# Dynamics of natural gas conversion in the throttling mode under VUV-irradiation

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Effect of irradiation by a $Xe_2$-excilamp ($\lambda = 172$ nm) on conversion dynamics of natural gas containing water vapor in the throttling mode is studied. A gain in the gas condensate yield by a factor of 2–3 is achieved under hard VUV irradiation of the flowing natural gas. It is pointed, that separation of the condensate from natural gas is based on the effect of induced condensation under the action of VUV photons, which form active centers (excited particles, ions, and radicals). In this case, non-equilibrium condensation occurs around active centers, such as positive and negative ions, and the induced condensation is provided for at vapor pressures essentially lower than the saturated one. Performed calculations have shown that energy consumption for the induced condensation is one–two orders of magnitude less than the energy spent for formation of one active particle, namely, excited molecule, radical, or ion. Measurements of water content in the gas flow demonstrate that VUV-irradiation of the gas, when throttling, reduces the concentration of water by a factor of ~1.5. Thus, gas irradiation in the throttling mode allows a gain in the condensate yield and the decrease of the $H_2O$ concentration.

## Introduction

Processes of structural change of hydrocarbons under impact of hard VUV irradiation are important for understanding ecological problems of atmospheric chemistry. In addition, they play an essential part in modern techniques of hydrocarbon processing.

When preparing gas to transportation, there appear technological problems of primary processing and treatment of the produced gas mixture for the most effective condensate separation and its piping. Any enhancement of the efficiency, even relatively small, results in a noticeable benefit at the industrial scale.

A necessary condition for a gain in condensate yield is providing for conditions for retrograde condensation, when the liquid phase drops out from the multicomponent gas mixture near its critical point at the isothermal pressure decrease.

A necessary condition for reduction of transportation losses and providing for reliability of the gas supply is stabilization of the gas phase, i.e., some complex of technological processes, including gas drying. The water dew-point is the gas mixture temperature, at which the gas becomes water-vapor saturated at a given pressure value. Further temperature decrease, even small, results in condensation of water vapors. To prevent this effect, harmful for the gas transportation and most probable in vulnerable points of the gas pipeline, the water dew-point is to be decreased. It is necessary to decrease moisture content in gas ("to dry" gas) at some fixed gas temperature and pressure.

Extraction of heavy hydrocarbon components and dewatering of natural gas at gas-condensate fields are carried out using low-temperature processes in field and plant conditions.[1,2] In this work, a principally new approach is considered, based on photochemical processes in the gas flow with the use of powerful UV sources.[3,4] Besides, an effect of $Xe_2$-excilamps irradiation ($\lambda = 172$ nm) in the throttling mode on dynamics of conversion of the natural gas, containing water vapors, is reported.

## 1. Instrumentation for diagnostics of quantity and content of natural gas conversion products

Three photoreactors were used in the experiment. The first one[5] was a pipe cell with an inner diameter of 40 mm and a working volume of 510 cm$^3$, operating with a $Xe_2$-excilamp up to 45 atm. The length of the lamp working surface was 24.5 cm, radiation density at a wavelength of 172 nm was 15 mW/cm$^2$, and total radiation power was about 4 W.

The second photoreactor consisted of a pipe cell with an inner diameter of 100 mm and working volume of 6330 cm$^3$, which worked with a set of four similar excilamps. The working surface length of a lamp was 100 cm, radiation density at a wavelength of 172 nm was 20 mW/cm$^2$, and total radiation power of four lamps was about 60 W.

The third photoreactor consisted of four pipe cells, each of 1300 mm in length and 46 mm in diameter,

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located in parallel to each other, sequentially connected, and working with four excilamps. The working surface length of a lamp was 100 cm, radiation density at 172 nm was 20 mW/cm$^2$, and total radiation power of a lamp was about 15 W.

