RADIATION-THERMAL PURIFICATION OF WASTE WATER FROM OIL POLLUTION

I. Mustafayev, R. Rzayev, N. Guliyeva
Institute of Radiation Problems, Azerbaijan National Academy of Sciences, 31-a H. Javid ave Baku-370143, Azerbaijan, imustafaev@iatp.az

ABSTRACT

In this work the results of radiation-thermal decomposition of n-heptane micro-admixtures in water medium are adduced. The main parameters of radiolysis change within the bounds: temperature 20-400°C, absorbed dose – 0÷10.8 kGy at dose rate 3.6 kGy/h.

The correlation of n-heptane concentration and water steam changed within $[C_5H_{12}]/[H_2O] = (1\text{-}100)\ 10^{-5}$. Total concentration of steam was about 10^{20} molec/ml.

As a product of decomposition are observed H_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, C_4H_8, hydrocarbons C_5, and C_6. The changes of n-heptane concentration in the reactor also were established. The chain regime of n-heptane decomposition at high temperatures in the irradiated mixture is observed.

The critical value of temperature and mixture ratio of components, under which the break of chain process of normal n-heptane occurs are defined.

The mechanisms of proceeding radiation thermal processes in hydrocarbons-water system are discussed.
Key words: water, heptane, radiolysis, purification, γ-radiation

1. INTRODUCTION

During the extraction, preparation, transportation and refining of oil the sewages containing oil contaminations are produced. The concentration of oil content in the water depends on used technology and may vary from a thousandths parts up to tens percents. There is a necessity of cleaning this pollution up to a permissible level. There are numerous methods (adsorption, mechanical, chemical and etc) of treating of waster water from oil contaminations [1-2]. Radiation-chemical method is one of the effective among the above mentioned methods [3-4]. Early it have been established that under conjugate effect of heat and radiation decomposition of raw hydrocarbon happens in chain regime [5]. In that case the radiation-chemical yield of water decomposition does not exceed 7-8 molec/100eV [6]. The experimental researches of radiation-chemical processes in water containing micro-impurity of oil were not conducted. At the same time for perspective evaluation of radiation-thermal purification method for refining sewages from oil contaminations it would be useful to have those data.

The experimental researches of radiation-thermal conversion of hydrocarbon micro-impurities in water medium are adduced in this paper.

2. EXPERIMENTAL

The experiments on study of the kinetics of radiation-thermal process were conducted on mixtures of water with n-heptane as a oil hydrocarbon model. The simulated mixtures have prepared in vacuum equipment. The water vapor and n-heptane sequentially were frozen in the glass ampoule of 30 ml volume and were sealed. The total concentration of the mixture in the ampoule was 10^{20} molec/ml, and the components ratio changed in the limits $[C_7H_{16}]/[H_2O] = (1\text{-}100)\cdot10^{-5}$. Irradiation of the ampoule has been carried out in γ-radiation source of Co^{60}, by dose rate 3.6 kGy/h. In the all studied interval of temperature the n-heptane was in a vapor phase. Determination of the rate of the dose of gamma-radiation was conducted by ethylene and ferrosulphate dosimeters, and results of the measurements were agreed within the limits of 12-15%. The concentration of gas products of the radiation-thermal decomposition of mixtures of water with n-heptane was determined chromatographically on the devices Gasokhrom-3101 and Svet-102.

In all cases kinetics of the process has been investigated, and the generation rate and the radiation-chemical yields of products were determined on initial segments of kinetic curves.

3. RESULTS AND DISCUSSIONS

The radiation-chemical processes of decomposition of water, containing micro-impurity of n-heptane is studied in the temperature range of 100-400°C and absorbed dose of D=1.8÷10.8 kGy. The kinetics of gas production at the components ratio $[C_7H_{16}]/[H_2O] = 1.4\ 10^{-3}$ and at the temperature of 400°C is shown on fig. 1.

