Variation of natural gas composition under the action of Xe_2-ecxilamp radiation

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Received February 14, 2006

We present the results of the research into the Xe_2-excilamp radiation action (λ = 172 nm) on the phase transitions in natural gas containing water vapor in the temperature range from −30 up to +22°C at a gas pressure of 22.2 bar in the reactor with an active volume of 5000 cm^3. The Xe_2-excilamp radiation power was 4.4 W; exposure time was 1 min. Determination of the gas mixture composition before and after irradiation was performed by means of gas- and liquid chromatography. It has been shown that irradiation causes a twofold decrease in water vapor concentration and a considerable increase in hydrocarbon content (alcohols and dimers) with a number of carbon atoms greater than 6. After irradiation, the temperature dependence of natural gas pressure was measured within the range from −30 up to +22°C and was compared with temperature dependence of unirradiated gas pressure within the same temperature range. The comparison showed two representative parts of the dependence, which demonstrate that products formed in the reactor gave a considerable increase of gas pressure (about 0.4 bar) in the temperature range from −30 to −15°C.

Introduction

Investigation of the hydrocarbon structure changes under the action of a hard ultra-violet radiation is important for consideration of ecological problems in the atmospheric chemistry. Besides, oxidation processes and hydrocarbon structure changes play a significant role in modern plasma chemical techniques of processing of the raw hydrocarbons.

The natural gas dewatering and extraction of heavy hydrocarbon components at gas-condensate fields are carried out by means of the low-temperature processing both under field and factory conditions.[1–3] Temperature level in the extracting the C_{5+} hydrocarbons out of gas is usually being performed in the temperature range from −20 up to −30°C. At the same time, almost complete amount of ethane and more than 50 to 60% of propane and butanes remain (i.e., are actually lost) in the tank gas prepared for the long-distance transportation. The considered process is imperfect as regards the energy consumption as the extraction of a small amount (up to a few percent) of heavy components and a fraction of a percent of water vapor the processing is applied to the whole gas mixture. Besides, the low-temperature process has an awkward hardware implementation that leads to high capital outlays. Therefore, search for physically new technologies to affect the main components of natural gas of the gas-condensate fields and development of the physicochemical intensification methods of traditional low-temperature processes are the problems of topical urgency nowadays.

Several approaches to the low-temperature intensification technology are known: acoustic action and corona discharge for intensification of the condensation process from the gas phase, gasdynamic separation aimed at decreasing the equipment awkwardness and increase of technology reliability, especially, under field conditions. A new direction based on photochemical processes in gas flow with application of the high-power ultra-violet radiation is considered in the present paper.

In recent years, oxidation of the organic trace contaminants by means of UV radiation has assumed even greater importance.[4] The use of such sources of ultra-violet (UV) and vacuum ultra-violet (VUV) radiation as excilamps seems quite promising.[4,5] Depending on the choice of the working molecule and the pressure, excilamps allow obtaining incoherent narrow band radiation that opens new prospects for sewage and different process of waters treatment aimed at removing trace contaminants of the organic matters.[4,6,7] It should be noted that emitters of different shapes have already been developed that allowed conducting the UV irradiation in flow photoreactors thus making the considered process technological.

The paper presents the results of laboratory investigations on irradiation treatment of natural gas by a vacuum UV radiation ($\lambda \sim$ 172 nm).

1. Experimental hardware and measuring techniques

In earlier investigations,[8] the experiments on natural gas irradiation by a UV radiation were

0235-6880/06/09 734-04 $02.00

carried out at $\lambda \sim 172$ nm and power of 2 W under the atmospheric pressure and room temperature. The Table presents the natural gas composition of the Myl'dzhin gas-condensate field in Tomsk Region and the experimental results.

Table. Component composition of natural gas, mole %

Component	Before irradiation	After irradiation, Xe_2 excilamp, $\lambda \sim 172$ nm
Methane	92.38	92.52
Carbon dioxide	0.39	0.39
Ethane	3.48	3.48
Water	0.25	0.14
Propane	2.10	2.04
i-Butane	0.57	0.55
n-Butane	0.52	0.52
i-Pentane	0.16	0.16
n-Pentane	0.11	0.11
C_{6+}	0.04	0.09

Note. Relative variation of methane concentration is less than chromatograph error.

As follows from the component composition of the initial natural gas, the content of methane makes 92.38%, of hydrocarbons C_2 and the higher ones make 6.98%; water comprises about 0.25% of the total content.

The Table demonstrates that the C_{6+} and H_2O compounds undergo the highest relative changes moreover, the content of C_{6+} increases approximately twice. Concentration of water vapor decreases from 0.25 to 0.14 mole % (by 1.5 times). According to the absolute concentration value, the water vapor concentration ($\Delta[C_{6+}]$ – 0.05%, $\Delta[H_2O]$ – 0.1%) experiences the highest change.

