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Mechanochemical Conversion of Gaseous Oil Hydrocarbons in the Systems Gas–Solid

O. E. GAMOLIN[1], A. K. GOLOVKO[1], O. I. LOMOVSKIY[2], V. F. KAMYANOV[1] and S. G. MAMYLOV[1]

[1]Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademicheskiy 3, Tomsk 634021 (Russia)

E-mail: golovko@ipc.tsc.ru

[2]Institute of Solid State Chemistry and Mechanochemistry,
Siberian Branch of the Russian Academy of Sciences,
Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: lomov@solid.nsc.ru

Abstract

The effect of mechanical treatment on complex systems containing a solid phase and the components of casing-head gas is considered. The process is carried out in planetary ball mills with the acceleration of milling bodies (steel balls) up to 600 m/s^2. An intense mechanical action on the material of balls and mill walls causes the formation of active centres initiating transformations of the gaseous components. The possibility to obtain hydrogen and methane from hydrocarbon gases by means of mechanochemically initiated destruction was demonstrated. The presence of a solid phase, *i.e.* crystal quartz, which efficiently generates active centres of radical nature during mechanical treatment, increases the transformation degree of initial components.

INTRODUCTION

The development of new technologies involving the use of natural hydrocarbon raw material in hydrogen power engineering implies obtaining hydrogen and hydrogen-containing gases for application in oil-processing, petrochemical, metallurgical and other hydrogen-consuming branches of industry.

At present, the problem of reasonable utilization of oil-accompanying gas (casing-head gas) arising during the development of oil fields remains unsolved. The main components of casing-head gas are C_1–C_5 hydrocarbons (HC). Due to the absence of an economical method of processing at mining sites and expensiveness of transportation, these gases are flared, thus a large amount of combustion products including carbon oxides and carbon black is emitted into the atmosphere [1].

Investigation of the consequences of mechanical treatment (MT) of gaseous HC in intense mills of planetary type showed potential possibility of non-thermal initiation of radical processes in the gas phase [2]. An important role in mechanical activation is played by the type and nature of the material of activator and milling bodies in the system, as well as the presence of specially introduced solid phases [3]. For instance, mechanical treatment and grinding of crystal silica (quartz) results in the formation of many structural defects of different types. The most active ones are the centres of radical nature which can serve as the initiators of chemical transformations of gaseous HC [4]. Investigation of these processes could be the basis for the development of new, non-conventional technologies of processing the components of casing-head gases and obtaining ecologically safe energy sources.

The goal of the present work was to demonstrate the possibility of mechanochemical initiation of conversion of propane, isobutane and pentane.

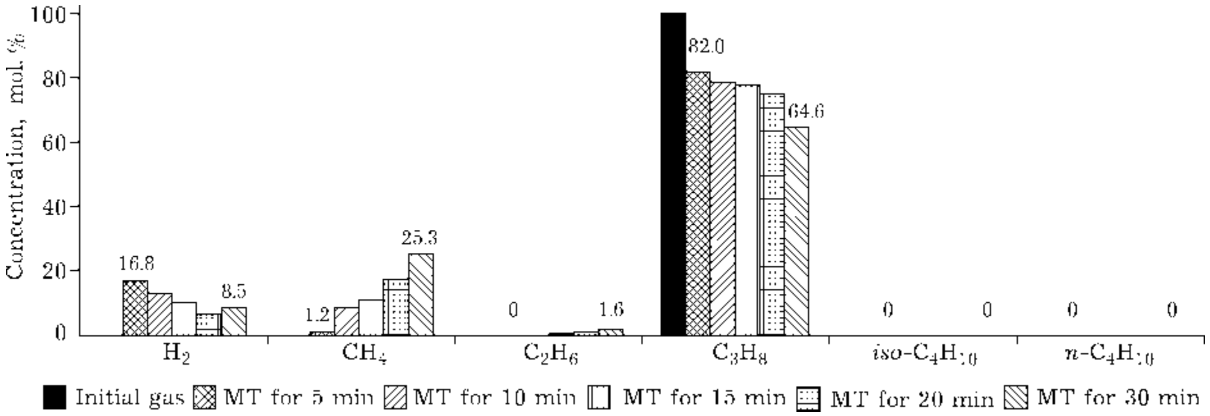

Fig. 1. Dependence of gas concentrations on the time of MT of propane without additives.

