6H_{14}/O_2 ratios (see Fig. 2). It can be assumed that hexane is converted much in the same way in different gaseous environments (see Fig. 3).

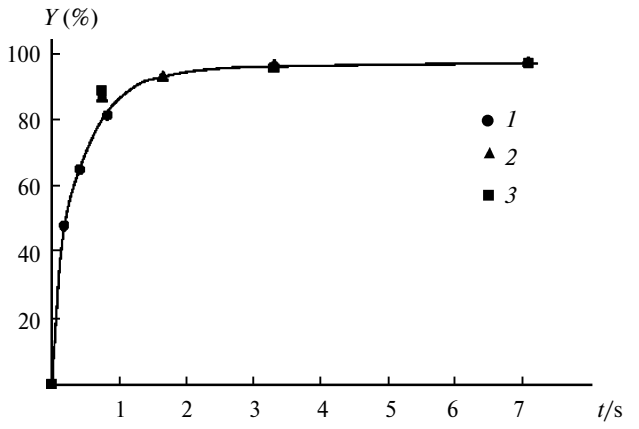

Fig. 3. Conversion of hexane (*Y*) at 730 °C *vs* residence time of the reactants in the empty reactor in a mixture with nitrogen at $[O_2]$ = 3.4% and the reactor diameter 3 (*1*) and 6 mm (*2*) and in a mixture with methane at $[O_2]$ = 1.6% and the reactor diameter 6 mm (*3*).

Table 3. Dependences of the yield of the products of hexane oxidative cracking in the empty reactor on the discharge of a methane—air mixture (730 °C, reactor diameter 6 mm)

Discharge of mixture /mL min^{-1}	Yield of product (%)		
	CO	C_2H_4	C_2H_6
	Concentration of oxygen 1.6%		
7	2.9	33.0	1.8
15	3.1	38.0	2.2
30	1.2	35.0	3.0
66	0.9	35.0	2.2
	Concentration of oxygen 1.0%		
7	3.5	43.0	2.6
15	2.0	43.7	3.0
30	1.1	41.5	3.0
66	Traces	33.7	2.3
	Concentration of oxygen 0.5%		
7	Traces	38.5	2.0
15	Traces	38.3	3.1
30	Traces	39.3	2.0
66	Traces	30.0	2.7
	Concentration of oxygen 0%		
7	—	41.2	3.6
15	—	39.3	1.8
30	—	35.8	2.0
66	—	26.3	2.0

The total yield of all identified conversion products (hydrocarbons C_1—C_2, CO, CO_2) did not exceed 60—63%. In addition, hydrogen is formed, whose yield was not quantitatively determined. Other products, being saturated and unsaturated hydrocarbons, as well as oxygen-containing organic compounds, were observed as several poorly separated chromatographic peaks in the chromatogram obtained using a capillary column packed with the ZB-1 phase. The experiments showed that the major products of hexane conversion in the empty reactor are ethylene, methane, ethane, and carbon monoxide (Table 3).

The dependence of the methane yield during hexane cracking in the empty reactor on the consumption of a nitrogen—air mixture (730 °C, reactor diameter 6 mm, without oxygen) is given below.

Gas consumption /mL min^{-1}	Yield of methane (%)
7	14.8
15	13.4
30	8.0
66	6.9

The yield of the cracking products depends on the composition of the mixture in the reactor and its residence time in the reactor. The changes in the oxygen concentration from 0 to 1.6 vol.% and the residence time in the reactor from 0.75 to 7.1 s result in the following variations in the yield of the products: methane, 7—15%; ethane, 1.8—3.6%; ethylene, 26—44%. No formation of carbon monoxide is observed without oxygen feeding, while in the presence of 1.6 vol.% oxygen the yield of CO exceeds 3% at the maximum residence time. Carbon dioxide is absent from the hexane conversion products in the empty reactor, but its yield reached 7.5% in the presence of the catalysts at the high (2—4 vol.%) oxygen concentration at 700 °C.

According to the data presented above, the cracking reactions with the formation of hydrocarbons C_1—C_2 proceeds more slowly in the absence of oxygen. In addition, the deposition of tar substances and soot on the reactor walls is observed without oxygen feeding to the reaction mixture. At the oxygen concentration 0.5 vol.%, the size of deposits on the walls decreases sharply, whereas they are almost absent at the concentration 1.0—1.6 vol.%. The addition of water vapor (0.5 mL min^{-1}) instead of oxygen to the nitrogen or methane flow shows that water is hardly able to prevent the formation of tar substances and the presence of oxygen in small concentrations is necessary.

Available works on oxidative hexane cracking are mainly aimed at producing low olefins.[8–10] To provide the autothermal conditions and to achieve a high yield of the target products, the process is usually carried out at the ratio $C_6H_{14}/O_2 = 0.7$—0.8, *i.e.*, at a higher oxygen concentration than in the present study. However, the regularities obtained correlate well with our results on studying the oxidative activation of pyrolysis of small hexane admixtures in methane.

1. The presence of oxygen in even small concentrations accelerates the hexane conversion (or decreases the temperature of the process). In the both cases, the conversion higher than 90% is achieved at the residence time 1—2 s and temperature 730—750 °C.

2. An increase in the oxygen concentration increases the conversion of hexane and selectivity of CO formation, which is especially pronounced at a short residence time in the reactor (see Fig. 2).

3. In the both cases, at rather high temperature the gas-phase conversion has almost the same efficiency as the catalytic conversion.

4. The presence of oxygen even in small concentrations prevents soot formation almost completely.

Although for the oxygen-free gas-phase pyrolysis of hexane the conversion rate and the composition of the products (except for oxygen-containing products) are close to analogous parameters of oxypyrolysis, this process is accompanied by the formation of a large amount of soot,[16] which is nearly entirely suppressed in the presence of oxygen. As in the absence of oxygen, the major products of oxidative pyrolysis are light olefins and alkanes; carbon monoxide also appears in the products. All these compounds are highly resistant to knocking and, therefore, have high octane numbers. They are acceptable as combustible gases for power plants of any type. Almost no carbon dioxide is formed in the gas-phase reaction, but in the presence of the catalyst its yield becomes significant at rather high concentrations of oxygen.

The data in Table 3 show that the yields of ethylene and ethane remain almost unchanged but the CO yield increases noticeably with an increase in the oxygen concentration at the same residence time in the reactor. The same regularity was observed for the oxidative hexane cracking.[10] Thus, under these conditions, at the high rate of hexane conversion more stable hydrocarbons C_2 remain almost unconverted. This is the large difference in the conversion rates of light hydrocarbons with different numbers of carbon atoms that makes it possible to selectively purify their complicated mixtures from small admixtures of high hydrocarbons. In this case, no noticeable decomposition of lower representatives of the considered class of compounds is observed. Therefore, the homogeneous pyrolysis (cracking) of small admixtures of heavy hydrocarbon fractions in natural and casing-head gases can be recommended as a method for the pretreatment of these gases for the use in power plants, in particular, for increasing their octane (methane) number.

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