Effect of VUV Radiation on Phase Transition in Natural Gas

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Abstract – the effect of Xe_2-excilamp (λ=172 nm) radiation on the phase transitions in the natural gas containing the water vapour is studied in the temperature range from -30 to +25°C at pressure up to 30 bar. The gas mixture composition was determined using gas and liquid chromatography methods. It was shown, that irradiation of the gas by the VUV photons results in decrease by a factor of 2 concentration of the water vapour, while considerable increase of hydrocarbons (alcohols and dimers) with the number of carbon atoms greater than 6 was observed. Temperature dependence of the gas pressure versus the gas temperature in the range -30 ÷ +25 °C was measured after irradiation and compared with that one for initial gas. Comparison of these dependences features two characteristic temperature intervals, which show, that products formed in the illuminated gas give sufficient rise of the pressure (of the order of 1 atm) in the temperature range under study.

Dynamics of the condensate yield in the gas flow was studied and 2–3 times gain for the condensate yield was obtained under exposure of the natural gas by the vacuum UV radiation.

1. Introduction

Refining of the natural gas from water vapour and separation of heavy hydrocarbons components at the gas-condensate deposit are carried out using low temperature processes, which are applied both in the field, and industrial conditions [1–3]. There are several known ways of intensification of the low-temperature engineering processes for elimination of the bulk and for reliability enhancement of applied facilities, especially for the field conditions – an acoustic action and a corona discharge for intensification of the condensation process in the gas phase, a gas-dynamic gas separation. In the present work a new approach based on the application of the photochemical processes in the gas stream is considered with usage of intense sources of ultraviolet radiation.

In the last years the oxidation of organic trace contaminant by means of ultraviolet radiation gains the increasing importance [4]. Application of such ultraviolet- (UV) and vacuum ultra-violet (VUV) sources as excilamps are realized as perspective [4, 5]. Depending on selection of the active molecule and the operating pressure of the gas mix, it is possible to obtain incoherent narrow-band radiation, which opens new prospects for sewage treatment, various processes of water purification from trace organic contaminants [4,6,7]. It is important to note, that various UV light sources appropriate for use in the flowing photoreactors are already developed and provide adaptability of considered process for technological applications.

In this paper the results of investigations on irradiation of natural gas by the vacuum ultraviolet radiation (the wave length λ ~172 nm) are presented.

2. Experimental.

In our former publications [8, 10] were presented experimental results on the natural gas treatment by the ultra-violet radiation sources λ ~172 nm with a light power of 2 W and 10 W at the natural gas pressure of 1 and 17.1 bar at the ambient temperature. The greatest relative changes undergo C_{6+} and H_2O species, while concentrations of C_{6+} components are decreased approximately twice. Concentration of water vapour drops from 0.25 to 0.15 % (in 1.5 time). On an absolute value of concentration the greatest variation were observed for water vapour concentration $\Delta[H_2O]$ ($\Delta[C_{6+}] \sim 0.05$ %, $\Delta[H_2O] - 0.1$ %). The analysis of the stable products composition of the natural gas at pressure 17.1 bar obtained after irradiation was carried out using chromatography technique. The composition of the natural gas before- and after exposure (in parenthesis) was as follows: methane was 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%).

Thus, essential processes at the irradiation by ultra-violet radiation are the processes of higher hydrocarbons formation and conversion of the water vapour. The reaction pathway for formation of the higher hydrocarbons C_{6+} in reactions with hydroxyl radicals in the barrier discharge has been considered earlier in [9]:

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

$$C_nH_{2n+1}^\bullet + C_mH_{2m+1}^\bullet \rightarrow C_{n+}mH2_{(n+m+1)} \quad (2)$$

As to reaction route of water elimination under the action of Xe_2-radiation on the natural gas involving a great diversity of organic and inorganic gaseous components, this problem requires special consideration. To this end a numerical simulation of the complex multi-component mixture of hydrocarbons C_1-C_6

containing water vapour under the action of Xe_2-radiation has been performed.

3. Numerical simulation.

In present work the numerical simulation of kinetics processes of hydrocarbons C_1-C_6 conversion in Xe_2 – excilamp photoreactor has been done. The model of the reactor comprised calculation of formation rates for the radicals $H^{\bullet}$, $C_nH_{2n+1}^{\bullet}$ and $OH^{\bullet}$·under the action of the ultra-violet radiation, and the rate constants calculations for free radicals reactions. For calculation of the gas phase kinetics for chemical transformations of the gas species a kinetic scheme including 200 reactions has been used.