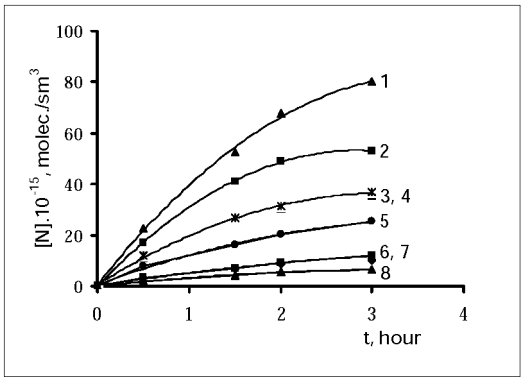


Fig. 1. Kinetics of formation H_2(6), CH_4(2), C_2H_4(1), C_2H_6(3), ΣC_3(4), ΣC_4(5), ΣC_5(7), ΣC_6(8) at the radiation-thermal decomposition of C_7H_{16} in the water medium; $[C_7H_{16}]/[H_2O]$=0.02, T=400 ^{0}C, I=3.6 kGy/h.

It is clear, that at absorbed doses more than 7 kGy (for irradiation time 2 hours) have been observed tendency to the saturation. It is connected with decreasing of concentration of n-heptane in the mixture and decreasing of the rate of sensibilization of its decomposition by the water vapor. The total yield of gases in linear area of kinetic curves makes G=379 molec/100 eV, that corresponds to the yield of the heptane's decomposition of 122 molec/100eV.

The dependence of the radiation-chemical yield of heptane's decomposition on its initial concentration in the mixture with water at the different temperatures is shown on fig. 2.

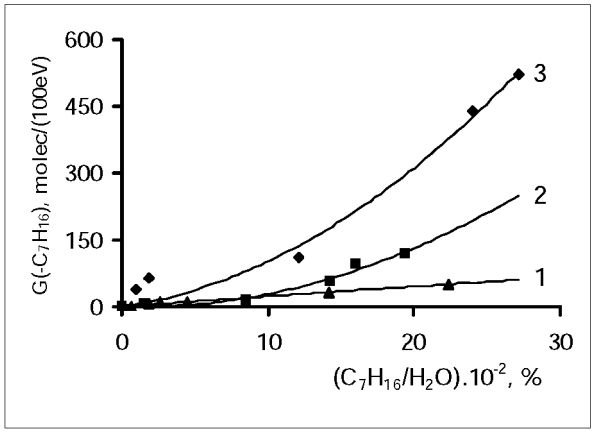


Fig. 2. Influence of ratio of concentration $[C_7H_{16}]/[H_2O]$ to the radiation-chemical yield of decomposition of C_7H_{16} in the water medium; 1-100 ^{0}C, 2-300 ^{0}C, 3-400 ^{0}C.

In all range of studied temperatures the radiation-chemical yield of heptane's decomposition decreases with decreasing of concentration of n-heptane. This fact approves the above-stated explanation of the kinetics of gas generation at T=400°C.

The temperature dependence of production and decomposition of C_7H_{16} within 100-400°C is depicted on fig.3.

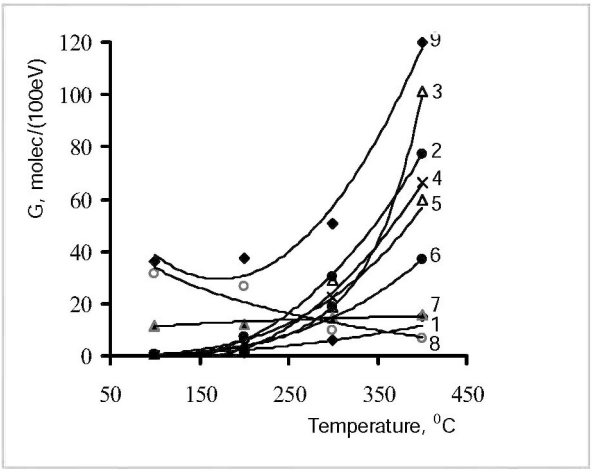


Fig. 3. The temperature dependence of the radiation-chemical yields of gases: H_2(1), CH_4(2), C_2H_4(3), C_2H_6(4), ΣC_3(5), ΣC_4(6), ΣC_5(7), ΣC_6(8), $G_{(-)}$(9); $[C_7H_{16}]/[H_2O]=14{,}2\cdot10^{-2}$%; J=3,5kGy/h.