The following techniques for diagnostics of quantity and composition of natural gas conversion products were used: gas-liquid chromatography of reaction products; measurement of total vapor pressure of the resulted products; measurement of liquid fraction volume; measurement of the gas flow rate.

## 2. Measurement of water vapor concentration variation in natural gas, affected by UV-radiation

Experiments[3,6] on UV-irradiation ($\lambda \sim 172$ nm) of natural gas have shown that basic processes are the formation of hydrocarbon complex molecules and the water vapor conversion.

Complex hydrocarbons $C_{6+}$ are formed in reactions with hydroxyl radicals by the scheme:

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

$$\bullet C_nH_{2n+1} + \bullet C_mH_{2m+1} \rightarrow C_{(n+m)}H_{2(n+m+1)}. \quad (2)$$

Water photolysis proceeds with formation of highly reactive radicals •OH и •H:

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

which later react with hydrocarbons.

Then the formed radicals recombine with each other or hydroxyl radicals. Therefore, the further development of the process realizes by the scheme:

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

$$\bullet OH + \bullet C_nH_{2n+1} + M \rightarrow C_nH_{2n+1}OH + M; \quad (5)$$

$$\bullet C_nH_{2n+1} + \bullet C_nH_{2n+1} + M \rightarrow u\text{-}C_{2n}H_{4n+2} + M, \quad (6)$$

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

Thus, dimmers and alcohols are synthesized in natural gas with water vapors.

Experiments on UV (172 nm) dynamics of water vapor concentration variations in natural gas were carried out at the first and second photoreactors at working gas pressures of 17.1 and 45 atm, respectively.

The variation dynamics of water vapor concentration depending on the irradiation time is shown in Figs. 1 and 2 for the first and the second photoreactors, respectively.

As is seen in Fig. 1, the water vapor concentration decreases by two times per 2 minutes. When increasing the gas cell pressure and total radiation density by a factor of 2.5, the time of water vapor concentration decrease by two times was 1.2 min (Fig. 2).

The composition of stable products of the formation gas, obtained after irradiation of hydrocarbons, was chromatographically analyzed at 17.1 atm. Here the results are presented before and after (in parentheses) irradiation: methane – 92.34 (92.52); carbon dioxide – 0.39 (0.39); ethane – 3.48 (3.48); water – 0.27 (0.13); propane – 2.1 (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 (0.1). The analysis proved the processes of formation of complex hydrocarbon molecules and water vapor conversion to be the most essential under the UV-irradiation.

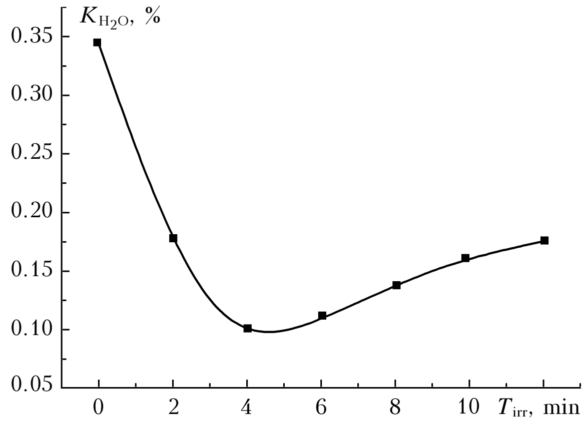


**Fig. 1.** Variation of water vapor concentration in natural gas as a function of irradiation time at a pressure in the photoreactor of 17.1 atm.

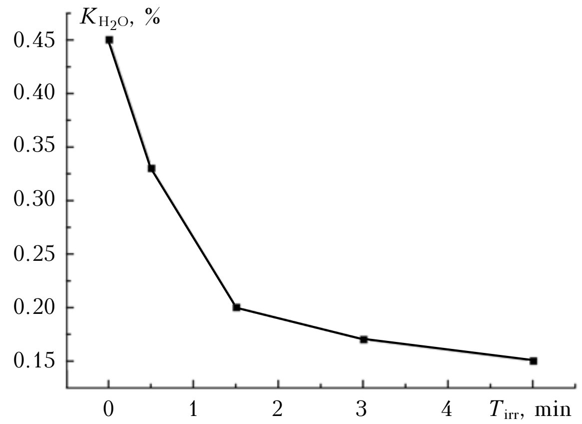


**Fig. 2.** Variation of water vapor concentration in natural gas as a function of irradiation time at a pressure in the photoreactor of 45 atm.