Except the direct solution of kinetic equations in the model the possibility has been envisioned for the analysis of the complex chemical reaction pathway consisting in selection of the most essential stages and in build-up of the processes hierarchy by the given criterion.

Numerical simulation of the gas phase kinetics processes in the natural gas under the action of Xe_2-excilamp has been done. According to our calculations, the kinetic scheme resulting in removal of water molecules from the mixture in this case looks as follows.

Under the action of ultra-violet radiation, in the natural gas containing water vapour, the formation of free radicals OH and H dominates ·in the photolysis of water molecule:

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

which react in the further chemical reactions with hydrocarbons. The reaction (3) is sufficient under exposure by UV radiation when the wave length λ <190 nm, therefore Xe_2-excilamp ideally matches to this aim.

The free radicals formed in the photolysis process recombine then with each other or with hydroxyl radicals. Therefore, the further evolution of process occurred in accordance with the following pathway:

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

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

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

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

Thus, in the natural gas with water vapour the synthesis of dimers and alcohols occur. In the above system the reaction (4) is most efficient with hydrocarbons C_{3+}. The rate constants for this reaction with C_{3+} is on 2–3 orders of magnitude higher, than those ones for similar processes of $OH^{\bullet}$ radicals·interaction with methane or ethane molecules. Therefore, despite the low C_3-C_6 concentrations in the composition of the natural gas, they are the basic precursors for $C_nH_{2n+1}^{\bullet}$·radicals. At the following stages the radicals transform to dimers or recombine with $OH^{\bullet}$. As a result, complex C_{6+} molecules with isomeric structure and oxygenated hydrocarbons (alcohols, aldehydes) are synthesized. The results of the experimental measurements and numerical simulation on concentrations of the natural gas components after exposure by Xe_2 - excilamp have correlation within the limits of 10 – 15 %.

4. Variation of the water vapour concentration in the natural gas

Irradiation of the natural gas with saturated water vapour at atmospheric gas pressure by Xe_2-excilamp radiation was carried out. The experiments were performed using the gas chamber made of the quartz tube (of 60 mm in diameter), closed by two steel flanges at the end faces. The quartz Xe_2-excilamp tube of 35 mm in diameter was placed inside the chamber along the tube axis. After pumping the gas chamber out it was filled by the natural gas with saturated water vapour.

Thus obtained results on the water vapour concentration measurements versus irradiation time using gas chromatography methods are presented in the Figure 1.

After three-minute gas exposure the percentage of water was diminished almost by 2 times (47 %), and subsequent exposures for 6, 9 and 12 minutes have yielded, accordingly, the variations of water concentrations 6.3, 7.5 and 4.8 %, respectively.

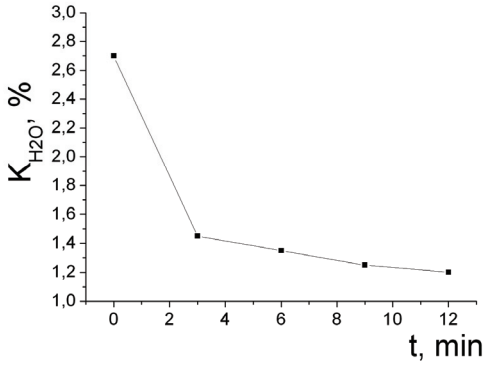

Fig. 1. Concentration of the water vapour in the natural gas versus irradiation time

5. Variation of the gas pressure versus the gas temperature

Under the action of Xe_2-radiation variations of the natural gas composition occurred which sufficiently influence its thermodynamic parameters. The reactor with Xe_2-excilamp operating at the pressure up to 45 bar has been developed for experimental study of this effect. The effective surface length of the lamp was of 24.5 cm, the radiation intensity of 26 mW/cm^{2}at the wave length 172 nm, and the overall radiation power of 4.4 W. The reactor was filled by the natural gas up to 22.2 атм (T = +22 ºC) and then cooled by the liquid nitrogen up to the temperature of -30 ºC. The initial content of water vapour in the gas composition was of 0.25 %. The dynamics of the cooling process for the non-irradiated- and irradiated natural gas (one-minute exposure) is shown in Figure 2.