EXPERIMENTAL

The components of oil-accompanying gas – individual HC: propane, isobutane, pentane – were chosen as the subjects of investigation. Quartz (natural mineral SiO_2) was used as a mineral additive because its mechanical grinding results in the formation of a large number of paramagnetic centres, which are necessary for radical reactions to proceed on the surface.

The gas mixture was introduced into a mechanochemical reactor which was preliminarily evacuated and purged with an inert gas; the reactor volume was 80 cm^3. An empty reactor was filled by 1/3 with milling balls 8 mm in diameter. The reactor and balls were made of stainless steel. Portions of mineral additives were 10 g, making about 1/4 of the reactor volume. After filling the reactor with the gas mixture, pressure in the reactor was 1.5–3.0 atm. Mechanical activation was carried out with AGO-2 apparatus (hydraulically cooled activator, ISSC&M, SB RAS, Novosibirsk, Russia) for 5, 10, 15, 20 and 30 min. The acceleration of balls in the activator mill was 600 m/s^2. Mechanical activation of gases was carried out at room temperature.

Experiments on MT of *n*-pentane were carried out as follows. Mechanochemical reactors were filled with milling bodies and the solid additive (quartz), then closed tightly and evacuated. After that, the reactors were purged with argon and heated directly in AGO-2 activator. At a temperature of 70 °C, 1 ml of liquid *n*-pentane was added into the heated reactors. So, pentane was in the gas state before activation started.

The initial hydrocarbons and reaction products were analyzed by means of gas liquid chromatography. The solid phase was examined by means of the X-ray phase analysis (DRON type diffractometer with monochromatic CoK_α radiation), IR spectroscopy (BOMEM MB-102 IR Fourier spectrometer). EPR spectra were recorded with ERS-221 instrument within the X range (9.5 GHz) with modulation amplitude of 5 Gs and microwave power of 3 mW. Elemental analysis of the solid phase (quartz) was carried out.

RESULTS AND DISCUSSION

In order to reveal optimal conditions of mechanical activation of propane, we carried out experiments differing in MT time. The results obtained for propane treatment without mineral additives (with the initial propane pressure of 3 atm) are shown in Fig. 1. The initial gas started to decompose as early as after 5 min of MT. Hydrogen, methane and ethane were detected in the resulting mixture.

Further MT causes HC conversion with an increase in the yield of methane. For instance, after half an hour treatment, the molar fraction of methane in the mixture was 25.3 %.

The introduction of quartz brought substantial changes into the process course. After activation for 5 min, the molar fraction of hydrogen in the gas mixture was 64 %, methane 17.1 % (Fig. 2).

The concentration of propane in the mixture was 18.2 %. As the time of MT increases, we observe accumulation of methane; a small

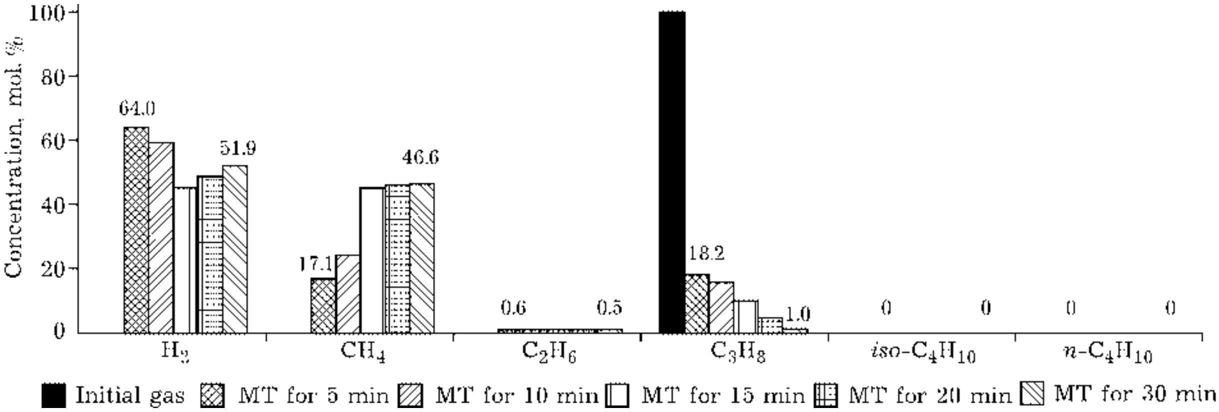

Fig. 2. Dependence of gas concentrations on the time of MT of propane in the presence of quartz.

amount of ethane is also present in the system. After MT for 30 min, only methane and hydrogen were detected as the reaction product.