Thus, significant processes at irradiation by the UV radiation are the processes of formation of the complex hydrocarbon molecules and water vapor conversion. The formation mechanism of the C_{6+} complex hydrocarbons in reactions with hydroxyl radicals in barrier discharge was considered earlier[9]:

$$C_nH_{2n+2} + OH^\bullet \rightarrow C_nH^\bullet_{2n+1} + H_2O, \quad (1)$$

$$C_nH^\bullet_{2n+1} + C_mH^\bullet_{2m+1} \rightarrow C_{(n+m)}H_{2(n+m+1)}. \quad (2)$$

The natural gas composition has a large set of organic and inorganic gaseous components. The dewatering mechanism under the action of UV radiation requires a special consideration. To do this, numerical modeling was carried out for the complex multicomponent hydrocarbon mixture C_1–C_6 with additives of the carbon dioxide and water vapor being under the action of UV radiation. The initial concentrations of these components were preset in correspondence with the tabular data.

2. Numerical modeling

We have conducted a numerical modeling of the hydrocarbon conversion processes C_1–C_6 in the reactors that use Xe_2-excilamps. A model of reactor included the calculation of formation rates of the radicals $H^\bullet$, $C_nH_{2n+1}{}^\bullet$, and $OH^\bullet$ under the action of UV radiation and rate constants of elementary processes involving free radicals. For calculations of gas phase kinetics of chemical transformations of the natural gas components, the kinetic scheme including about 200 reactions was used.

Except for solution of the primary kinetic problem, the model provided solving the problem of analyzing the complex chemical reaction mechanism that consisted in distinguishing of most significant elementary stages and construction of process hierarchy according to the preset criteria.

A numerical modeling of the kinetics of gas phase process is carried out for gas irradiated with a Xe_2 excilamp. The gas composition is presented in the Table. According to the calculations made, the scheme of processes leading to removal of water molecules from the mixture, in this case, is as follows. Under the action of UV radiation on the natural gas, containing water vapor, basically, water photolysis occurs with formation of the highly reactive $OH^\bullet$ and $H^\bullet$ radicals:

$$H_2O + h\nu \rightarrow H_2O^* \rightarrow H^\bullet + OH^\bullet, \quad (3)$$

which, henceforth, take part in the chemical reactions with hydrocarbons. Reaction (3) efficiently proceeds at irradiation by radiation at $\lambda < 190$ nm, therefore, the Xe_2 excilamp based on xenon dimers perfectly conforms to the photolysis.

Then the radicals formed recombine with each other or with hydroxyl radicals. Therefore, the further development of the process occurs according to the following scheme:

$$OH^\bullet + C_nH_{2n+2} \rightarrow i\text{-}C_nH^\bullet_{2n+1} + H_2O, \quad (4)$$

$$OH^\bullet + C_nH^\bullet_{2n+1} + M \rightarrow C_nH_{2n+1}OH + M, \quad (5)$$

$$C_nH^\bullet_{2n+1} + C_nH^\bullet_{2n+1} + M \rightarrow i\text{-}C_{2n}H_{4n+2} + M, \quad (6)$$

$$C_nH_{2n+1}OH + h\nu \rightarrow C_nH_{2n+1}OH^* \rightarrow C_nH^\bullet_{2n+1} + OH^\bullet. \quad (7)$$

Thus, synthesis of dimers and alcohols occurs in natural gas with water vapor. In the given system, the reaction (4) proceeds most efficiently with the C_{3+} hydrocarbons. The rate constants of this reaction with C_{3+} are by 2 to 3 orders of magnitude greater, than the rate constants of similar processes of the $OH^\bullet$ interaction with methane or ethane molecules. Therefore, in spite of low-level concentrations of the C_3–C_6 combinations in the natural gas composition, they are the major precursors of $C_n{}^\bullet H^\bullet_{2n+1}$ radicals. At the next stage, the formed radicals are dimerized or recombine with $OH^\bullet$. As a result, the complex C_{6+} molecules of isomeric structure and products of partial hydrocarbon oxidation (alcohols, aldehydes) are synthesized. Figure 1 presents the results of experimental measurements and numerical modeling of concentrations of the natural gas components after irradiation by Xe_2 excilamp.

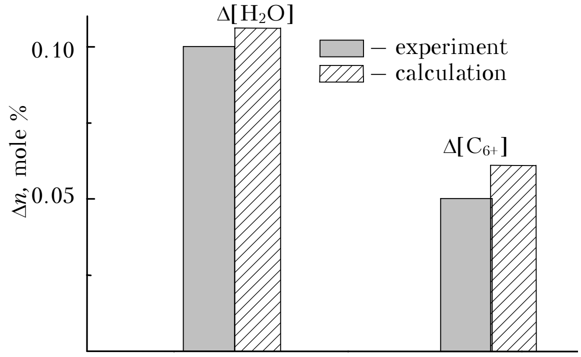

Fig. 1. Change of concentrations of natural gas components after the Xe_2-excilamp irradiation (measurements and calculation).