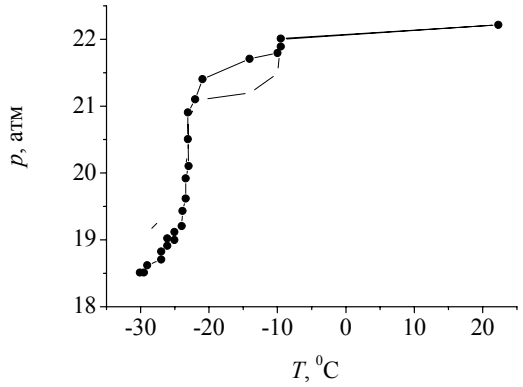

Fig. 2. Variations of the gas pressure in the reactor versus temperature for unexposed gas (●), and for that one after irradiation by Xe_2-excilamp (■)

The gas pressure dependences versus the temperature obtained in the reactor for irradiated natural gas have shown that there is first a pressure drop and then, by the further temperature decrease, some pressure rise occurs as compared to non-irradiated components. At -30 ºC an overpressure about 0.4 bar occurs for the irradiated gas mix. As a result, one can observe two characteristic temperature intervals for pressure *p(T)* dependence: a) in the temperature range from -20 ºC to -10 ºC; b) from -30 ºC to -20 ºC. Though the quantitative analysis of the phase changes in a multicomponent mixture of hydrocarbons with water vapour is a complex computational task, the following qualitative interpretation of the observed effect is possible. According to our kinetics simulation results, under the action of UV-radiation the formation of dimers and alcohols occurs. Thus obtained higher hydrocarbon molecules getting then into liquid phase, what leads to a pressure decrease as consequence of an efficient dissolution of the gas components in the temperature range from -20 ºC to -10 ºC. By the further temperature decrease, the condensation of water vapour starts, and the solubility of the gas components in the liquid products drops owing to occurrence of the water-alcohol fraction in the condensate [9]. The gas pressure under these conditions should be higher. This pressure variation features were also noticed in the experiments.

6. A study of the gas condensate formation processes on the basis of the field tests

Tests on the condensate extraction from the natural gas in a flowing type photo-reactor at the gas deposit was simulated on a photo-reactor with Xe_2-excilamp of 25 cm in length, a radiant density of 25 mW/cm^2 and a wave length $\lambda \sim 172$ nm. The initial natural gas pressure in the experiments was of 45 bar.

Dependencies of condensate yield **V** from 1 m^3 of natural gas versus gas flow rate **A** for the first test series are presented in the Figure 3. The condensate yield from irradiated gas over the range of the gas flow rate from 10 to 30 m^3/h was higher than for non-irradiated gas. The maximal condensate yield for this test series was of 95 ml at the gas flow rate ~ 10 m^3/h. The exit of a condensate without an exposure of gas in similar conditions was of 46 ml.

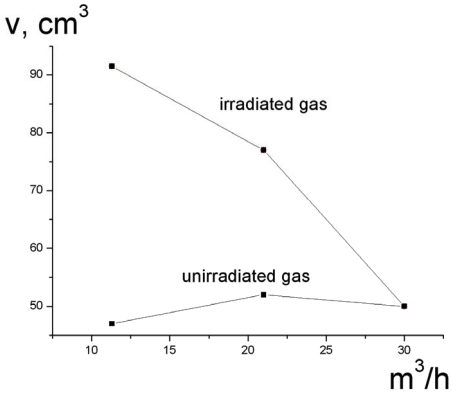

Fig. 3. Association of an exit of a gas condensate on a velocity of pumping of gas

For the second test series the maximal condensate yield at the gas flow rate ~7 m^3/h for irradiated gas was of 88 ml and for non-irradiated one of 44 ml, respectively. For the last test series the condensate yield at the gas flow rate ~ 5 m^3/h was for the irradiated gas of 80 ml and for non-irradiated one of 18 ml, respectively.

The chromatography analysis of the gas condensate obtained under conditions of a steady pressure gradient, for non-irradiated- and irradiated gas has shown that in case of the condensate yield magnification the concentration of C_4-C_5 hydrocarbons increase and reduction of hydrocarbons C_{6+} is observed. Thus, a retrograde condensation occurs in the multicomponent gas system accompanied by the liquid phase formation near to the critical point under isothermal decompression.

7. Conclusion

1. It is shown, that under the action of ultra-violet radiation at the wave length of 172 nm (Xe_2-excilamp) on the natural gas the concentration of water vapour decreases by 2.5 times.
2. Thus obtained results show, that the action of an intense ultra-violet radiation at the above wave length on the wet natural gas result in magnification of heavy molecules content due to the selective photochemical processes of propane-butane dimerization.
3. The dependence of the pressure versus gas temperature has been measured for irradiated- and non-irradiated components of the natural gas at the gas pressure of 22.2 bar and an interpretation of observed effect of the gas pressure rise at temperature -30 ºC is given.
4. A magnification of the gas condensate yield by 2–3 times is obtained under irradiation of the flowing natural gas by the vacuum UV radiation.

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