In order to achieve maximal conversion and to investigate the solid phase in detail, we carried out an experiment with the MT of propane with quartz for 15 min varying the initial gas pressure. The results are shown in Fig. 3. One can see that the larger the amount of quartz present in the system, the more profound mechanical cracking of HC. For example, for the initial pressure of 2 atm and for 10 g of quartz, after MT the system was observed to contain 61.5 % of hydrogen, 36.5 % methane, as well as ethane and propane. After mechanical treatment under the same conditions but with 15 g of quartz, hydrogen concentration increases to 70 %, methane concentration decreases. A decrease in the initial propane pressure to 1.5 atm and an increase in the mass of quartz to 20 g resulted in the full conversion of propane into methane and hydrogen.

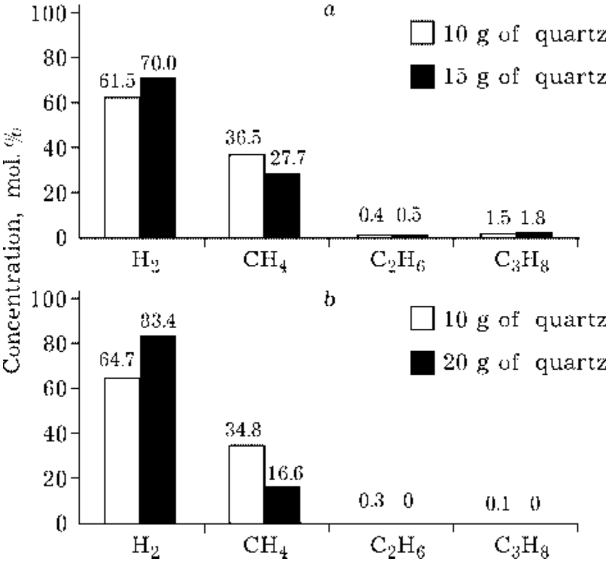

Fig. 3. Composition of the gas mixture obtained after MT of propane for 15 min in the presence of quartz. Initial pressure of propane in reactors: 2 (*a*) and 1.5 atm (*b*).

The composition of the solid phase is observed to change during the experiment. Elemental analysis of the quartz components of the solid phase after MT showed that the mass concentration of carbon is about 0.86 %.

The X-ray diffraction patterns of mechanically activated quartz (Fig. 4, *b*) show a decrease in the intensity of characteristic peaks. This is an evidence of particle grinding and possible amorphization of the solid phase, which in fact happens during MT of quartz [5–7].

Chemical transformations accompanying MT in the systems containing solid phases can be either of thermal or non-thermal character. It was shown in [8] that temperature in the sites of collisions of milling bodies can reach 800 °C. If we assume that in the case under our consideration the destruction of propane occurs due to local heating between the balls during their collisions, it seems logical to apply the mechanism of thermal cracking of propane to our system. However, along with hydrogen and methane, thermal cracking of propane should result in the formation of unsaturated HC. Nevertheless, the chromatographic analysis of the products of MT of propane did not indicate the presence of unsaturated HC in the mixture. Therefore, one cannot unambiguously state that propane cracking during mechanical treatment is thermal.