## 3. Calculation and estimation of energy efficiency of photolysis of UV-irradiated methane

The UV radiation absorption by methane at $\lambda = 172$ nm is negligible in comparison with absorption by water vapors. Therefore, no methane conversion occurs in the absence of water vapors or other absorbing admixtures. Initiation of $CH_4$ decomposition occurs with $H_2O$ admixture in the process of water photolysis.

The concentration of products, formed as a result of $CH_4$–$H_2O$ mixture irradiation by the UV $Xe_2$-excilamp, is determined by the numerical simulation of kinetics of methane and water vapor decomposition processes. More than 100 processes of $CH_4$ oxidation were taken into account in the kinetic model. According to the calculations, the composition of the produced products essentially depends on the gas temperature. For water vapor conversion, the region of low temperatures is optimal (293 K is a minimal value taken in the calculations); ethane, methanol, and hydrogen are the main products of methane conversion. Methyl radicals, necessary for producing these compounds, resulted from the reactions

$$CH_4 + OH \rightarrow CH_3 + H_2O, \quad (8)$$

$$CH_4 + H \rightarrow CH_3 + H_2. \quad (9)$$

Despite a large variety of processes, considered in the model, other reactions contribute negligibly in the methane conversion process. The reaction

$$OH + CH_3 + M \rightarrow CH_3OH + M \quad (10)$$

contributes about 90% in the process of methane conversion and about 100% in the water conversion at a reactor temperature of 293 K.

According to calculations, to produce one $CH_3OH$ molecule, about two photons of UV $Xe_2$-excilamp radiation, or about 14 eV of irradiation energy are expended at worst (7 eV at best). If to take the excilamp efficiency equal to 50%, then the equivalent electric power consumption is about 15–30 kW · h per 1 kg of methanol, which is essentially more than for its production. In terms of 1 kg of water, driven off while synthesizing methanol in the photoreactor, it is consumed up to 60 kW · h per 1 kg of water; therefore, direct process of gas dewatering is unprofitable. The use of this process along with standard field systems of methanol regeneration, it is possible to reduce the consumption for the dewatering by more than the order of magnitude and to decrease the reactor sizes by the corresponding factor.

Estimate the efficiency of experimental water decomposition processes under static irradiation in the first photoreactor at a natural gas pressure of 17.1 atm. The natural gas was irradiated by a $Xe_2$-excilamp (a wavelength of 172 nm, a radiation density of 15 mW/cm$^2$, a radiating surface of 192 cm$^2$). The $H_2O$ concentration in natural gas varied from 0.28 to 0.14% per 3 min, which was $21.4 \cdot 10^{-6}$ kg for the first photoreactor of 510 cm$^3$ in volume. The irradiation energy for this period was 522 J or $145 \cdot 10^{-6}$ kW · h. Then the energy consumption for water decomposition is $145 \cdot 10^{-6}$ kW· h/$21.4 \cdot 10^{-6}$ kg = = 6.8 kW · h/kg. This is in a good agreement with the above calculation results.

## 4. Study of natural gas conversion in the throttling mode under VUV-irradiation

Tests on formation-gas condensate production in the field throttling mode at a flow photoreactor were carried out at the first and second photoreactors at an initial gas pressure of 40–45 atm.

