Natural Gas Conversion under Influence of VUV Radiation

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Abstract – In field conditions (gas pressure in a field well is 8 MPa) influence of VUV radiation (l = 172 nm) on phase transitions in natural gas containing water vapors in a mode of throttling was investigated. It is shown, that processing of a gas stream by VUV irradiation leads to increase of condensate extraction in 2–16 times and to decrease of water concentration in 11 times (the dew-point changes to 25 °C).

1. Introduction

Processes of structural modifications of hydrocarbons are of vital importance for modern technologies of hydrocarbon raw material processing. In the context of preparation of gas for transportation there are technical problems of primary processing, and preparation of the extracted gas mix to more effective allocation of a condensate and transport of gas through pipes. Any, even rather small increase of efficiency in branch scales leads to appreciable economic benefit, that attaches great importance to the decision of the problem.

Low-temperature processes which are carried out both in field and industrial conditions allow removing water from natural gas and to extract heavy hydrocarbon components in gas condensate fields [1–3]. In the present work, a fundamentally new direction based on carrying out of photochemical processes in a stream of gas with use of powerful sources of VUV radiation is considered. It is important to note, that various configurations of the radiators are already developed and allow irradiating by VUV rays in flow photoreactors that makes the considered process technological.

In this work, results of investigations of VUV irradiation of native natural gas (wave-length λ ~ 172 nm) in a flow photoreactor (mode of throttling) are given.

2. Hydrocarbon conversion and modification of water vapor concentration in natural gas under influence of VUV radiation

Researches [4–7] on VUV irradiation of native natural gas (λ ~ 172 nm) demonstrate that the basic processes at irradiation by VUV light are the processes of formation of hydrocarbon complex molecules and water vapor conversion. A mechanism of complex hydrocarbons C_{6+} formation in reactions with hydroxyl radicals is the following:

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

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

Water photolysis is accompanied by formation of high reactive OH and •H radicals

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

that react in the sequel with hydrocarbons. The formed radicals recombine then each other or with hydroxyl radicals. Thus, further process is the following:

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

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

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

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

So, synthesis of dimers and spirits in natural gas with water vapor takes place.

Experiments on dynamics of change of water vapor concentration in natural gas under influence of VUV radiation with wave-length 172 nm show that water concentration reduction depending on time occurs in two stages – sharp reduction and a slow rise on a standard. At that, dependence of fast reduction on intensity has not linear character, so the intensity increase of VUV radiation in 4 times leads to decrease of time of sharp reduction in 2 times.

Numerical simulation shows that the reaction (4) is more efficient with hydrocarbons C_{3+} in this scheme. Reaction rate constants with C_{3+} are in 2–3 orders above than rate constants of similar processes of interaction of •OH radicals with methane or ethane molecules. Therefore, though low concentration of compounds C_3–C_6 in natural gas composition, they are principal precursors of radicals C_nH_{2n+1}. At the next stage, the formed radicals make dimers or recombine with OH. As a result the complex molecules C_{6+} of an isomeric structure and products of partial oxidation of hydrocarbons (spirits, aldehydes) are synthesized. Results of experimental measurements and numerical simulation of concentration of natural gas components after irradiation by an Xe_2 excilamp have correlation in the range 10–15%.

3. Setup and methods of measurements

A flow photoreactor KU-01 with natural gas pressure of 8 MPa is used in a test stand. An excilamp with

wavelength 172 nm and total power 5–15 W is used in the photoreactor.

Tests are carried out in the Myldzhino gas field. The test stand is shown in Fig. 1.

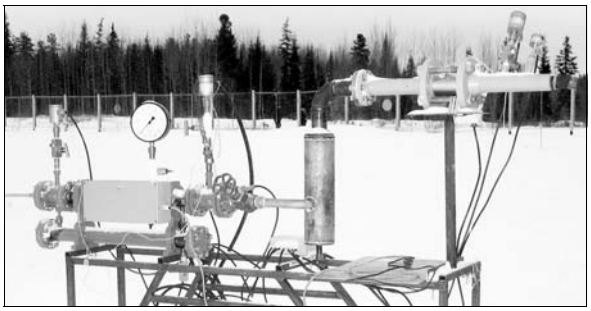

Fig. 1. Photoreactor KU-01

Valves of a gas main line, adjustment of quantity of consumption of gas, gas and condensate extraction are used in the stand. The stand is equipped by sensors of pressure, temperature. There are units of a cleaning filter, a nozzle, a meter of consumption of gas, a gas gauge, gas gathering and gas recycling, gas extraction for humidity measurement in the stand.

The scheme of tests allows to control temperature and pressure at an inlet, an outlet and directly in the photoreactor during experiences. The scheme provides for an opportunity of sampling for gas chromatography and condensate extraction from the unit of condensate gathering and gas recycling.

As a gauge for the control of water content a flow hygrometer "Zima" made by Ltd TPK "Vega: with the assistance of IAO SB RAS is used during tests of the photoreactor.

All data from sensors are collected in the control block and output on a computer.

A nozzle with one, two, four channels and an annular nozzle are used in tests. Natural gas is placed in the photoreactor, the mode of throttling with change of pressure at the input and in the photoreactor without irradiation and with irradiation by VUV light is provided for. After each test, condensate and natural gas samples for determination of a component structure of hydrocarbons and samples for determination of the dew-point, and a structure of stable products of natural gas before and after irradiation are taken. Time of tests is 5–20 min. The component structure of condensate received during tests is investigated by the chromatographic method in the laboratory of Myldzhino gas field.