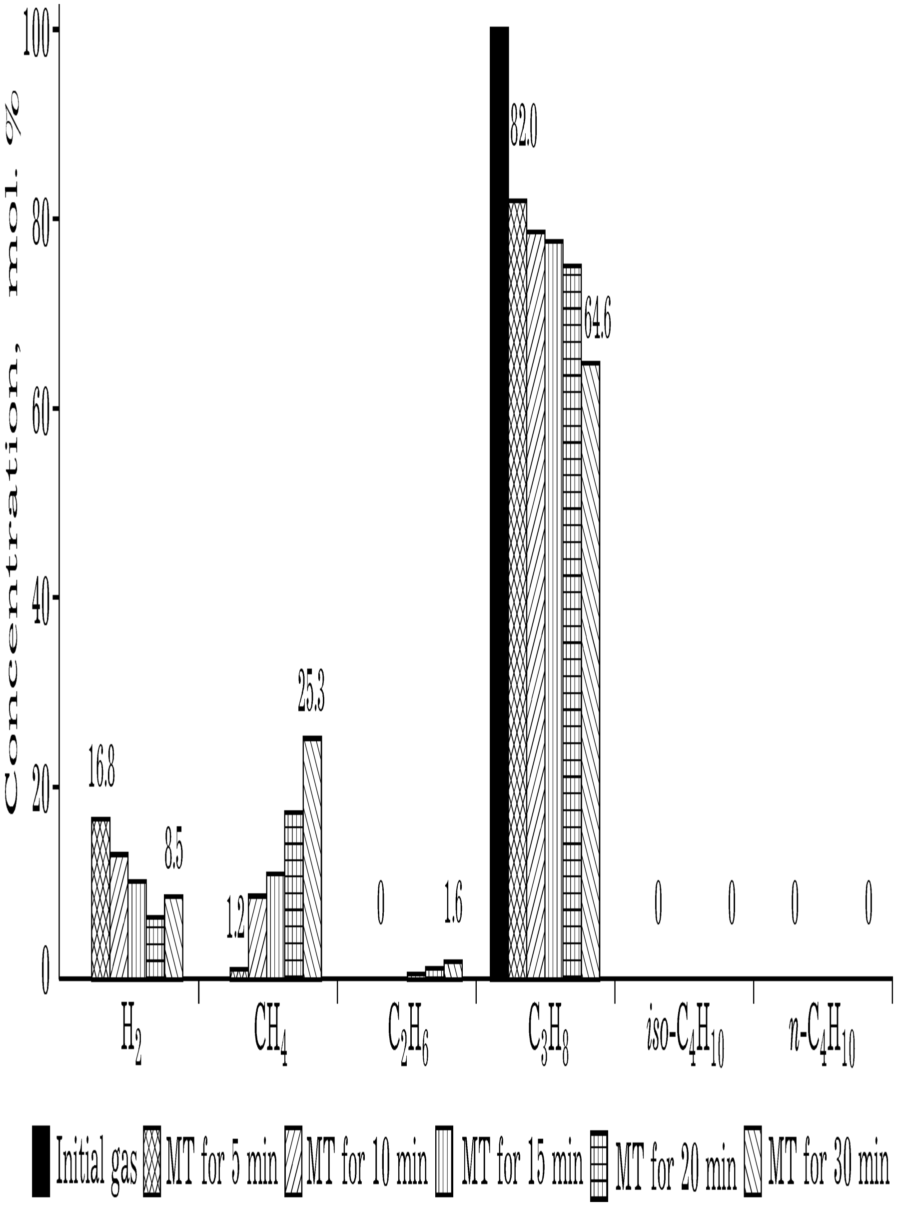

Fig. 4. X-ray diffraction patterns of quartz used in the experiments on mechanical activation, before MT (*a*) and after MT with propane for 15 min (*b*).

In our opinion, the mechanism of destruction is complex. The initiation of radical process is likely to occur during mechanical destruction of quartz crystals. It is possible that broken or deformed silicon-oxygen bonds can form chemisorption centres [6]. The molecules of the initial gas can get sorbed on these paramagnetic centres. Subsequent splitting of the least strong bond with the formation of radical products can occur. These products initiate a chain transformation in the gas phase. The occurrence of paramagnetic centres is confirmed by EPR spectra of quartz samples (Fig. 5). For instance, the EPR spectrum of a quartz sample after MT exhibits a signal with the *g* factor of free electron, which points to possible occurrence of carbon-containing deposits on the surface; they may be formed as a result of chemical transformations of HC during mechanical activation. The analysis of this signal is hindered because the signal is strongly broadened (to about 300 Gs) due to the dipole-dipole interaction with ferromagnetic iron particles formed due to wearing during MT. The presence of these ferromagnetic particles manifests itself by the appearance of EPR signal