As shown, the yields of all gases rise with temperature and their activation energy are: E (H_2) =34.6, E (CH_4) = 34.6, E (C_2H_4) =51.8, E (C_2H_6) = 38.5, E (C_3H_8) =40.9, E (C_4H_{10}) = 44.3 kJ/mole. The temperature dependence of the rate of heptane's decomposition (curve 7) is also studied. Thus the values of activation energy is equal E =11.3 kJ/mole.

The temperature variation of the radiolysis significantly influences to the ratio of yields of gas and liquid products (Table 1).

Table 1. Influence of temperature on formation of gas and liquid products at the radiation-thermal decomposition of heptane admixtures in the water

T, °C	G_{gas}	G_{liq}	G_{gas}/G_{liq}
100	3.0	43.2	0.07
200	20.2	38.7	0.52
300	125.3	24.1	5.2
400	356.5	22.5	15.8

From the table 1, it is clear, that with increasing the temperature from 100 up to 400°C the ratio G_{gas}/G_{liq} changes from 3 up to 15. It evident that at radiation- thermal cleaning of water of hydrocarbon products are separated to the gas phase that is advantage of this process. At that effective activation energy of gas production is 11.3 кJ/mol.

At the temperature higher than 300°C hydrocarbon component decomposes with negligible rate even at the thermal process. In that case the ratio of rates of thermal and radiation-thermal processes significantly depends on temperature (see table 2).

Table 2. The influence of temperature on ratio of radiation-thermal and thermal reactions rates

T, °C	300	350	375	400
W_{tr}/W_t	101,2	55.2	26.1	1.9

Earlier we, on an example of pentadecane as a hydrocarbon model [5], have explicitly studied the relationships between that rate on temperature and dose rate, and have found optimum conditions for observation high sub-thermal effect in the radiation-thermal processes.

The observation of high values of radiation-chemical yields counted for a total absorbed dose by the system C_7H_{16}-H_2O, testifies the proceeding of sensitized radiolysis of C_7H_{16}. It is impossible to judge the precise mechanism of transfer of radiation energy from water to hydrocarbon now. Nevertheless it is possible to ascertain the fact that these processes flow through exited and ionized conditions of molecules of water. At

the radiation-thermal decomposition of water the radiation-chemical yield of molecular hydrogen does not exceed 7-8 molec/100eV [6]. At the temperatures is higher than 300°C anatomic hydrogen generated at radiation decay of molecules of water (1. $H_2O \rightarrow H + OH$), reacts with a molecule of water and produces H_2 (2. $H + H_2O \rightarrow H_2 + OH$). However at the presence of hydrocarbon there can be more easily way its consumption in the reaction with C_7H_{16} (3. $H + C_7H_{16} \rightarrow H_2 + C_7H_{15}$). At presence of hydrocarbonic radicals at the high temperatures the chain regime of decomposition of hydrocarbon to the gas products can be originated. Thus it is possible to achieve high cleaning of water from oil. However, at very low concentrations of hydrocarbon ($<10^{-2}$ %), the rate of a sensitization can decrease, and in these conditions the self-radiolysis of macro-components prevails. For example, at ratio concentrations of components $[C_7H_{16}]/[H_2O] < 10^{-4}$ in a competition of reactions (1) and (2) can prevail (3). In these conditions the yield of products of a radiolysis is determined by decomposition of more radiation-stable component of H_2O. The competition of the ionic reactions should be studied separately in that case.

4. CONCLUSION

At the temperatures higher than 300°C the radiation-thermal decompositions of hydrocarbon micro-impurities in water into gas products occurs according a chain mechanism and the radiation-chemical yield of the decomposition exceeds 100 molec/100eV. This method can be used for purification of sewages from oil contaminations.

5. REFERENCES

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