Figure 3 shows the test results for the first run at the first photoreactor. The condensate yield at the gas rate $A$ from 10 to 30 m$^3$/h was higher under the gas irradiation then without it. The maximum condensate yield was 95 cm$^3$ per 1 m$^3$ at a flow rate of about 10 m$^3$/h (curve *2*), while the condensate yield of the unirradiated gas was 46 cm$^3$ per 1 m$^3$ (curve *1*). In the second test run, at a gas rate of 7 m$^3$/h, the maximum condensate yield in the given test conditions was 88 cm$^3$ per 1 m$^3$ for irradiated and 44 cm$^3$ per 1 m$^3$ for unirradiated gas.

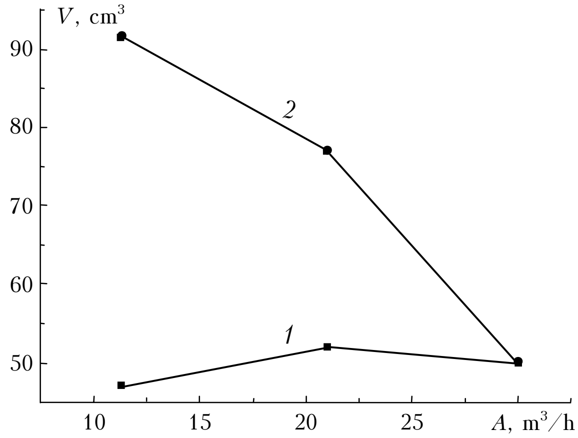


**Fig. 3.** Gas condensate yield as a function of gas rate.

Tests at the third photoreactor at a gas rate of 27 m$^3$/h have shown a 10-fold gain in condensate yield under UV irradiation.

Let us estimate the energy efficiency of condensate yield. In tests at the first reactors, the crude gas rate was 11.3 m$^3$/h, the working time was 5 min, and the supply power was 250 W; in those conditions, the condensate yield was 0.0623 kg. In addition, the energy consumption was determined to be 0.334 kW · h per 1 kg of condensate.

The analysis of chromatograms of gas condensate, produced in the throttling mode for irradiated and unirradiated natural gases, has shown that concentrations of $C_4$, $C_5$, and $C_6$ hydrocarbons increase and of $C_7$ hydrocarbons decrease with the increase of condensate yield under irradiation (Fig. 4).

Experiments on natural gas dewatering were carried out at a small reactor in laboratory conditions. Field crude gas was fed into the reactor from a cylinder under the 42-atm pressure through an aperture; in the reactor it was irradiated by an excilamp ($\lambda$ = 172 nm). The lamp was 27 cm in length, 2.2 cm in diameter, and had a radiation density of about 7 mW/cm$^2$. The pressure was controlled by an output valve and changed from 35 to 16 atm during a 5-min throttling. The water concentration in gas was chromatographically measured by means of sampling while throttling.

The dynamics of water concentration variation is shown in Fig. 5.

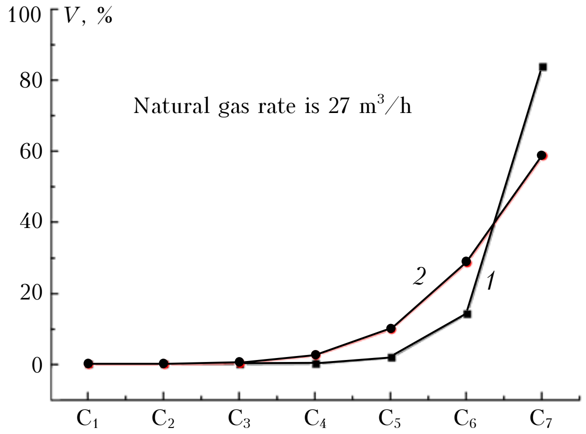


**Fig. 4.** Content of natural gas before (*1*) and after (*2*) irradiation. The pressure at the photoreactor inlet is 45 atm.