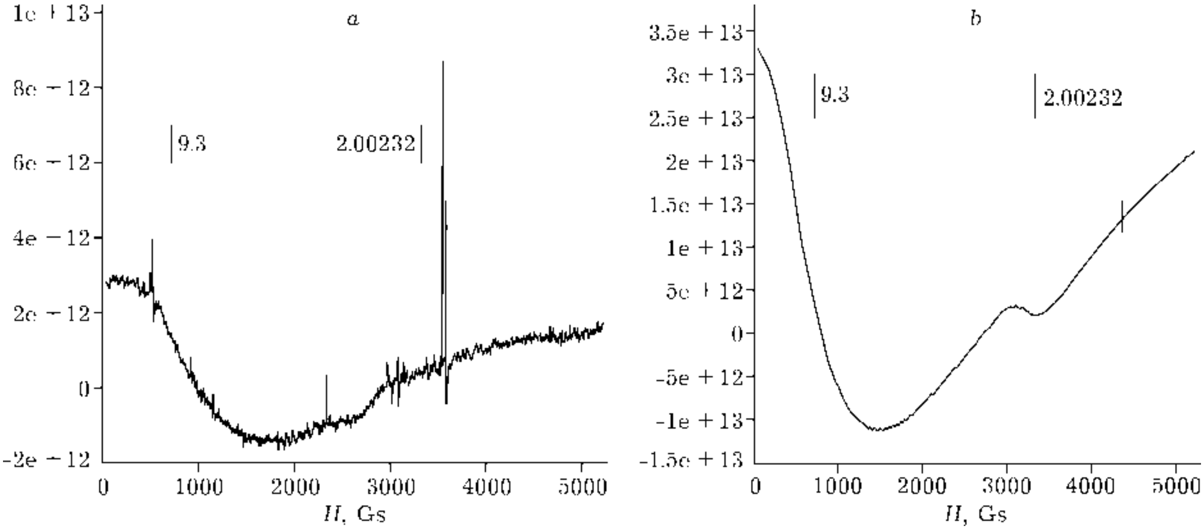

Fig. 5. EPR spectra of quartz before MT (*a*) and after MT with propane for 15 min (*b*).

with *g* factor near 9.3. It is necessary to note that, though the signal from ferromagnetic particles is clearly observed in the EPR spectrum of the initial quartz, the signal amplitude for this sample is two orders of magnitude less than that in the case of mechanically activated quartz.

In the absence of special additives, the main factor may be local heating in the sites of collisions of milling bodies. One cannot exclude the effect of iron from milling bodies and reactor walls. According to the results of elemental analysis, the mass fraction of iron in mechanically activated quartz reaches 24 %. This worn material is ferromagnetic and can participate in chemical reactions, too.

Thermodynamic investigation of possible reaction routes shows that non-thermal radical transformations are admitted in hydrocarbon mixtures of this kind [9].

No hydrocarbon structures grafted on the surface of the solid additive (the region 2950–2850 cm^{-1}) were detected in the IR spectrum of mechanically treated quartz (Fig. 6). This