4. Test results and their interpretation

Dependences of condensate extraction vs. rate of gas consumption for a single-channel nozzle (the area is 50 mm^2) placed before the cleaning filter are shown in Fig. 2. In tests with a two-channel nozzle (the area of apertures is 2 mm^2) located after the filter of clearing, there is a tendency to increase condensate extraction at irradiation of natural gas by VUV light.

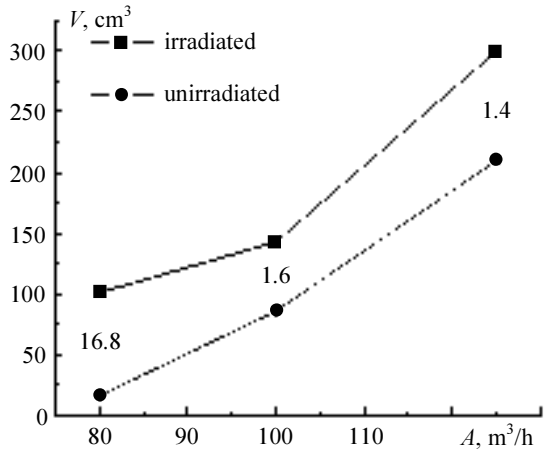

Fig. 2. Dependence of condensate extraction vs. rate of gas consumption

The change of water vapor concentration and a component structure has tendencies similar to tests with the single-channel nozzle. It is necessary to note, that in tests with the two-channel nozzle we have increase of difference of temperatures at the photoreactor input and in the photoreactor for an operating mode with VUV irradiation from 22 up to 36 °C.

In tests with a four-channel nozzle (the area of apertures is 4 cm^2) located after the filter, it is important to note the tests for observation of natural gas dewatering at VUV irradiation (Fig. 3). Tests are carried out at change of pressure at the photoreactor input and in the photoreactor of 14atm and at temperature difference of 24 and 30 °C. Water vapor concentration decreases more intensively at VUV irradiation. Note also, that in tests at a switched on and a switched off source of VUV radiation the inflexion of a curve is observed at change of a mode (Fig. 3, curve *3*).

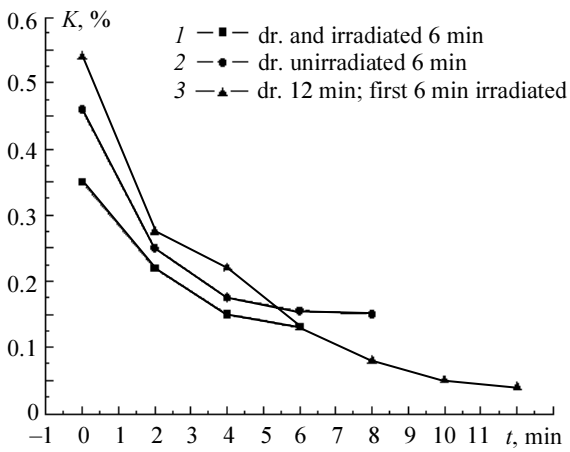

Fig. 3. Dependence of water concentration vs. irradiation time

A following condensate extraction corresponds to these tests: (*1*) 70.5 cm^3 at 6 min throttling with VUV irradiation; (*2*) 64 cm^3 at 6 min throttling without irradiation; (*3*) 550 cm^3 at 12 min throttling, first 6 min with VUV irradiation.

It is essential to note the test *3* as in this case we could reach the minimal water vapor concentration and receive the maximal condensate extraction of 30 cm^3/min as well as in the case of a single-channel nozzle. Probably, such cyclic processing of a gas stream can become the basis of technology of gas processing. At the heart of technology of condensate extraction from natural gas, in our case, there is the effect of stimulated condensation under influence of VUV irradiation generating the active centers: the excited particles, ions and radicals.

There is so-called nonequilibrium condensation. Germs growth at low pressure of hydrocarbon vapor occurs at external initiation of ions and radicals by sources owing to intensive processes of cluster formation having very high rate.

The process is chain and dozens and hundreds of germ molecules suit each formed particle. So, power inputs for stimulated condensation are dozens and hundreds of times less than consumption for formation of one active particle – the excited molecule, a radical or an ion. Photolysis of a water molecule with formation of high reactive hydroxyl radicals and their subsequent compound with hydrocarbon complex molecules is the result of quantum radiation effect as shown in calculations. Thus, gas dewatering is accompanied by self-recycling of water, increase of complex molecule content and synthesis of products of partial oxidation (spirits and aldehydes).

The tests with the annular nozzle placed after the filter (the total area of three sections is 4.08 mm^2) gave condensate extraction at a level of 10 cm^3. There is at the same time increase of condensate density received at natural gas stream irradiation by VUV light. Chromatograms of processes, in case of use of the annular nozzle for gas consumption 120 m^3/h show the reduction of components C_3, C_4 and the augmentation of C_7 and above in a condensate received at natural gas stream irradiation by VUV light in contrast to previous nozzles, that is concerned with nozzle form which has a small gap and the developed surface.

5. Conclusion

It is shown that influence of power VUV radiation with wave-length 172 nm on natural gas containing water vapor leads to increase of heavy component content at the expense of directed photochemical processes of propane and butane dimerization.

The increase of condensate output at natural gas throttling in a mode of irradiation in 2–16 imes is received and it is shown that the maximal changes of the dew-point correspond to the maximal condensate outputs.

Water concentration decrease in 11 times (the dew-point changes to 25 °C at processing of a gas stream by VUV irradiation is received.

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