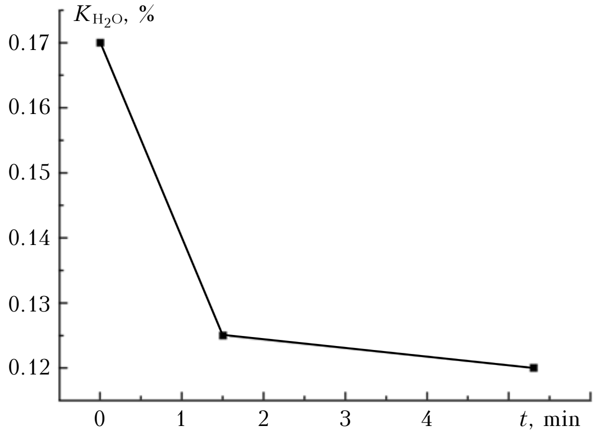


**Fig. 5.** Time behavior of water concentration in gas flow.

While throttling, the water concentration in gas decreased by 1.5 times. Note that the concentration in crude gas was slightly lower than in the field one. Usually it is 0.25–0.35% and its decrease by 2.5–3 times is expected in the throttling mode.

Thus, when irradiating the field gas in the throttling mode, the condensate yield increases and $H_2O$ concentration decreases simultaneously.

In our experiments, the retrograde condensation takes place, i.e., the drop out of the liquid phase in a multicomponent gas mixture near its critical point under the decrease of the usually isothermal pressure and UV irradiation.

The technology of the condensate separation from natural gas is based on the effect of external-source induced condensation (UV radiation in our case); the source generates active centers, such as excited particles, ions, and radicals. In this case, a so-called nonequilibrium condensation occurs. The process of aerosol origination therewith essentially differs from ordinary kinetics of drop formation from saturated vapor at its cooling (e.g., in throttling). Under external initiation by sources of ions and radicals, nuclei grow at low hydrocarbon vapor pressure owing to intense clustering:

$$(C_{5+})_n^{\pm} + C_{5+} \rightarrow (C_{5+})_{n+1}^{\pm}. \qquad (11)$$

Here $C_{5+}$ are heavy hydrocarbons present in natural gas as vapors; $(C_{5+})_n^{+}$ is the ion cluster. When the number of particles in a cluster attains a certain limit (usually several tens of molecules), process (11) slows down due to discharge screening. Further growth of drops occurs due cluster coagulation with drop formation. Thus, induced vapor condensation is provided for at pressures essentially lower then saturated. Essential difference of this process from ordinary condensation is evident: an external source, generating active centers, is required.

Note an important peculiarity in terms of technological applications: process (1) is a chain with tens and hundreds of nucleus molecules account for each formed particle. Thus, the energy consumption for the induced condensation is tens and hundreds time lower than those for formation of one active particle (excited molecule, radical, or ion). An alternative technique for $C_{5+}$ hydrocarbons inducing condensation is the use of UV radiation sources.

Preliminary field tests of an UV reactor have clearly shown that the wall tarring of the reactor and pipeline is absent in this case, condensate yield increases by about one order of magnitude, and discharge is safed from the natural gas flow by thick quartz walls, holding the working pressure in the pipeline.

The absence of tarring processes in pipelines is explained by the intensity of the process (1). Since OH radical is the most active particle in the oxidation processes of organic compounds, tar films do not form. Hydrocarbon oxidation with participation of OH radical produces alcohols, aldehydes, and ketones, which favor the aerosol stabilization and, hence, a gain of the condensate yield.

## Conclusion

1. It is shown that UV-irradiation at $\lambda \sim 172$ nm (Xe-excilamp) of 40–45-atm natural gas results in a 2–2.5-fold decrease of water vapor concentration in the gas.

2. When irradiating the field gas in the throttling mode, the condensate yield increases with simultaneous decrease of $H_2O$ concentration, while the energy consumption for the induced condensation is by the order of magnitude lower than those for formation of one active particle, i.e., excited molecule, radical, or ion.

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