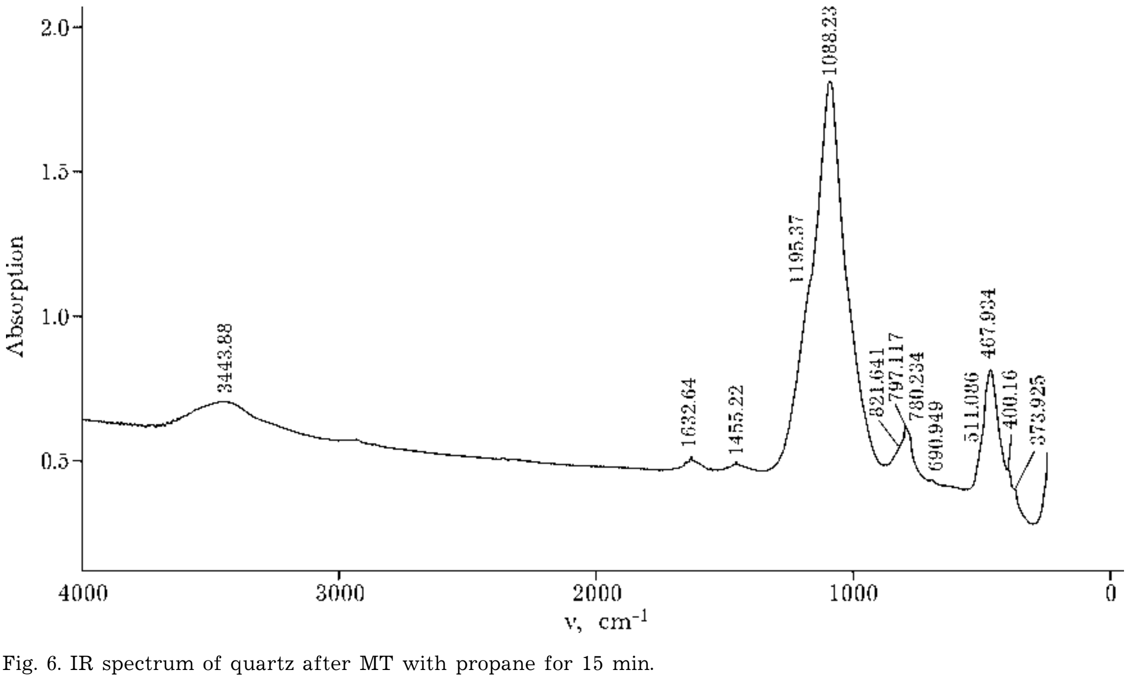

Fig. 6. IR spectrum of quartz after MT with propane for 15 min.

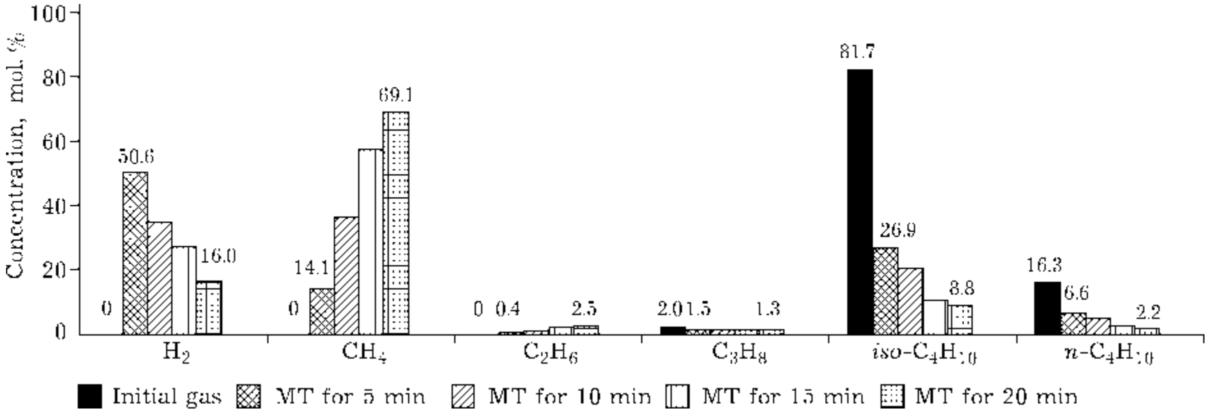

Fig. 7. Dependence of gas concentrations on time of MT of isobutane without additives.

provides evidence that MT does not result in the formation of hydrocarbons that cannot be detected chromatographically.

The presence of carbon in mechanically activated quartz points to the fact that propane decomposes completely into methane, hydrogen and carbon during MT with quartz.

In order to study the effect of MT on hydrocarbons with larger molecules, we carried out experiments on mechanical activation of isobutane. The results are shown in Fig. 7. One can see that in the case of MT of isobutane without any solid additive (isobutane pressure: 2 atm) the initial gas starts to decompose after 5 min activation, similarly to the case of propane. Hydrogen, methane, ethane and propane were detected in the resulting mixture. Further MT results in increased HC conversion accompanied by an increase in methane yield. After the experiment was finished, methane concentration was about 70 %, hydrogen 16 %. However, after MT for half an hour isobutane was still present in the system. In general, the trend of transformations is similar to that observed in experiments with propane.