3. Change of water vapor concentration in natural gas

Natural gas at the atmospheric pressure was irradiated by the UV radiation with saturated water vapor. The experiments were carried out in a gas cell made of quartz tube (internal diameter of 60 mm), closed on two sides by steel flanges. The quartz tube of the Xe_2 excilamp of 35-mm diameter was arranged inside the cell, along the tube axis. After the evacuation of the gas cell, it was filled with natural gas with saturated water vapor.

The measurement results on water vapor concentration obtained by methods of gas chromatography are shown in Fig. 2.

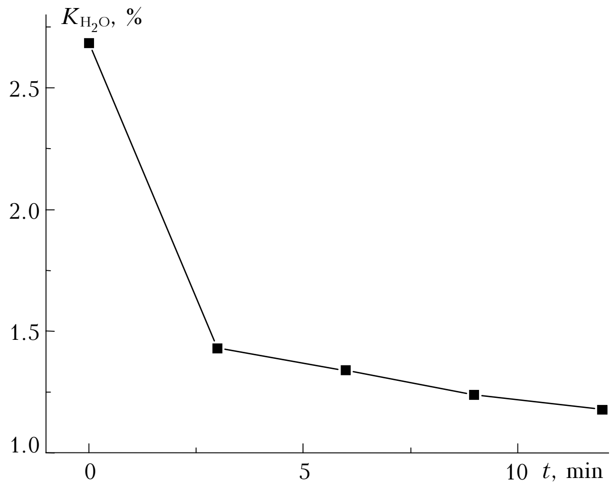

Fig. 2. Water vapor concentration in gas depending on irradiation time.

After the three-minute irradiation, the water percentage decreased approximately twice (47%), the subsequent irradiations in 6, 9, and 12 min gave the change of 6.3; 7.5, and 4.8 %, respectively.

4. Change of pressure depending on gas temperature

The natural gas composition changes under the action of UV radiation that exerts an essential influence upon its thermodynamic parameters. For experimental investigation of this effect, the reactor has been developed that operated with the Xe_2 excilamp up to 45 bar. The working surface length of a lamp made 24.5 cm, radiation density at the wavelength of 172 nm was 26 mW/cm^2, total radiation power was 4.4 W. The reactor was filled with natural gas up to the pressure of 22.2 bar ($T = +22$°C) and was cooled by means of liquid nitrogen down to the temperature of -30°C. Thus, the water vapor content in gas corresponded to the tabular data. The cooling dynamics for the unirradiated and irradiated natural gas (exposure time was 1 min) is presented in Fig. 3.

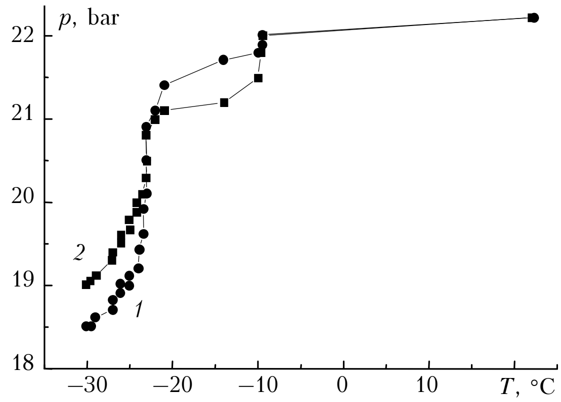

Fig. 3. Dependences of gas pressure in the reactor on temperature before (*1*) and after (*2*) irradiation by the Xe_2 excilamp.

The obtained pressure dependences in the reactor on the temperature show that pressure decrease is observed for the irradiated natural gas components and then, within the limits of the subsequent temperature reduction, there occurs a pressure increase as compared with the pressure of the unirradiated gas. At a temperature of -30°C, the excess pressure of irradiated gas makes approximately 0.4 bar. As a result, there are two representative sections of temperature dependence of pressure $p(T)$ in the temperature interval from -20 up to -10°C and from -30 up to -20°C. Although, quantitative analysis of phase transitions in multicomponent hydrocarbon mixture with water vapor is a complex calculation problem, there is the following qualitative interpretation of the observed effect. The modeling results show that under the action of radiation, the synthesis of dimers and alcohols takes place. The formed complex hydrocarbon molecules convert into the liquid phase that leads to the decrease in pressure due to efficient dissolving of a gas component at temperatures from -20 up to -10°C. The subsequent decrease in temperature causes water vapor condensation and solubility of a gas component in liquid products falls down owing to the aqueous-alcoholic fraction in the condensate.[9] Gas pressure under these conditions should be higher. Just this behavior of pressure has been recorded in the experiment.

Conclusions

1. It is shown that under the action of a UV radiation with $\lambda \sim 172$ nm (Xe_2 excilamp) on natural gas, the water vapor concentration in natural gas decreases more than twice.

2. The results obtained show that action of the high-power UV radiation in the above-stated range on natural gas containing water vapor leads to an increase in content of heavy components due to the directed photochemical processes of propane and butane dimerization.

3. Dependence has been revealed of the gas pressure change on temperature for the irradiated and unirradiated natural gas at a pressure of 22.2 bar, and interpretation of the observed effect of gas pressure increase at -30°C has been proposed.

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