The addition of quartz into the system causes a sharp increase in the conversion degree of isobutane. One can see in Fig. 8 that propane and butane disappeared form the system completely after MT for 20 min, while ethane concentration was only 2.5 %, methane 56.4 %. These data confirm the important role of quartz as a component initiating the radical-assisted conversion of hydrocarbon gas.

In order to confirm the decisive role of the gas phase, we carried out the experiments on MT of pentane in liquid and in the gaseous state. It was established that the treatment of pentane in the liquid phase did not result in its substantial transformation.

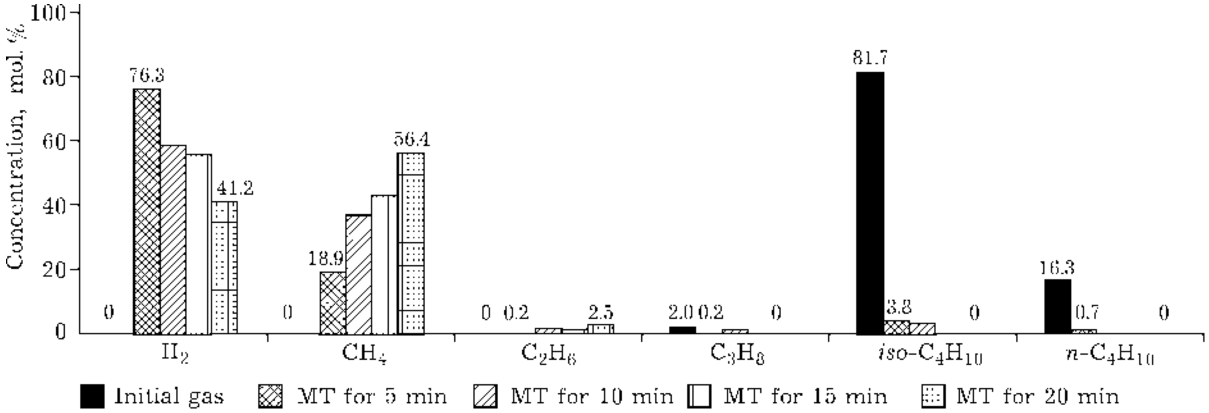

Fig. 8. Dependence of gas concentrations on time of MT of isobutane in the presence of quartz.

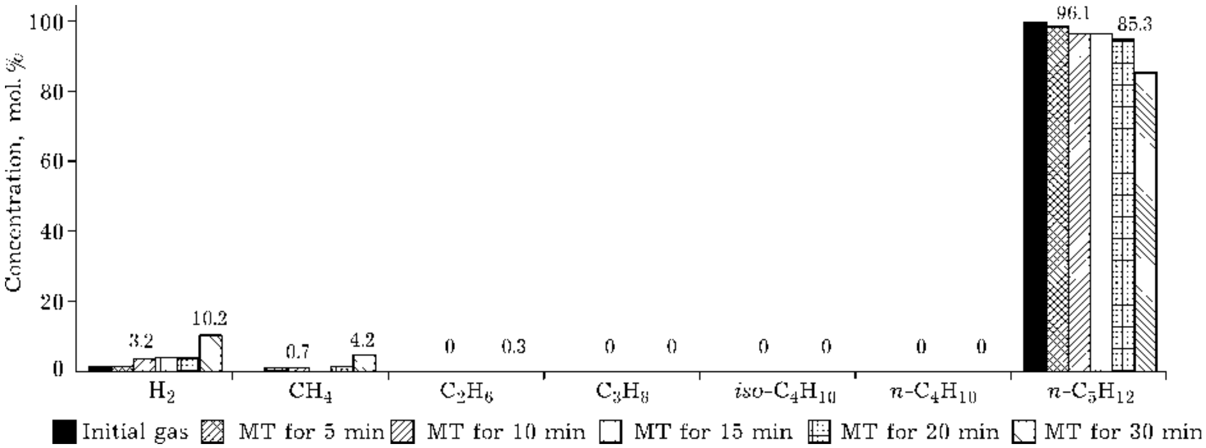

Fig. 9. Dependence of the concentrations of gaseous HC on the time of MT of n-pentane without additives.

The experiments in the gas phase were carried out with permanent heating of the reactors to the temperature exceeding pentane boiling point. The data obtained in the experiments are shown in Fig. 9. One can see that mechanical action has no significant effect on pentane. Only after MT for a long time (up to 30 min), methane and hydrogen are accumulated in the system: 4.2 and 10.2 %, respectively. One can see in Fig. 10 that the changes caused by the presence of quartz are essential. For example, after MT for 5 min, the system was observed to contain 61 % of hydrogen, 14.1 % of methane and 0.6 % of ethane. Further MT causes almost complete destruction of pentane. After MT for 30 min, the molar fraction of the initial hydrocarbon in the system is only 0.3 %.

On the basis of the data obtained on the mechanical activation of HC – components of accompanying and casing gas – one may propose a method of processing hydrocarbon-containing raw material into hydrogen-containing gas. Such a mixture of gases forms crystal hydrates under more rigid conditions than the gases containing easily condensable HC C_2–C_5 do [10]. Therefore, it will not bring about problems of transportation and storage. The relative density of this mixture is smaller than the density of any liquid HC that can be obtained from the casing-head gas; therefore, expenses for transmission through pipelines will decrease. Hydrogen-containing gases are needed in petrochemical industry, which shows the possibility to use the mechanochemically obtained gas mixtures in petroleum processing.

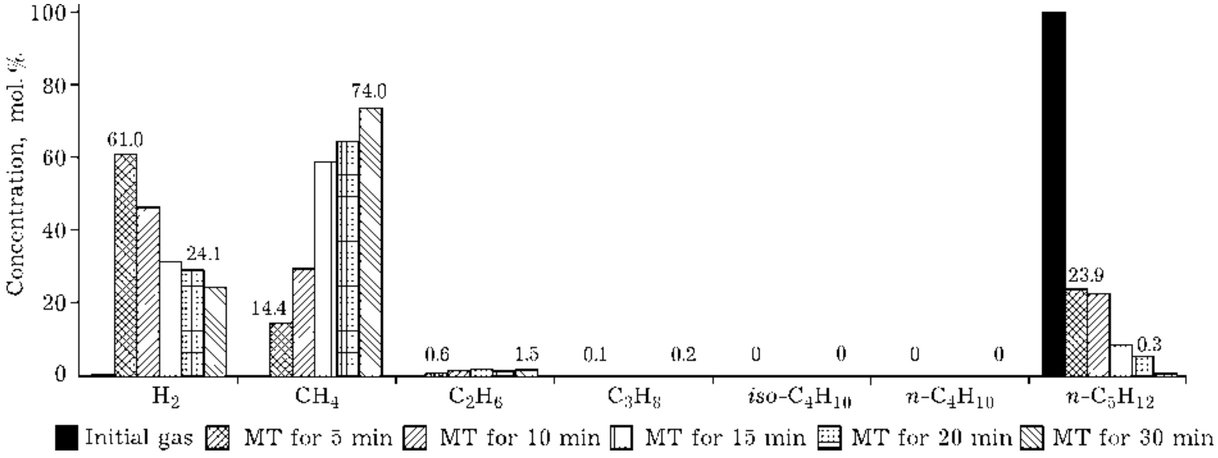

Fig. 10. Dependence of the concentrations of gaseous HC on the time of MT of n-pentane in the presence of quartz.

CONCLUSIONS

Mechanical activation of the heterophase system containing a gaseous HC and a solid body involves chemical reactions. The main route of the process is a mechanical destruction of HC into low-molecular homologues, hydrogen and carbon.

The possibility of mechanochemical conversion of propane, isobutane and n-pentane is demonstrated. Treatment in a planetary ball activator mill in the presence of quartz for 15 min results in a complete decomposition of propane into methane, hydrogen and carbon. Varying the conditions of mechanical activation one may vary the yield of methane to achieve its maximal value. Mechanical treatment of mixtures with isobutane proceeds in a similar way. Gaseous pentane more readily undergoes mechanochemical destruction into lighter-weighed hydrocarbons and hydrogen than pentane in the liquid state does.

Chemical reactions of HC during MT are likely to be initiated by radical paramagnetic centres on the surface of the mechanically treated solid. The presence of active centres was confirmed by means of EPR spectroscopy. The possibility of an initiation of the chemical transformations of HC due to local heating in the sites of collisions of milling bodies cannot be excluded.

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